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Nanostructured poly(aniline-co-metanilic acid) as platinum catalyst support for electro-oxidation of methanol

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ABSTRACT

Nanostructured poly(aniline-co-metanilic acid) is prepared using the chemical oxidative polymerization of aniline (Ani) and metanilic acid (Maa). The copolymerization of poly(aniline-co-metanilic acid) with various molar feed ratios of Ani/Maa is conducted to attain highly porous nanowire copolyanilines. The as-prepared copolyanilines are characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The XPS results indicate that a saturated doping state is achieved when the Ani/Maa ratio is less than 20/1. The SEM images reveal that these films are composed of highly porous nanowires when the feed molar ratio of Ani/Maa is more than 4/1. The copolyanilines are used as Pt catalyst supports. Transmission electron microscopy (TEM) results indicate that Pt particles disperse more uniformly onto the highly porous nanowires of P(A10-M) (feed molar ratio = 10:1) than onto other copolyanilines, and that the P(A10-M)-Pt electrode has the highest active surface area. Cyclic voltammetry results and chronoamperometric response measurements show that the P(A10-M)-Pt electrode has the highest electrocatalytic activity and the best long-time stability toward methanol oxidation among polyaniline-Pt and copolyaniline-Pt electrodes.

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Introduction

The electrocatalytic oxidation of methanol has been widely studied due to its promising usage in direct methanol fuel

cells (DMFCs) [1–3]. The reaction of methanol electro-oxidation is sensitive to the catalytic nature of the electrode surface because it involves several adsorption steps, including the formation of chemisorbed species, which decreases the

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catalytic activity of the electrode surface. Accordingly, poor methanol oxidation at the anode and methanol crossover from the anode to the cathode remain challenges to the commercialization of DMFCs [4,5]. Recent research has indicated that the negative influence of methanol crossover can be diminished by the addition of a second metal to platinum, to form platinum-based alloys such as PtRu, PtCo, PtPb, PtRh, PtSn, and PtAu, to promote methanol electro-oxidation of electrode [6–11]. Although bimetallic alloy structures can effectively improve the utilization efficiency of Pt-based catalysts, their high cost makes them prohibitive. Conducting polymers (CPs) are promising catalyst supports due to their porous nanostructure, highly accessible surface area, and high stability. Recent research has shown that modifying the electrode surface with polymeric films in place of conventional supports allows the practical application of electrochemically modified electrodes. The films are stable and provide active sites.

CPs exhibit interesting optical and electrochemical properties, and hence are attractive candidates for composite components [12–16]. A number of polymeric films, such as polypyrrole (PPY) [17,18], polyaniline (PANI) [19,20], polythiophene [21,22], poly(diallyldimethylammonium chloride) [23], polycarbazole [24,25], and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS) [26], have been investigated as conducting catalyst supports for methanol oxidation. PANI has received a great deal of attention due to its high conductivity and good redox reversibility. A number of studies have modified PANI to improve its electrochemical properties [27]. Three modification methods are commonly used [27,28], namely the homopolymerization of aniline (Ani) derivatives, the modification of PANI via post-polymerization reactions, and copolymerization. Among them, copolymerization provides a simple route for preparing a specific polymer with unique physical and chemical properties. The copolymerization of Ani with other monomers has received increasing attention [29] because it allows the preservation of good properties and the addition of new ones. The copolymerization of Ani and other monomers can be carried out via chemical and electrochemical methods. Although electrochemical methods can obtain Ani-based polymer films on conductive substrates directly, the deposition amount is less than that for chemical routes.

