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Enhanced methanol electro-oxidation activity of Pt/MWCNTs electro-catalyst using manganese oxide deposited on MWCNTs

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ABSTRACT

Electro-oxidation of methanol on platinum nanoparticles supported on a nanocomposite of manganese oxide (MnO_x) and multi-wall carbon nanotubes (MWCNTs) is investigated. The morphology, structure, and chemical composition of the electro-catalysts are characterized by TEM, XRD, EDS, TGA, and H_2-TPR. The electro-catalytic properties of electrodes are examined by cyclic voltammetry, CO-stripping, electrochemical impedance spectroscopy (EIS), and linear sweep voltammetry (LSV). Compared to Pt/MWCNTs, the Pt/MnO_x-MWCNTs electro-catalyst exhibits about 3.3 times higher forward peak current density, during cyclic voltammetry, and 4.6 times higher exchange current density in methanol electro-oxidation reaction. In addition, deposition of manganese oxide onto MWCNTs dramatically increases the electrochemical active surface area from 29.7 for Pt/MWCNTs to 89.4 $m^2\,g^{-1}{}_{Pt}$ for Pt/MnO_x-MWCNTs. The results of long-term cyclic voltammetry show superior stability of Pt nanoparticles upon addition of manganese oxide to the support. Furthermore, the kinetics of formation of the chemisorbed OH groups improves upon manganese oxide incorporation. This leads to a lower onset potential of CO_{ads} oxidation on Pt/MnO_x-MWCNTs than on Pt/MWCNTs.

1. Introduction

Direct methanol fuel cells (DMFCs) have become attractive as portable power sources because of their low pollutants emission, low operating temperature, and high theoretical energy density of methanol (6.1 W h g^{-1}). Methanol electro-oxidation, as the anodic reaction of DMFCs, is a relatively complex electrochemical reaction consisting of several intermediates, which some are strongly adsorbed on the catalysts surface and block their active sites. Therefore, slow kinetics of methanol oxidation reaction (MOR) and poisoning of active sites with residual intermediates are two major problems in commercialization of DMFCs. Among all employed electro-catalysts, platinum-based ones are known as the best choice in low temperature fuel cells such as direct methanol fuel cells [1,2]. However, pure platinum is a rather poor electro-catalyst for methanol oxidation reaction, due to severe poisoning problems. Incorporation of transition metals or their oxides into the electro-catalysts structure is considered as a proper way to enhance the electro-catalytic activity and stability of Pt nanoparticles and reduce the overall cost of DMFCs [3]. Generally, the effect of promoters on electro-catalytic activity of Pt nanoparticles can be explained using two major phenomena: "bi-functional mechanism" and/or "ligand effect" [4–6]. Methanol electro-oxidation reaction on Pt nanoparticles promoted with different metals or metal oxides has been widely addressed in the literature [7–11].

MnO_2 has been utilized as a support for noble metals in catalytic oxidation of CO_{ads} at low temperatures [12]. MnO_2 is also used as a promoter in anodic reaction of light alcoholic fuel cells [13,14]. Zhou et al. reported that MnO_2/PtRu/CNT showed a higher stability for electro-catalytic oxidation of methanol compared to PtRu/MWCNTs [15]. In addition, they have shown that manganese dioxide can prevent dissolution of noble metal clusters on supports. Zhao and his co-workers have studied Pd-MnO_2/MWCNTs electro-catalyst for methanol oxidation in alkaline media and suggested that Pd-MnO_2/MWCNTs had higher electro-catalytic performance than Pd/MWCNTs and Pd/vulcan carbon [16]. Moreover, Peng et al. have reported high ability of CO_{ads} oxidation and excellent methanol electro-oxidation activity for Pt/RuO_2-MnO_2/CNTs [17].

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This work investigates the promoting effect of MnO_x-MWCNTs nanocomposite as a support for Pt nanoparticles in methanol electro-oxidation. The results indicate that MnO_x-MWCNTs support significantly improves the electro-catalytic activity and stability of platinum active sites in MOR.

2. Experimental

2.1. Electro-catalysts preparation and characterizations

Multi-wall carbon nanotubes (MWCNTs) were purified by several washing steps in aqueous solution of hydrochloric acid and nitric acid. The dried sample was then treated at 400 °C in air for 1 h, to eliminate the amorphous carbon. The graphitic surface of purified MWCNTs was treated ultrasonically in a mixture of H_2SO_4 and HNO_3 (3:1 V/V) at 60 °C. In order to prepare MnO_x-MWCNTs nanocomposite, the MWCNTs were dispersed in deionized water. Next, an aqueous solution of manganese nitrate ($Mn(NO_3)_2.4H_2O$) was added drop-wise to the suspension and mixed vigorously. The black colored suspension was treated in an ultrasonic bath for six 10 min intervals. The aqueous suspension was uniformly dried in a rotary evaporator, and then heated in an oven at 80 °C for 12 h. The thus obtained powder was placed into a microwave oven (Black and Baker, MY26 PG, 1000 W), and radiated several times in a pulse mode [18].

In order to precipitate platinum nanoparticles on the supports, a specific amount of MWCNTs (for Pt/MWCNTs) or MnO_x-MWCNTs (for Pt/MnO_x-MWCNTs) was ultrasonically dispersed in 20 ml deionized water. Then, 3.4 ml aqueous solution of hexachloroplatinic acid (75.4 mM) was added dropwise and stirred for 15 min. The pH of the solution was adjusted at 9.0 via addition of proper amount of NaOH aqueous solution. Next, a solution of sodium borohydride ($NaBH_4$) was slowly added to the suspension under vigorous stirring followed by sonication for 30 min. Finally, the reduction reaction was conducted at 30 °C for 24 h. The resultant sample was rinsed with an ample amount of deionized water and dried in a vacuum oven at 70 °C for 8 h.

