Applied Surface Science 257 (2011) 2923–2928

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

High catalytic performance of Pt nanoparticles on plasma treated carbon nanotubes for electrooxidation of ethanol in a basic solution

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ARTICLE INFO

Article history:
Received 14 September 2010
Received in revised form 12 October 2010
Accepted 18 October 2010
Available online 23 October 2010

Keywords:
Multi-walled carbon nanotubes
Plasma surface modification
Electrocatalysts
Direct ethanol fuel cells
Pt utilization efficiency

ABSTRACT

Nanosized Pt particles deposited on plasma treated multi-walled carbon nanotubes have been used in electrocatalytic oxidation of ethanol in a basic solution. These Pt nanoparticles have very narrow size distribution and exhibit significant higher catalytic activities, higher Pt utilization efficiency (93.77%) and improved durability in comparison to the commercial available Johnson Matthey Pt/C catalyst.

1. Introduction

Direct alcohol fuel cells (DAFCs), identified as an important power source in applications ranging from portable electronic devices to fuel cell vehicles, have been the subject of intense research [1,2]. Currently, research in this field is largely focused on the methanol based fuel cells, e.g. direct methanol fuel cells (DMFCs), due to the easy availability, handleability and transportation of the methanol fuel [3–6]. However, some disadvantages, such as its toxicity, low boiling point and unrenewability, provoke researchers to use other alcohols. Among various alcohols, ethanol is considered most attractive, because it has less toxicity, higher energy density and boiling point relative to other alcohols, and can be easily produced with great quantities by the fermentation of sugar containing raw materials [7–9]. Despite these obvious advantages of ethanol over other alcohols, the recent experimental results [4,10,11], consistent with theoretical analysis, show that the ethanol based DAFCs usually exhibit low performance, which stresses the need for the development of more active electrocatalysts and the optimization of the reaction condition where the formation of poisoning reaction intermediates is minimized.

Pt nanoparticles (NPs) have been demonstrated as an important electrocatalyst in DAFCs [4,12–14]. Due to large surface to volume ratio, these Pt NPs usually exhibit improved catalytic activities relative to their bulk material. Recently, a great deal of synthetic work has been focused on the development of Pt/MWCNTs (multiwalled carbon nanotubes) composites, constructed from deposition of Pt NPs onto the surface of MWCNTs [6,15–17]. It has been demonstrated the deposition onto the surface of MWCNTs can not only prevent Pt NPs from aggregating, but also improve their catalytic activities for their application in DAFCs. However, the chemical inertness of the surfaces of MWCNTs usually leads to weak adhesion and low loading and poor dispersion of metal NPs on MWCNTs [18]. Surface functionalization processes used to create appropriate surface properties for the deposition are therefore required to enhance the adhesivity of the metal NPs and improve the loading and dispersion of metal NPs. Such surface functionalization processes include chemical or electrochemical oxidation of MWCNTs at defect sites [19,20], addition of radicals, nitrenes, or carbenes [21], supramolecular complexation with detergents, proteins, or polymers [22–24], electro-deposition [25], ultrasonication with organic materials [26–28], etc. These surface functionalization approaches, however, inevitably cause the damage to MWCNTs, which may affect their electrical and mechanical properties, or enhance the resistance at the NPs/MWCNTs interface because of insertion of organic materials in between Pt and MWCNTs, which may be the major source of internal resistance, such that the catalytic activities

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doi:10.1016/j.apsusc.2010.10.091

of the Pt/MWCNTs composites will be decreased to a certain extent. Recently, we developed a new, mild surface functionalization process, e.g. plasma surface modification method, to modify the surface of MWCNTs for the deposition of metal Pt NPs [29]. Such plasma treatment technique can offer the MWCNTs appropriate surface for the deposition of Pt NPs, but introduces no exotic organic compounds into the interspace of Pt NPs and MWCNTs and causes less damage to MWCNTs [29–31]. The Pt NPs on these plasma treated MWCNTs (Pt/PS-MWCNTs) exhibit much higher electrocatalytic activities in methanol oxidation in comparison to those on MWCNTs functionalized with other methods [29]. The improvement of the electrocatalytic activities of these Pt/PS-MWCNTs are ascribed to the enhanced metal-support interaction and less structure damage of MWCNTs caused by plasma treatment [29]. Enlightened by this result, we attempt to apply Pt/PS-MWCNTs to the electrocatalytic oxidation of ethanol in a basic solution.

Actually, researches in ion-exchange membrane fuel cells operated at a basic environment, e.g. basic anion-exchange membrane fuel cells (AEMFCs), are receiving growing interests [32,33]. The high pH environment might address some of the shortfalls associated with DAFCs. In an AEMFC, the transportation of charge carriers and the electro-osmosis of water in the membrane are from the cathode to the anode, a direct that is opposite to the transportation of the alcohol crossover from the anode to the cathode. Consequently, a reversed electro-osmotic effect is formed, which may depress alcohol crossover through the membrane accordingly [34]. Furthermore, both electrochemical oxidation of ethanol and oxygen reduction reaction in an alkaline media are much easier than those in an acidic media [35]. However, to become commercially viable, the ethanol based DAFCs have to overcome the barrier of low activity and poor durability of electrocatalysts in the fuel cell electrode [4,36]. The deposition of catalysts onto the surface of PS-MWCNTs is expected to address these issues, because of the enhanced catalyst-support interaction and less structure damage of MWCNTs caused by plasma treatment.

