Chinese Chemical Letters Vol. 16, No. 4, pp 551-553, 2005
http://www.imm.ac.cn/journal/ccl.html

Preparation and Electrocatalytic Activity of Polyaniline-poly(propylene oxide)

Mei Chao LI*, Chun An MA

College of Chemical Engineering and Material Science, State Key Laboratory Breeding Base of Green Chemistry-Synthesis Technology, Zhejiang University of Technology, Hangzhou 310032

Abstract: A novel copolymer of polyaniline-poly(propylene oxide) (PAN-PPO) was prepared by cyclic voltammetry (CV) and characterized by FTIR and SEM. It showed good electroactivity for methanol oxidation in H_2SO_4 solution.

Keywords: Polyaniline, poly(propylene oxide), electrocatalysis, methanol**.**

Polyaniline (PAN) has become one of the most extensively studied materials and attracted great interest from electrochemical viewpoint recently [1-3]. However, in order to obtain the most suitable material, the physical and chemical properties of the polymer had to be modified. One of the most important methods was copolymerization, the precursor solution, containing the mixture of the monomers. Copolymers of aniline with vinyl alcohol[4], toluidines[5], *o*-toluidine[6], and ethylene terephthalate[7] were synthesized *via* chemical or electrochemical method. Propylene oxide was often added to the electrolyte during electrochemical polymerization to improve some properties of the polymer[8], while copolymer of aniline with propylene oxide has never reported. In this study, copolymer of polyaniline-poly(propylene oxide) (PAN-PPO) was synthesized for the first time. Its electrocatalytic activity was studied with electrooxidation of methanol in sulfuric acid solution.

Experimental

Aniline was distilled before use, other chemicals were of analytical grade. The ultrapure water employed in all experiments was obtained from a Millipore-Milli-Q system. All the electrochemical experiments were carried out using EG&G M273A potentiostat/galvanostat under nitrogen atmosphere at room temperature (25℃). PAN-PPO and PAN were prepared on glassy carbon (GC) electrode by cyclic voltammetry at a sweep rate of 50 mV/s between 0.0 V and 1.3 V in 0.1 mol/L aniline solution with and without propylene oxide, respectively. A saturated calomel electrode (SCE) was used as reference electrode, and a platinum sheet (2.5 cm^2) as counter

---

[*] E-mail: limc@zjut.edu.cn

electrode. All the potentials reported in this paper were relative to this reference electrode. Electrocatalytic oxidation of 1.0 mol/L methanol on PAN-PPO was examined by cyclic voltammetry at a scan rate of 50 mV/s.

PAN-PPO was characterized by FTIR with pressed KBr pellets on thermo Nicolet Nexus 670 FTIR spectrometer. Scanning electron microscopy (SEM) measurements were made using HITACHI S-4700 scanning electron microscope.

Results and Discussion

Electrochemical copolymerization of PAN-PPO on GC electrode surface is achieved by applying potential cycling between 0.0 V and 1.3 V at 50 mV/s. The cyclic voltammograms corresponding to the PAN-PPO film growth up to the seventh cycle obtained during the electropolymerization are shown in **Figure 1**. It is much different in shape from PAN film growth[5] in the similar condition. In the first cycle, there is only one high anodic current peak (0.97 V *vs.* SCE), which shows the electropolymerization of PAN-PPO on GC electrode has a nucleation-loop character and proceeds *via* a radical cation mechanism[9]. From the second cycle on, four anodic peaks are observed at about 0.17 V, 0.47 V, 0.56 V and 0.77 V, and four cathodic peaks at about 0.08 V, 0.44 V, 0.52 V and 0.62 V. These redox current peaks show good reversible character. In addition, all the peak currents increase with the number of potential cycles.

Figure 2 exemplifies FTIR spectrum of PAN-PPO. Peak 1740 cm^{-1} is attributed to carbonyl group, and peak 1055 cm^{-1} is attributed to C-O-C stretching band[8]. It indicates that during the electropolymerization the ring of propylene oxide is opened with a consequence of formation of ether bonds and carbonyl groups in PAN-PPO chain.

Figure 3 shows that PAN-PPO is composed of many uniform nanotubes about 70 nm in diameter. A regular and cross-linked network structure is formed, which helps to improve conductivity and electron transfer capability of PAN-PPO.

