

Electropolymerization of *O*-Phenylenediamine in an Ionic Liquid

Yan Fang DU, Xi Min QI, Peng ZHAO, Jia Xing LU*, Ming Yuan HE

Shanghai Key Laboratory of Green Chemistry and Chemical Process,
Department of Chemistry, East China Normal University, Shanghai 200062

Abstract: Ionic liquid like 1-ethyl-3-methylimidazolium bromine ([EMIM]Br) has been used as electrolyte for the electropolymerization of *O*-phenylenediamine at glassy carbon electrode by cyclic voltammetry. It is found that poly (*O*-phenylenediamine) film modified electrode has favorable electrochemical activity in acid solution.

Keywords: *O*-Phenylenediamine, cyclic voltammetry, electropolymerization, ionic liquid.

Ionic liquids are widely used as solvents for green organic and polymer synthesis, because they exhibit non-flammability and non-volatility¹. Ionic liquids as electrolytes have also excellent properties such as high-ionic conductivity, wide potential window², and have been extensively utilized for a variety of electrochemical processes^{3,4}. From the above points of view, ionic liquids are expected to be peculiar medium for electroorganic synthesis and electropolymerization. 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMICF₃SO₃) was used as electrolyte for the electrooxidative polymerization of pyrrole⁵, and polythiophene was electrochemically prepared in ionic liquid 1-butyl-3-methylimidazolium hexafluoro-phosphate ([BMIM]PF₆)⁶.

Poly(*O*-phenylenediamine) (POPD) has drawn much attention in recent years owing its attractive applications such as pH response, electrochemical diode properties, permselectivity for a dissolved species, electron-transfer mediation, and photovoltaic properties, *etc.* Electrochemical polymerization is a convenient way to prepare polythiophene (PTh), polypyrrole (PPy) and polyaniline (PAN). In this paper, we report for the first time on the direct electropolymerization of *O*-phenylenediamine on the glassy carbon electrode, using the ionic liquid [EMIM]Br as solvent and electrolyte.

Experimental

O-Phenylenediamine, the monomer was recrystallized from distilled water before use. 1-Ethyl-3-methylimidazolium bromine ([EMIM]Br) was synthesized according to the literature⁷. The electrochemical experiments were carried out using a CHI600

* E-mail: jjaxlu@online.sh.cn

electrochemical working station. 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 (GC) disk with an area of 0.071 cm^2 , the reference electrode was saturated calomel electrode and the counter electrode was platinum spiral wire. Prior to use, the working electrode was polished with $0.05 \text{ }\mu\text{m}$ alumina powder, then rinsed with acetone and water respectively in an ultrasonic bath. Poly(*O*-phenylenediamine) was deposited on the GC electrode by cyclic potential-scanning under the following electrolytic conditions: potential scanning range, $+0.6 \sim -1.2 \text{ V vs. SCE}$; scanning rate, 100 mV/s ; temperature, $75 \text{ }^\circ\text{C}$; *O*-phenylenediamine monomer concentration, 0.1 mol/L ; the cycles $N = 20$. After electropolymerization, the POPD-coated GC electrode was thoroughly rinsed with distilled water and H_2SO_4 solution ($\text{pH} = 2.0$), then used for further electrochemical measurements.

Results and Discussion

Cyclic voltammetry (CV) is a versatile electrochemical method, which has been widely employed in the study of electrode reactions and the characterization of electrode surface in electrocatalysis. Cyclic voltammograms of pure ionic liquid and *O*-phenylenediamine in [EMIM]Br are shown in **Figure 1**.

As seen from **Figure 1b**, the strong oxidation of *O*-phenylenediamine starts at $+0.3 \sim +0.4 \text{ V}$, and the current strength diminishes with potential scanning because the electrode surface was passivated gradually. On the other hand, the CV of the pure [EMIM]Br shows no current waves in the same potential scale (**Figure 1a**). The CV waves in **Figure 1b** could be assigned to the polymerization of *O*-phenylenediamine.

Figure 1 Cyclic voltammograms of pure [EMIM]Br (a) and 0.1 mol/L *O*-phenylenediamine in [EMIM]Br(b) on GC electrode at scan rate of 100 mV/s .

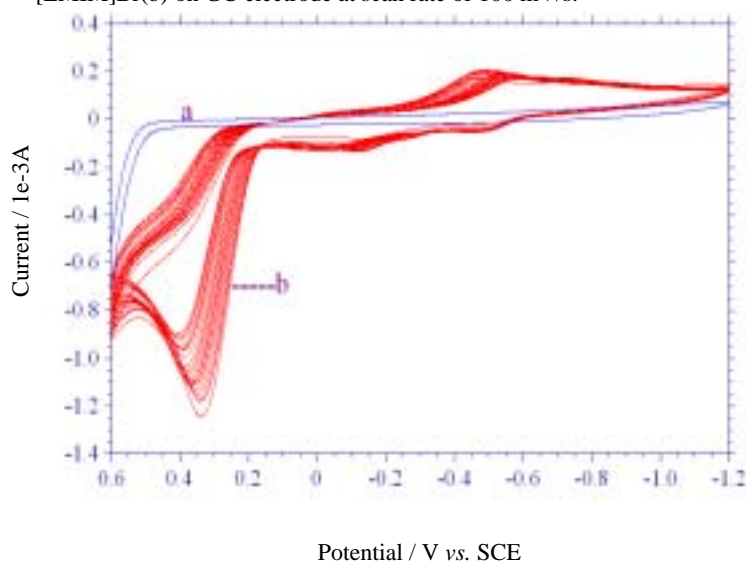
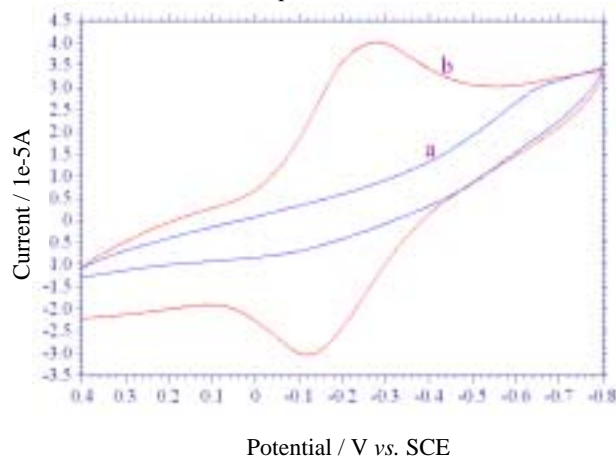


Figure 2 Cyclic voltammograms of blank GC electrode (a) and POPD film modified GC electrode (b) in H₂SO₄ solution (pH = 2) at scan rate of 100 mV/s.



The blank GC electrode shows no electrochemical activity (**Figure 2a**), however, POPD film modified GC electrode (**Figure 2b**) shows a pair of oxidation-reduction peak, the cathodic and anodic peak potentials (E_p^c and E_p^a) are about -0.27 V and -0.12 V, respectively. So POPD film modified electrode has favorable electrochemical activity in acid solution.

Conclusion

The electropolymerization of *O*-phenylenediamine in [EMIM]Br has been demonstrated on the glassy carbon electrode. Ionic liquids are expected to be peculiar medium for electroorganic synthesis and electropolymerization. Further investigations about mechanistic aspects and the application of electrochemical activity are currently in progress in our laboratory.

Acknowledgments

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