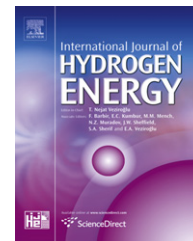


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High efficient electrocatalytic oxidation of formic acid at Pt dispersed on porous poly(*o*-methoxyaniline)

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ABSTRACT

A Pt-based composite electrode material has been developed by dispersing Pt nanoparticles on a porous poly(*o*-methoxyaniline) (POMA) film, which was produced via electropolymerization on a glassy carbon (GC) electrode. As-formed Pt/POMA/GC electrode was characterized by SEM, EDX and electrochemical analysis. Furthermore, the composite electrode material was evaluated by its electrocatalytic performance for formic acid oxidation using cyclic voltammetry and chronoamperometry methods. Compared to Pt deposited on bare GC (Pt/GC), Pt/POMA/GC exhibits higher catalytic activity and stronger poisoning-tolerance ability towards formic acid electro-oxidation. The improved performance is attributed to the synergetic effect between Pt and POMA. Also, as demonstrated by CO stripping voltammograms, the interference of CO on Pt/POMA/GC is greatly weakened. These results suggest that the POMA film has great potential to serve as a promising support material for the electrocatalytic oxidation of formic acid.

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1. Introduction

Direct formic acid fuel cell (DFAFC) has attracted great attention as a power source for portable electronic devices because of its advantages over direct methanol fuel cell (DMFC) [1–3]. Although methanol has higher theoretical energy density than formic acid, it has some disadvantages such as the inherent toxicity, slow electrocatalytic oxidation kinetics, having a high crossover through the polymer membrane and a complicated reaction process [4,5]. In contrast, formic acid is non-toxic and has low crossover, which makes it possible for DFAFC to work at high concentrations [6–8].

Pt has been extensively used for the electrocatalytic oxidation of formic acid [9–11]. It is universally acknowledged that formic acid oxidation on Pt follows a so-called dual pathway, i.e., a direct oxidation pathway occurring via the dehydrogenation reaction to form CO₂ and an indirect reaction pathway forming adsorbed CO as a reaction intermediate by dehydration [12,13]. Moreover, formic acid oxidation on Pt surface occurs dominantly through the second pathway, which leads to Pt poisoned by CO_{ads} and thus reducing its catalytic performance. Many efforts have been devoted to reduce the poisoning effect by modifying Pt surface, such as Pt-based bimetallic catalysts [14–20], Pt-macrocyclic co-catalysts [21,22], and manganese oxide single crystalline nanorod

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modified Pt catalysts [23]. Although these approaches work effectively to some extent, they have a disadvantage, i.e., involving highly costly materials.

Recently, composites of platinum on conducting polymers (CPs), such as polyaniline [19,24], polypyrrole [11] and polythiophene [25,26], have been becoming attractive objects in the field of electrocatalytic research. The enhanced activity of Pt-based catalysts on CPs for the oxidation of organic molecules is associated with their high surface area and the synergistic effect between CPs and relevant Pt catalysts [27–30]. As one of polyaniline derivatives, poly(*o*-methoxyaniline) (POMA) has been extensively investigated due to its excellent electrochromism [31,32], good solubility [33–35], good electroactivity [36,37] and high thermal stability [38,39]. Additionally, Pt supported on POMA has been studied for methanol electro-oxidation, which showed improved catalytic activity [34]. To the best of our knowledge, up to now, there are limited reports on using POMA as support for Pt nanoparticles in DFAFC, which is advantageous over DMFC in many aspects as stated before.

In this paper, a Pt/POMA composite has been successfully prepared by electrodeposition of Pt on a POMA film. Compared to its counterpart Pt on the bare GC, to our delight, as-formed Pt/POMA shows superior performance in electrocatalytic oxidation of formic acid.