Figure 1 Film growth of PAN-PPO at 50 mV/s in 0.5 mol/L H_2SO_4 solution

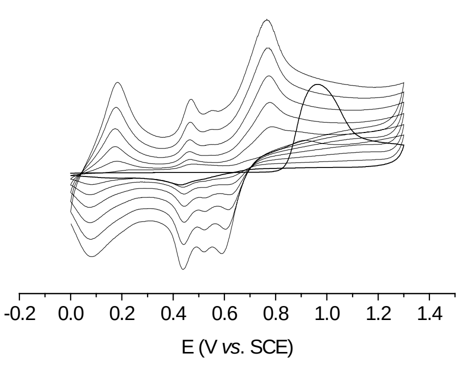


Figure 2 FTIR spectrum of PAN-PPO

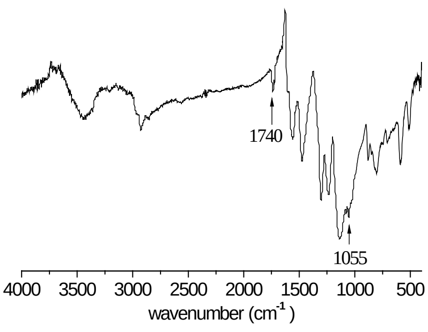


Figure 3 SEM of PAN-PPO

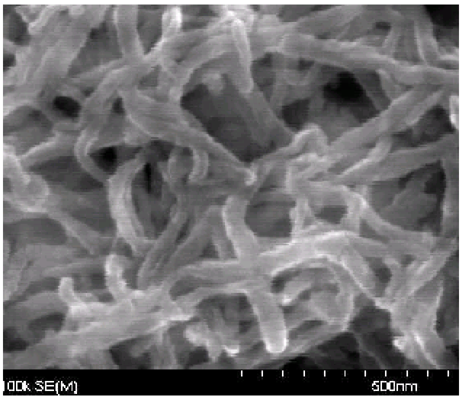
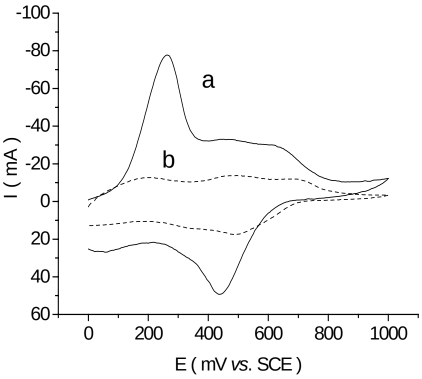


Figure 4 Cyclic voltammegrams of CH_3OH oxidation on PAN-PPO and PAN



(a) PAN-PPO; (b) PAN

The electrooxidation of methanol is important in view of its application in fuel-cell technology[10]. **Figure 4** shows a comparison of methanol oxidation on PAN-PPO and PAN in 0.5 mol/L H_2SO_4 solution containing 1.0 mol/L methanol between 0.0 V and 1.0 V at a sweep rate of 50 mV/s. The first anodic peaks in curve (a) (265 mV) and (b) (220 mV) are corresponding to the following oxidation process[11].

$$CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$$

As shown in **Figure 4**, the oxidation peak current is obviously higher on PAN-PPO (-77.78 mA) than on PAN (-12.6 mA) with equal geometric area. With a high electrocatalytic activity to methanol oxidation, PAN-PPO will have a promising application in fuel-cell in the future.

References

1. W. K. Maser, A. M. Benito, M. A. Callejas, *et al.*, *Mater. Sci. Eng. C*, **2003**, *23*, 87.
2. J. H. Sung, S. J. Kim, K. H. Lee, *J. Power Source*, **2004**, *126*, 258.
3. P. K. Kahol, K. K. Satheesh Kumar, S. Geetha, D. C. Trivedi, *Synth. Metal.*, **2003**, *139*, 191.
4. A. Mirmohseni, G. G. Wallace, *Polymer*, **2003**, *44*, 3523.
5. D. Shan, S. L. Mu, *Synth. Metal.*, **2002**, *126*, 225.
6. D. D. Borole, U. R. Kapadi, P. P. Kumbhar, D. G. Hundiwale, *Mater. Lett.*, **2002**, *56*, 685.
7. A. A. Pud, S. P. Rogalsky, G. S. Shapoval, A. A. Korzhenko, *Synth. Metal.*, **1999**, *99*, 175.
8. P. Jannasch, *Polymer,* **2001**, *42*, 8629.
9. L. T. Cai, H. Y. Chen, *J. Appl. Electrochem.,* **1998**, *28*, 161.
10. K. R. Prasad, N. Munichandraiah, *J. Power Source*, **2002**, *103*, 300.
11. R. Parsons, T. V. Noot, *J. Electroanal. Chem.*, **1988**, *257*, 1.

Received 5 April, 2004