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Electrochemical fabrication of novel platinum-poly(5-nitroindole) composite catalyst and its application for methanol oxidation in alkaline medium

Weiqliang Zhou^a, Chunyang Zhai^a, Yukou Du^{a,*}, Jingkun Xu^{b,**}, Ping Yang^a

^a College of Chemistry, Chemical Engineering and Materials Science, Suzhou University, Suzhou 215123, PR China

^b Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, PR China

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ABSTRACT

A novel composite catalyst, Pt nanoparticles supported on poly(5-nitroindole) (Pt/PNI), has been successfully prepared by the electrochemical method and used for the electrooxidation of methanol in alkaline media. As-prepared Pt/PNI was characterized by SEM, EDX and electrochemical methods. The results of the catalytic activity for methanol oxidation showed that Pt/PNI had higher catalytic activity and stronger poisoning-tolerance than Pt/Pt, Pt/GC and the common Pt electrode. The effects of different parameters related to the methanol oxidation reaction kinetics, such as Pt loading, mass of PNI film, concentration of methanol and KOH, potential scan rate, have also been investigated. The present study showed a promising choice of Pt/PNI as composite catalyst for methanol electrooxidation in alkaline medium.

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1. Introduction

The direct methanol fuel cell (DMFC) is suited for portable devices and transportation applications due to its high energy density at low operation temperature and ease of handling a liquid fuel [1,2]. However, two problems block the DMFC from commercialization: (1) the poisoning intermediates during the oxidation methanol can be bound easily and strongly to Pt in acid media, which leads to severe limitations in the oxidation kinetics [3] (2) the high loading of Pt catalysts. To date, much effort has been devoted to the development of catalysts by increasing catalytic activity and reducing Pt loadings. It is reported that the alcohol oxidation kinetics will

be significantly improved when oxidation processes in an alkaline electrolyte instead of an acidic electrolyte [4–9]. However, alkaline medium are not stable for DMFC owing to the carbonation of alkaline electrolyte. Besides, carbonate precipitation in the cathode will cause performance degradation and electrolyte leakage through the electrode. If the advantages of alkaline media are to be made use of, alkaline membranes should be used [10]. The DMFC with alkaline membrane shows reasonable performance stability.

It is well-known that conducting polymers (CPs) have been proved to be a suitable host material for dispersing metallic particles [11–17]. The composites of CPs with metal nanoparticles permit a facile flow of electronic charges through the

* Corresponding author. College of Chemistry, Chemical Engineering and Materials Science, Suzhou University, Industrial Park, Renai Road, Suzhou 215123, PR China. Tel.: +86 512 65880361; fax: +86 512 65880089.

** Corresponding author.

E-mail addresses: duyk@suda.edu.cn (Y. Du), xujingkun@tsinghua.org.cn (J. Xu).

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polymer matrix during electrochemical processes. However, the studies of CPs as host material of Pt nanoparticles were centered on the polyaniline, polypyrrole, polythiophene and their derivatives. However, as far as we know, few CPs as catalyst support was used in alkaline medium. This limitation is possibly due to the rapidly activity loss and the destruction of the conjugated structure of polymer in alkaline medium [18]. Therefore, it would be quite interesting to extend such studies to other CPs which might be suitable as host materials of the catalyst nanoparticles in alkaline medium.

On the other hand, nitro-substituted aromatic rings, such as 5-nitroindole, currently have attracted great attention because of the lower band gap of CPs obtained from nitro-substituted aromatic rings [19] and their hydrogen-bonding capabilities [20,21]. This class of compounds was also used to prepare polyindole films for extending applications in various domains. Kokkinidis et al found that poly(5-nitroindole) (PNI) can be prepared electrochemically from 5-nitroindole monomer in acetonitrile [22], but the quality of as-formed PNI films was very poor due to the high oxidation potential of corresponding monomers in neutral solvent. Presently, the high quality PNI from boron trifluoride diethyl etherate (BFEE) has been successfully prepared by our group [23], which had good thermal stability, good conductivity in its oxidized state (measured to be 0.016 S cm^{-1}), good adhesion to the electrode substrate and good electrochemical activity. Here, we found that as-prepared PNI from BFEE in alkaline solutions had also good electrochemical activity and stability in the potential range from -0.6 to 0.5 V versus SCE. However, up to now, there have been no reports on the electrodeposition of Pt nanoparticles on PNI-modified electrode.

