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Platinum–Iron nanoparticles supported on reduced graphene oxide as an improved catalyst for methanol electro oxidation

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ABSTRACT

Platinum–Iron nanoparticles supported on reduced graphene oxide powder are synthesized by chemical reduction method as an anode catalyst for the methanol electro oxidation. The characterization of the catalyst has been investigated using physical and electrochemical methods. Prepared catalyst was characterized by scanning electron microscopy (SEM), TEM (Transmission electron microscopy), FT-IR (Fourier-transform infrared spectroscopy), Raman spectroscopy and, X-ray diffraction (XRD) and energy dispersive analysis of X-ray (EDX). Pt and Pt-Fe nanoparticles are uniformly dispersed on the surface of reduced graphene oxide (rGO) powder nanocomposite support. The catalytic properties of the catalyst for methanol electro-oxidation were thoroughly studied by electrochemical methods that involved in the cyclic voltammetry, linear sweep voltammetry (LSV), chronoamperometry and electrochemical impedance spectroscopy (EIS). The Pt-Fe/rGo exhibits high electrocatalytic activity, catalyst tolerance for the CO poisoning and catalyst durability for electro-oxidation of methanol compared to the Pt/rGo and commercial Pt/C catalyst. Therefore, the Pt-Fe/rGo catalyst is a good choice for application in direct methanol fuel cells.

Introduction

In the last decades, the use of the fuel cells as power sources was brought into focus [1,2]. The various types of fuels and their processing for use in fuel cell systems are suggested and studied such as methanol [3–5], ethanol [6–8], formic acid [9], ethylene glycol [10], hydrazine [11], dimethyl ether [12], glycerol [13] and glucose [14]. Among the fuels used, methanol has been attracted considerable attention due to unique physical and chemical properties such as sustainable, ease of transportation and identified as the applicable fuel [15]. Hence, it is an alternative selection as a fuel in a direct combustion fuel cell. In direct methanol fuel cell (IMFC) systems need fuel processing device, thus presenting an attractive alternative to the direct methanol fuel cells

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(DMFCs) [16,17]. Therefore, the use of DMFCs as combustion fuel cell has several advantages in comparison to IMFC. Although a lot of progress has been made in the improvement of DMFCs, some of the problems include slow anodic methanol oxidation reaction (MOR) and high cost of noble metal should be overcome [18].

Development electrocatalytic activity toward methanol oxidation is one of the major factors affecting DMFCs performance [19,20]. The production of new catalyst materials with non-noble and noble metals can be improve DMFC anode catalyst performance. Platinum (Pt) catalysts are generally used as best anode catalyst materials in low temperature fuel cells [21]. Pt could hold high electro-oxidation catalytic activity and Pt nanoparticle as an electrode material has recently received much attention due to its some distinguished advantages such as reliability, high stability and significantly large surface areas [22]. The limitation in the use of the Pt for catalyst layers performance comes from high production cost and finite resource of Pt. The use of alloy nanoparticles supporting approach could significantly reduce the Pt content in the DMFC anode catalyst layer without performance decrease [23]. Besides, in the last years, the Pt [24] electro catalysts coupled with row transition metals as catalysts materials such as ruthenium (Ru) [25], nickel (Ni) [26,27], cobalt (Co) [28], iron (Fe) [29], have been improve electrocatalytic oxidation of methanol. Mirzaie et al. [17] studied that synthesis of Pt-Ni/carbon paper electrode for the oxidation of methanol in alkaline direct. Pt-Ni/carbon paper electrode has been successfully synthesized by electrochemical reduction method. Their cyclic voltammetry, chronopotentiometry and electrochemical impedance spectroscopy studies showed that the Pt-Ni/carbon paper electrode indicates a high catalytic activity for the electro oxidation of methanol in an alkaline medium. The carbon materials such as carbon nanofiber (CNF) [30], carbon nanotube (CNT) [31,32] and graphene [33,34] carbon black powder [35] and other [36–39] as catalyst support for DAFCs have been used. In principle, with respect to the mechanism of methanol electro-oxidation on the Pt catalyst, the proposed mechanisms for the adsorption of methanol and the oxidation of CO, according to the simplified reaction:

