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Pt and Pt–Ru nanoparticles decorated polypyrrole/multiwalled carbon nanotubes and their catalytic activity towards methanol oxidation

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Abstract

Conducting polymer composite films comprised of polypyrrole (PPy) and multiwalled carbon nanotubes (MWCNTs) [PPy–CNT] were synthesized by in situ polymerization of pyrrole on carbon nanotubes in 0.1 M HCl containing $(NH_4)S_2O_8$ as oxidizing agent over a temperature range of 0–5 °C. Pt nanoparticles are deposited on PPy–CNT composite films by chemical reduction of H_2PtCl_6 using HCHO as reducing agent at pH = 11 [Pt/PPy–CNT]. The presence of MWCNTs leads to higher activity, which might be due to the increase of electrochemically accessible surface areas, electronic conductivity and easier charge-transfer at polymer/electrolyte interfaces allowing higher dispersion and utilization of the deposited Pt nanoparticles. A comparative investigation was carried out using Pt–Ru nanoparticles decorated PPy–CNT composites. Cyclic voltammetry demonstrated that the synthesized Pt–Ru/PPy–CNT catalysts exhibited higher catalytic activity for methanol oxidation than Pt/PPy–CNT catalyst. Such kinds of Pt and Pt–Ru particles deposited on PPy–CNT composite polymer films exhibit excellent catalytic activity and stability towards methanol oxidation, which indicates that the composite films is more promising support material for fuel cell applications.

Keywords: Multiwalled carbon nanotubes (MWCNTs); Methanol oxidation; Polypyrrole; Pt nanoparticles; Pt–Ru nanoparticles; Fuel cells

1. Introduction

The direct methanol fuel cell (DMFC) is an extremely promising power source for portable applications due to its simple handling and processing of fuel. The recital of DMFC has improved manifestly in the past five years [1–3]. Despite many efforts devoted to the DMFC development, there still remain difficulties to be overcome in terms of efficiency and power density. One of the reasons is the relatively slow kinetics of the methanol oxidation reaction at the anode, which leads to high over-potentials [4]. Platinum has towering activity for methanol oxidation and was used as anode electrocatalysts for many years [5–7]. However, Pt electrocatalyst is poisoned by the intermediate of methanol oxidation, such as CO_{ads}. Since the mid-1970s, modification of the catalyst surface has been made by the addition of a second metal to platinum to promote methanol electrooxidation at platinum [8–10]. The Pt–Ru binary metallic catalyst is commonly accepted as the preeminent electrocatalyst for methanol oxidation. The fundamental mechanism studies for Pt–Ru catalysts indicate that methanol is oxidized according to a bifunctional mechanism [11].

The electrocatalytic activity of platinum particles for methanol oxidation is reliant on many factors [12,13]. Of these, the supporting materials and their surface condition are indispensable for the Pt catalyst to produce high catalytic activity [14–18]. The significance of the structure of the supporting materials for dispersion of the catalyst has been concerned [14]. The supporting materials with high surface

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area are vital to disperse catalyst particles and to reduce the catalyst loading under the condition of keeping high catalytic activity. Hence much efforts are in the underway in the development of various conducting supports for fuel cell applications. Besides traditional carbon support materials (XC-72), the appearance of novel carbon materials, such as graphite nanofibres (GNFs) [19,20], carbon nanotubes (CNTs) [21–23] and mesocarbon microbeads (MCMB) [24,25] provide new candidates of carbon supports for Pt and Pt based electrocatalysts.

Carbon nanotubes (CNTs), because of their appealing properties like high chemical stability and a large surface to volume ratio, have received a rising attention in recent years for their use as catalyst support materials [26,27]. Several papers have focused on the application of carbon nanotubes in fuel cell as catalyst supports [21,28,29]. Carbon nanotubes (CNTs) have become a hub of attraction due to its immense interest from both a fundamental and an applied point of view since their discovery. On the other hand, noble metal nanoparticles are exclusive materials and have a wide application in the homogeneous and heterogeneous catalysts. The synthesis of such nanoparticles with uniform size and good dispersion over the carbon supports as an electrocatalytic materials remains to be a challenging and demanding work. Many researches have demonstrated that CNTs can be used as catalyst supports where catalytically active metal particles, such as Pt, Ru, PtRu, may decorate along the external walls or be filled in the interior of the CNTs and the resulting materials displayed good catalytic behavior [21,27,28,30–32].