Morphology of the synthesized electro-catalysts was characterized by transmission electron microscopy (TEM, ZEISS EM 900). The structure of the electro-catalysts was determined by X-ray powder diffraction (XRD) using a PW 1840 Philips diffractometer in the 2θ range of 15–90° at a scanning rate of 0.02 $(2\theta)\ s^{-1}$. Hydrogen temperature-programmed reduction (H_2-TPR) was performed using a Quantachrome CHEMBET-3000 apparatus. The TPR experiments were conducted under a flow of 10 sccm 7.0% hydrogen in argon stream with a heating rate of 10 °C min^{-1} in a temperature range of 100 to 750 °C. Thermal gravimetric analysis (TGA) was carried out under nitrogen atmosphere with a heating rate of 10 °C min^{-1} by a PerkinElmer thermogravimetric analyzer.

2.2. Electrochemical measurements

All electrochemical measurements were carried out in a conventional three electrode cell, in which a Pt plate (5.2 cm^2) and an Ag/AgCl electrode were applied as counter and reference electrodes, respectively. In order to fabricate modified working electrode, 5 mg of prepared electro-catalysts powder was dispersed in a mixture of 50 μl nafion solution and 2 ml ethanol under ultrasonic stirring for 30 min. Then, 6.3 μL of the prepared ink was dropped on the surface of a glassy carbon electrode (0.0314 cm^2) and dried under an ordinary 100 W lamp. Finally, the modified working electrode was heated in an oven at 80 °C for 30 min. All the potentials in this work are given versus Ag/AgCl reference electrode at 25 °C. In addition, all the experiments were carried out in nitrogen bubbled electrolytes using Ivium Stat electrochemical analyzer (Ivium Technologies, Ivium Stat type 10 V/5A).

In order to determine the electro-catalytic activities toward methanol oxidation reaction (MOR), cyclic voltammetry (CV) experiments were conducted in a potential range of -200 to 1200 mV at a scan rate of 50 mV s^{-1}. The electro-catalytic active surface areas (ECSA) were estimated by cyclic voltammetry in 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1}. The exchange current density and Tafel slope for each electro-catalyst were obtained using linear sweep voltammetry (LSV) performed at 25 °C in a deaerated solution of 1 M methanol and 0.5 M H_2SO_4 at a scan rate of 1.25 mV s^{-1}. CO-stripping experiment was performed to investigate the CO tolerance of the electro-catalysts. This experiment was carried out by first bubbling nitrogen gas into the electrolyte for 30 min, then purging CO through the cell for another 30 min. In order to allow the adsorption of CO on the electro-catalyst layer, the potential working electrode was adjusted at -200 mV for 5 min. The dissolved CO was removed by Ar bubbling, and then the CV profile during the first cycle was recorded in a potential range of -200 to 1200 mV at scan rate of 50 mV s^{-1}. Moreover, electrochemical impedance measurements were carried out over a frequency range of 100 kHz - 100 mHz in a constant potential mode at amplitude of 5 mV.

3. Results and discussion

3.1. EDS and TEM analyses

In order to determine the chemical composition of Pt/MnO_x-MWCNTs, energy-dispersive X-ray spectroscopy (EDS) results of Pt/MnO_x-MWCNTs are depicted in Fig. 1. The results confirm that both platinum and manganese oxide species are present on the surface of multi-wall carbon nanotubes. The Pt:Mn atomic ratio is 2.2:1 very close to the nominal ratio of 2:1.

Fig. 2 illustrates the TEM images of the synthesized electro-catalysts, along with the corresponding size distribution of Pt nanoparticles. In the case of Pt/MWCNTs, it is observed that Pt nanoparticles are successfully deposited on multi-wall carbon nanotubes, nevertheless the size distribution is wide from 1 to 10 nm with an extended tail to 14 nm. There is no significant sign of agglomeration of Pt nanoparticles on the composite support, even at the open ends of MWCNTs. On the other hand, in the presence of manganese oxide, very small platinum nanoparticles are

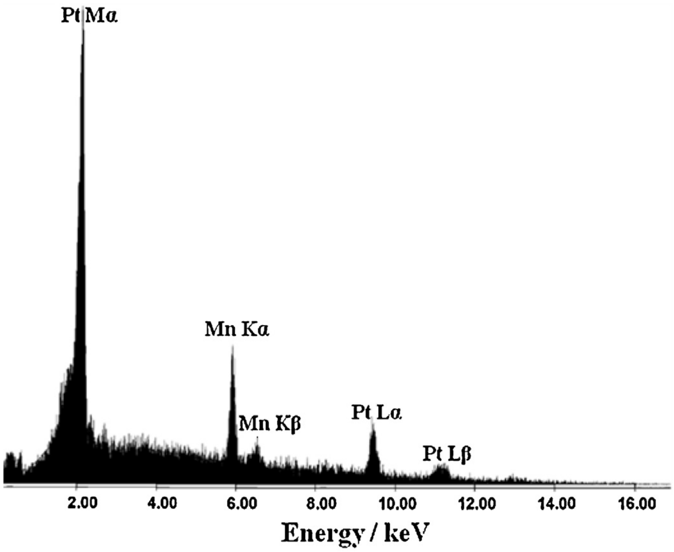

Fig. 1. Energy dispersive spectroscopy analysis of Pt/MnO_x-MWCNTs.