2. Experimental

2.1. Materials and apparatus

o-Methoxyaniline (99%) (Johnson Matthey Company) and H_2PtCl_6 (Shanghai Shiyi Chemicals Reagent Co., Ltd., China) were used as received. Formic acid and H_2SO_4 were of analytical-grade. Doubly distilled water was used throughout the work. The electrochemical experiments were carried out using a CHI 660B potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd., China) at room temperature. A glassy carbon electrode (GC, 3 mm diameter) was used as the substrate electrode. The counter electrode and the reference were platinum wire and saturated calomel electrode (SCE), respectively. Electrolyte solutions were deaerated by a dry nitrogen stream and maintained under a slight nitrogen overpressure during experiments. A scanning electron microscope (SEM, FEI Quanta 200) equipped with an energy-dispersive X-ray analyzer (EDX, S-4700, Japan) was used to determine morphology and composition of the sample composite.

2.2. Electrode preparation

Before modification, GC surface was polished with 0.3 mm alumina slurry, and then rinsed with doubly distilled water in an ultrasonic bath. The electrodeposition of POMA was performed in a 0.1 M *o*-methoxyaniline + 0.5 M H_2SO_4 solution at the constant potential of 0.7 V under controlled deposition time, and the thickness of the polymer film (d_n) was derived from the total charges passed through the cell during the film growth process (Q_{dep1}) with an assumption of a 100% current efficiency (η) according to Eq. (1) [40]:

$$d_n = \frac{(Q_{\text{dep1}})(M)}{nF\rho S} \quad (1)$$

where M is the molecular weight of *o*-methoxyaniline (126.16 g/mol), n is the number of electrons transferred per monomer attached to the polymer (here n is estimated to be 2), F is the Faraday constant (96485 C/mol), ρ is the density of POMA (1.50 g/cm³) [41], and S is the surface area of GC electrode (0.07 cm²).

After modification, the POMA-modified GC electrode (POMA/GC) was thoroughly rinsed with ethanol and water. Pt nanoparticles were deposited on POMA/GC in a 3 mM H_2PtCl_6 + 0.5 M H_2SO_4 solution at -0.2 V. The amount of Pt (W) loaded onto POMA/GC was determined by the following Eq. (2) [39,40]:

$$W = \frac{(Q_{\text{dep2}})(M)}{ZF} \quad (2)$$

where Q_{dep2} is the integrated charge during platinum deposition assuming a 100% current efficiency, M is the atomic weight of Pt, Z is the number of electrons transferred (taken as 4 for the formation of Pt), and F is the Faraday constant. For comparison, the same amount of Pt deposited on bare GC (Pt/GC) was prepared by a similar method as stated above.

3. Results and discussion

3.1. Electrochemical synthesis and electrochemical behavior of POMA

Fig. 1 shows the successive cyclic voltammograms (CVs) of 0.1 M *o*-methoxyaniline on GC in a 0.5 M H_2SO_4 aqueous solution. The processes include the oxidation of the monomer and the polymer in a positive scan, and the reduction of the polymer during a negative scan. As the CV scan continues, a polymer film is formed on the GC surface. The increase in the redox wave currents implies that the amount of polymer on the electrode is increasing [42]. In the first positive sweep, the monomer oxidation starts at about 0.64 V, and then polymer is obtained by the electropolymerization of

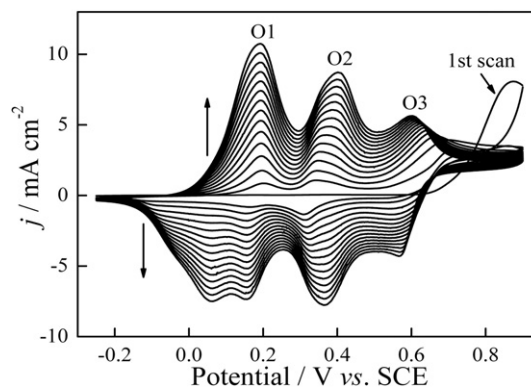


Fig. 1 – The cyclic voltammograms of 0.1 M *o*-methoxyaniline on GC in the presence of 0.5 M H_2SO_4 at 50 mV s⁻¹.

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