2. Experimental

2.1. Materials

Ethanol, hexachloroplatinic(IV) acid, sodium hydroxide and ethylene glycol (EG) were purchased from Shanghai Chemical Reagent Co. Ltd. Nafion solution DE520 (Dupont®, 5% in isopropanol and water), Johnson Matthey (JM) Pt/C (Johnson Matthey Corp., Pt loading: 40 wt%). These were used without additional purification. The deionized (DI) water through Millipore system (Milli-Q®) with resistivity ∼18.0 MΩ cm^{-1} was used.

2.2. Preparation and purification of MWCNTs

MWCNTs used in this work were synthesized by using chemical vapor deposition (CVD) of acetylene in hydrogen flow at 760 °C using Ni–Fe nanoparticles as catalysts [29]. The obtained MWCNTs were then purified by a strong oxidant and calcined at 500 °C for 4 h in argon to remove carbon nanoparticles and carbonaceous impurities. The catalyst Ni and Fe in purified MWCNTs were measured by inductively coupled plasma-mass spectroscopy (ICP-MS), and the results showed that the contents of Ni and Fe in MWCNTs were less than 0.01% and 0.03%, respectively.

2.3. Plasma surface modification procedure

The synthesis of PS-MWCNTs was performed in a custom-built plasma generator induced by a radio frequency (RF) inductively coupled plasma (ICP). Prior to ignition of the N_2 plasma, the pressure in the reactor was evacuated to 4.0 Pa. Pure N_2 gas was then introduced into the reactor via a gas mass flow controller (MFC) at a flow rate of 10 sccm. Plasma ignition occurred at ∼16 Pa with a frequency of 13.56 MHz and a supplied power of 150 W. MWCNTs were treated by N_2 plasma for 40 min under continuous stirring.

2.4. Preparation of Pt/PS-MWCNTs

The Pt/PS-MWCNTs catalysts were prepared by an EG reduction method [29]. Typically, 500 mg PS-MWCNTs was mixed with 50 mL of EG solution and ultrasonicated for 30 min to get a well dispersed solution. A predefined amount of hexachloroplatinic acid EG solution (7.4 mg Pt mL^{-1} EG) was then added to the solution under agitation. After 4 h, NaOH solution (2.5 M in EG solution) was added to adjust the pH value of solution up to 13, and the solution was then heated to 140 °C and kept at that temperature for 3 h under argon flow. The entire EG solution has a DI water content of ∼5 vol%. During the preparation, a refluxing condition was used to keep water in the reaction system. After reaction, the reaction system was cool down to room temperature. The solid was filtered and washed with 1.5 L of DI water and dried at 70 °C for 8 h.

2.5. Characterization

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) investigations were carried out in a JEOL JEM-2000EX operating at 100 keV and a JEOL JEM-2011 operating at 200 keV, respectively. An X-ray diffraction (XRD) patterns were performed on a D/Max-IIIA X-ray diffractometer (Rigaku Co., Japan), using Cu Kα ($\lambda_{K\alpha1}$ = 1.5418 Å) as the radiation source to identify the crystalline structure and average crystallite size of Pt particles. The weight percent of catalysts deposited on functionalized MWCNTs was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Jarrell-Ash model ICAP 9000).

2.6. Electrochemical measurements

1 M NaOH and 1 M NaOH + 1 M ethanol aqueous solution were selected as the electrolyte solutions for the electrochemically active surface area (ECSA) and ethanol electrooxidation measurements, respectively, and both solutions were deaerated with N_2. The electrochemical measurements were measured at the scan rate of 50 mV s^{-1} at 20 °C using an Autolab potentiostat/galvanostat (IM6e, Zahner, Germany) in a three electrodes and one compartment configuration cell. A Pt wire was served as the counter electrode and a KCl saturated Ag/AgCl electrode as the reference electrode. All potentials in this work were quoted against Ag/AgCl (KCl (sat.)). For comparison purposes, a conventional electrode made with commercially available JM Pt/C was also evaluated. A predefined amount of Pt/PS-MWCNTs catalysts with different weight percents of Pt loading and a commercially available JM Pt/C catalyst with Pt weight percent of 40 wt% were added to 1 mL 2-propanol, which were then shaken for 30 min in an ultrasonic bath to form slurry. This slurry was brushed onto a piece of carbon paper (0.4 cm × 0.6 cm; HCP020P) and dried in an oven at 80 °C for 20 min to remove the solvent. The weight of the carbon paper with dry Pt/PS-MWCNTs nanocomposites was measured and subtracted from that before coating of the slurry to obtain the loading of metal-carbon nanocomposites. Experiments were controlled so that Pt/PS-MWCNTs catalysts and JM Pt/C catalyst were obtained the predefined amount of Pt loaded on the electrode, which were later used as working electrodes for electrochemical measurements. A 100 μL amount of 5 wt% Nafion solution DE520 was spread on top of the carbon nanocomposite layer and dried at 80 °C. Nafion acted as a protective layer to prevent loss of catalyst powder into the electrolyte solution. The electrodes were activated by cycling