In this paper, we attempted to prepare a novel composite catalyst using PNI as host materials, namely, Pt/PNI. As-prepared composite catalyst was characterized by SEM and EDX. And the electrocatalytic activities of composite catalyst were examined by cyclic voltammetry, chronoamperometry and chronopotentiometry in 1.0 M methanol + 1.0 M KOH. The effect of variables related to the methanol oxidation reaction kinetics, such as concentration of methanol and KOH, potential scan rate, etc. were also investigated.

2. Experimental

2.1. Materials

5-Nitroindole (Shandong Pingyuan Hengyuan Chemical Co., Ltd., China) and H_2PtCl_6 (Shanghai Shiyi Chemicals Reagent Co., Ltd., China) were used as received. Boron trifluoride diethyl ether (BFEE, distilled before use) was a product of Sinopharm Chemical Reagent Co., Ltd. Diethyl ether (EE), Ethanol, Methanol, KCl and KOH were of analytical-grade purity. Doubly distilled water was used throughout.

2.2. Apparatus

The electrochemical experiments were carried out using a CHI 660B potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd., China). GC electrode (3 mm diameter) was used as the substrate electrode. The counter electrode and the

reference used were platinum wire (0.5 mm diameter) and saturated calomel electrode (SCE), respectively. The solutions were deaerated by a dry nitrogen stream and maintained a slight nitrogen overpressure during experiments. A scanning electron microscope (SEM, S-4700, Japan) equipped with an energy-dispersive X-ray analyzer (EDX) was used to determine the morphology and composition of composites.

2.3. Electrode preparation

Before modification, GC surface was polished with $0.3 \mu\text{m}$ alumina slurry, and then rinsed thoroughly with doubly distilled water in ultrasonic bath. According to our previous paper [23], PNI electrodeposition was performed in BFEE + 10% EE and 50 mM 5-nitroindole at the constant potentials of 1.2 V under controlling deposition time, and the mass of the polymer film (W_{polymer}) was calculated from the total charge passed through the cell during the film growth process, according to Eq. (1) [24]:

$$W_{\text{polymer}} = \frac{(\eta Q_{\text{dep1}})(M_1)}{F(Z_1)} \quad (1)$$

here, W_{polymer} was calculated by using the charge (Q_{dep1}), assuming a 100% current efficiency (η) (the total charge passed through the cell during the polymer film growth process). M_1 is the molecular weight of 5-nitroindole, F is the Faraday constant (96485 C/mol), and Z_1 is the number of electrons transferred per monomer attached to the polymer (here Z_1 is estimated to be 2.25).

After modification, the PNI-modified GC electrode (PNI/GC) was thoroughly rinsed with ethanol and water. The Pt nanoparticles were deposited on PNI/GC in a 3 mM H_2PtCl_6 + 0.1 M KCl solution at a constant applied potential of -0.2 V . In the constant potential deposition, the amount of Pt deposited is determined by the charge integrated during platinum deposition, assuming a 100% current efficiency. And the amount of Pt (m_{Pt}) loaded onto PNI/GC and bare GC was calculated from the following Eq. (2) [14]:

$$m_{\text{Pt}} = \frac{(Q_{\text{dep2}})(M_2)}{F(Z_2)} \quad (2)$$

here, m_{Pt} was calculated by using the charge (Q_{dep2}) (obtained from the charge passed during electrolysis) utilized for the deposition of Pt. M_2 is the atomic weight of Pt, F is the Faraday constant, and Z_2 is the number of electrons transferred (taken as four for the formation of Pt).

3. Results and discussion

3.1. Electrochemical synthesis of PNI

The successive cyclic voltammograms (CVs) of 0.05 mol L^{-1} 5-nitroindole in the mixed electrolytes on a GC electrode is shown in Fig. 1. The processes involved were the oxidation of the monomer and the polymer in the positive scan, and the reduction of the polymer during the negative scan. The broad peaks were due to the redox processes in the polymer and the large increase in anodic current at the positive potential was

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