$$CH_3OH \rightarrow (CH_3OH)_{ads} \quad (1)$$

$$(CH_3OH)_{ads} \rightarrow (CO)_{ads} + 4H^+ + 4e^- \quad (2)$$

$$(CO)_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \quad (3)$$

In the present study, the reduced graphene oxide powder was used as catalyst support to investigate effects of the Pt and bi-metallic Pt-Fe nanoparticles for methanol electro oxidation in acidic media. The Pt and Pt-Fe are synthesized by chemical reduction. The prepared catalysts were characterized by using several techniques such as scanning electron microscopy (SEM), TEM, FT-IR, Raman spectroscopy and, X-ray diffraction (XRD) and energy dispersive analysis of X-ray (EDX). Finally, the electro catalysts were studied by cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry and electrochemical impedance spectroscopy (EIS) in the MOR.

Material and methods

Reagents

Chemical reagents including Methanol, H_2SO_4 (95% purity), H_2PtCl_6 (≥37.50%), Fe $(Cl)_2$, $NaBH_4$ and commercial Pt/C with highest purify available were obtained from Merck (Darmstadt, Germany). All reagents were of analytical grade and used without any purification. All experimental studies were done in distilled water.

Electrochemical measurements

A conventional three-electrode system was used to carry out electrochemical experiments. Ag/AgCl electrode (saturated with KCl) and platinum sheet were used as reference and auxiliary electrodes, respectively. The electrochemical impedance spectroscopy is useful procedure that were carried out at the open circuit voltage (OCV). The frequency range of the EIS measurements was from 50 kHz to 10 mHz. All electrochemical experiments were performed with EG&G PARSTAT 2273 advanced electrochemical analyzer. The morphology of the nanoparticles was observed by field emission scanning electron microscopy (SEM: MIRAll TESCAN) under an acceleration voltage of 15 kV.

Catalyst preparation

Synthesis of Pt/rGO catalyst

The graphene oxide (GO) was prepared from natural graphite by Hummers method and as-synthesized GO was then purified [28]. The reduction of graphene oxide to reduce graphene oxide by the reaction with NaBH4 as a reducing agent. The synthesis of rGO was collected with filtration, several times washed with distillated water and ethanol then dried at 70 °C for 2h.The reduced graphene oxide powder was applied as a support improves properties of catalyst [40]. The samples was synthesized by chemical reduction with NaBH4 of H2PtCl6 as follow: In a typical experiment, the reduced graphene oxide powder were mixed with 2-propanol (1:3) and 25 ml H_2PtCl_6 (0.01 M) and distilled water in glass flaks. The flask was then put in the ultrasonic bath for 30 min. The pH value of the ink was adjusted by NaOH solution to 8 and then raised its temperature to 80 °C. 50 mL of 0.1 M solution of $NaBH_4$ was added into the ink drop by drop. After that, the mixture was washed repeatedly with distilled water. The catalyst powder was dried for 3h at 90 °C.

Synthesis of Pt-Fe/rGO catalyst

Reduced graphene oxide powder as a catalyst support was used in DMFCs. The catalyst was synthesized by chemical reduction with $NaBH_4$ of $FeCl_2$ and chloro platinic acid (H_2PtCl_6) as follow: the reduced graphene oxide powder was ultrasonically dispersed in a mixture of distilled water with 2-propanol (1:3) and 25 ml $FeCl_2$ (0.01 M) and 25 ml H_2PtCl_6 (0.01 M). The pH value of the ink was adjusted by NaOH solution to 8 and then raised its temperature to 60 °C. 100 mL of 0.1 M solution of $NaBH_4$ was added into the ink drop by drop