Another promising and intriguing area of developing science are the conducting polymers owing to their novel applications in electronic and electro optical devices [33]. New-fangled attempts have been developed to design and synthesize conducting polymer carbon nanotube composite materials for various target applications such as electrochemical devices, light-emitting diodes, chromatography, electrostatic discharge protection, corrosion protecting paint [34–36] and electrocatalyst. Among conducting polymers, polypyrrole (PPy) has superiority for commercial applications because of its unique properties, such as high conductivity, stability in air, and ease of preparation. Polypyrrole (PPy), also have potential applications in batteries [37,38], supercapacitors [39], sensors [40,41], microwave shielding and corrosion protection [42,43]. In order to increase the physical properties of PPy, various composites of PPy have been synthesized [44–47]. Carbon nanotubes are of interest for composite materials because of their good electronic and mechanical properties and high stability [48–51]. Composites of PPy and carbon nanotubes have been prepared by chemical or electrochemical oxidation, and the capacitance [52,53] and magnetic properties [54] of these composites have also been studied.

Therefore, the synthesis of hybrid materials consisting MWCNTs with PPy matrix for the fabrication of PPy–CNT composite supports is an interesting approach to improve the properties of electrocatalyst materials because composite structure may exhibit improved characteristics than the corresponding individual counterparts. To the best of our knowledge, there have been no reports on the use of platinum and Pt–Ru nanoparticles decorated PPy–CNT composite films or its use for support materials in the electrocatalytic oxidation of methanol. In the need of developing potent electrocatalysts for a better performance in fuel cell applications, the present work is focused on synthesis of Pt and Pt–Ru nanoparticles decorated polypyrrole–multiwalled carbon nanotube composites and its role in methanol oxidation. This is the continuation of our previous work on the role of nanoparticles in fuel cell applications [55,56].

2. Experimental

2.1. Materials

Reagent grade formaldehyde, methanol were obtained from SRL and electrocatalyst precursor salts $H_2PtCl_6 \cdot 6H_2O$ and $RuCl_3$, were purchased from Alfa Aesar. They were used as received without further purification. Multiwalled carbon nanotubes obtained from SIGMA, Aldrich were rinsed with double distilled water and dried. All chemicals were of reagent grade and double distilled water was used throughout the experiments. All the experiments were carried out at room temperature.

2.2. Equipment and methods

A CHI 660B instrument with a three-compartment cell was employed for the electrochemical measurement. The working electrode was a thin layer of nanoparticles modified PPy–CNT (or PPy) catalysts cast on a graphite electrode. A Pt foil and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All potentials in this study are reported with respect to SCE. The electrolyte solution was deaerated by high purity nitrogen gas prior to the measurement. For measurement of methanol electrooxidization reaction activities, cyclic voltammetry was performed in a solution containing 0.5 M CH_3OH and 0.5 M H_2SO_4 at room temperature. The surface analysis (SEM) was carried out using an LEO-stereoscan 440 microscope. The presence of metal nanoparticles in the polymer matrix was probed using energy dispersive X-ray analysis (EDAX) with an INCA200 instrument. The size of the particles was confirmed using TEM (TECHNIE 10) with an accelerating voltage of 80 kV.

2.3. Synthesis of polypyrrole–CNT composites (PPy–CNT)

CNT–PPy nanotubes were synthesized by in situ polymerization of pyrrole on carbon nanotubes in 0.1 M HCl solution-containing $(NH_4)_2S_2O_8$ as oxidant over the temperature range of 0–5 °C is as follows. One hundred and fifty millilitres of 0.1 M HCl solution containing CNTs