Several research groups have focused on the modification of conducting supports to increase Pt utilization and enhance the electrocatalytic properties toward methanol oxidation. Huguenin et al. [30] reported that a film of chitosan and poly(vinyl sulfonic acid) prepared via the layer-by-layer method could serve as a template for loading Pt particles. Kuo et al. [31] reported that PANI doped with poly(acrylic acid) (PAA) forms a spatial network structure. A PANI-PAA-Pt composite shows a significant enhancement of electroactivity for methanol oxidation. Huang et al. [32] reported that the electrochemical stability of PANI can be improved by the incorporation of PANI into poly(styrene sulfonic acid) (PSS). PANI-PSS acts as a matrix that leads to the uniform distribution of Pt particles. Hence, the electrocatalytic activity for methanol oxidation of PANI-PSS-Pt is much higher than that of PANI-Pt. Ho et al. [33] improved the deposition of Pt on carbonized PANI nanofibers by grafting sulfonic acid to

increase the hydrophilic surface. The electrochemically active electrode with this catalyst ink exhibited increased power and maximum current density. Accordingly, the introduction of sulfonic acid groups ($-\text{SO}_3\text{H}$) might affect the properties of supporting materials and the performance of methanol oxidation. This motivated us to investigate the feasibility of incorporating $-\text{SO}_3\text{H}$ groups into the backbone of CP as a support for Pt.

In the present study, $-\text{SO}_3\text{H}$ groups are incorporated into the side chain of the PANI backbone. The CPs (poly(aniline-co-metaniolic acid)s) are synthesized using the chemical oxidative polymerization of Ani and metaniolic acid (Maa) with ammonium peroxydisulfate. Ani/Maa molar feed ratios of 100:0, 40:1, 20:1, 10:1, 4:1, 2:1, and 1:1 are used. The characteristics of deposited homopolyaniline and copolyaniline films are characterized by Fourier transform-infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Platinum particles are doped into the homopolyaniline and copolyaniline films using K_2PtCl_6 as the precursor to obtain PANI-Pt, P(A40-M)-Pt, P(A20-M)-Pt, P(A10-M)-Pt, P(A4-M)-Pt, P(A2-M)-Pt, and P(A1-M)-Pt composite electrodes. The morphology and Pt particle size of the composite electrodes are characterized using transmission electron microscopy (TEM) and X-ray diffraction (XRD), respectively. The electrocatalytic activities and long-time stability of the composite electrodes are determined by carrying out cyclic voltammetry (CV) and chronoamperometry measurements in 1.0 M methanol + 0.5 M H_2SO_4 solution. It is expected that the methanol oxidation performance of copolyaniline films as the Pt catalyst support depends on the molar ratio of Ani/Maa.

Experimental

Preparation of PANI, P(A40-M), P(A20-M), P(A10-M), P(A4-M), P(A2-M), and P(A1-M) films

The polymerization of Ani was carried out in 5 mL of 1 M HCl solution using ammonium peroxydisulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, APS) as an oxidant. The molar ratio of [Ani]/[APS] was 0.8:1.0 and the concentration of Ani was 0.2 mol L^{-1} . The reaction mixture was allowed to react under stirring for 2–20 h, and then PANI was collected from the reaction by filtration. To remove unreacted monomers, the filtered solid product was washed with diluted HCl and deionized water, and then dried at 105°C for 24 h. In similar conditions, the chemical oxidative polymerization of P(A40-M), P(A20-M), P(A10-M), P(A4-M), P(A2-M), and P(A1-M) was carried out in mixture solutions with various Ani/Maa feed molar ratios (40/1, 20/1, 10/1, 4/1, 2/1, and 1/1), respectively.

Deposition of Pt into PANI, P(A40-M), P(A20-M), P(A10-M), P(A4-M), P(A2-M), and P(A1-M) matrices

Pt particles were deposited onto indium tin oxide (ITO)/PANI, ITO/P(A40-M), ITO/P(A20-M), ITO/P(A10-M), ITO/P(A4-M), ITO/P(A2-M), and ITO/P(A1-M) from 10.3 mL (4.6 mM) of K_2PtCl_4 solution, with 2.5 mL of formic acid used as a reduction agent. The mixtures were stirred at room temperature for 16 h. After

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