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Improvements of electrocatalytic activity of PtRu nanoparticles on multi-walled carbon nanotubes by a H_2 plasma treatment in methanol and formic acid oxidation

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ABSTRACT

A H_2 plasma has been used to treat the PtRu nanoparticles supported on the plasma functionalized multi-walled carbon nanotubes (PtRu/PS-MWCNTs). The plasma treatment does not change the size and crystalline structure of PtRu nanoparticles, but reduces the fraction of the oxidized species at the outermost perimeter of particles. The electrochemical results show that these plasma treated PtRu/PS-MWCNTs exhibit increased electrochemically active surface area, improved electrocatalytic activity and long term stability toward methanol and formic acid oxidation, and enhanced tolerance to carbonaceous species relative to the sample untreated with the H_2 plasma. The electrocatalytic activities of the plasma treated PtRu/PS-MWCNTs are found to be dependent upon the Pt:Ru atomic ratios of PtRu nanoparticles. The catalysts with a Pt:Ru atomic ratio close to 1:1 show superior properties in the electrooxidation of methanol and formic acid at room temperature and better tolerance to carbonaceous species.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs), such as direct methanol fuel cells (DMFCs) and direct formic acid fuel cells (DFAFCs), conducting the conversion of energy from organic fuels into electricity via direct electrochemical reactions, have been identified as one of the important energy sources showing a wide range of applications from small sensors and portable electronic devices up to automobiles [1,2]. Their desirable attributes, including high energy-conversion efficiency, high power density, and low pollutant emission, have triggered tremendous research interest across many scientific disciplines [3,4]. Over the years, a great deal of such research interest has been focused on the development of catalysts of higher activity and tolerance to carbonaceous species [5,6]. Because the occurrence of energy conversion in a PEMFC is mainly at the surface of catalysts used, the design of catalysts of higher efficiency and improved tolerance to carbonaceous species are of great importance to improve and maintain the performance of the PEMFC [7,8].

Currently, the most widely utilized catalysts in PEMFCs are platinum (Pt) or Pt-based nanoparticles due to their significantly higher electrocatalytic activities for fuel electrooxidation [9–12]. A severe problem associated with pure Pt nanoparticles is their lower tolerance to carbonaceous species, such as CO. The pure Pt catalysts are known to rapidly lose their activities due to the block of active sites by the adsorption of carbonaceous species produced in the electrooxidation of fuels [13]. Recent synthetic work therefore mainly focuses on the development of Pt-based alloy nanoparticles [4,14–16]. Studies have shown that Pt based bimetallic or multimetallic alloy nanoparticles exhibit improved electrocatalytic activities and enhanced tolerance to carbonaceous species [17,18]. Among various types of Pt-based alloy nanoparticles, PtRu nanoparticles have been reported to have high catalytic activities toward fuel oxidation and are considered the most effective in reducing the poisoning of carbonaceous species [13,19]. However, the catalytic activities of PtRu nanoparticles and their tolerance to carbonaceous species are strongly dependent upon their relative atomic compositions [4,5,14,20–22]. Although much work has been done to investigate the influence of the composition on the catalytic activities of PtRu nanoparticles and their tolerance to carbonaceous species, controversies still exist. For example, Hsieh et al. and Gu et al. [17,23] demonstrated that the PtRu nanoparticles with an atomic ratio close to 50:50 exhibited a higher electrocatalytic activity and better tolerance to carbonaceous species than those with other atomic ratios, while Xu et al. [24] reported that the PtRu nanoparticles with an atomic ratio of 70:30 possessed a higher electrocatalytic activity and best tolerance to carbonaceous

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species. Therefore, for the rational design of catalysts of higher efficiency, it remains important to optimize the composition of PtRu nanoparticles.

In PEMFCs, Pt and Pt-based alloy nanoparticles used as catalysts are required to be well separated to increase the surface area accessible to fuel electrooxidation. In this sense, special supports are usually employed [4,13,21,23,25–27]. It has been demonstrated that the use of the supports could effectively prevent the particles from aggregation, which improves the accessibility of nanoparticles to the redox reaction and correspondingly their catalytic activities [22,28–31]. The most widely applied supports are undoubtedly carbon nanotubes (CNTs) which are characterized to be with special electronic and mechanical properties that are beneficial for their use as supports in PEMFCs. Greater power densities for the Pt supported on CNTs (Pt/CNTs) in the oxygen reduction reaction of DMFCs than those on other supports has been reported in the literatures [18,19,27]. However, the problem is that the pristine surface of the CNTs is rather inert, which makes the deposition of metal nanoparticles difficult [32]. In addition, their hydrophobic graphene structure tends to form agglomerates due to van der Waals interaction, which further increases the difficulties for the dispersion of nanoparticles on CNTs. For being with suitable surface properties for metal deposition, CNTs are therefore necessary to be surface modified. Extensive studies have demonstrated that the approaches used for the CNTs surface modification had dramatic effects on the electrocatalytic activities of metal nanoparticles deposited on them [33,34]. A mild surface modification technique might be desired to obtain higher electrocatalytic activities of Pt/CNTs due to the preservation of the unique structures and properties, such as intact graphene structure, high surface area, good electronic conductivity, strong mechanical properties and high chemical stability, of CNTs during the surface modification processes. As reported in our previous work [33,34], the metal Pt nanoparticles supported on multi-walled CNTs (MWCNTs) functionalized by a mild plasma technique (Pt/PS-MWCNTs) exhibited a higher catalytic activity in the methanol electrooxidation.

Another important issue, as occasionally noted, is the effects of the surface composition and the state of metal nanoparticles on the electrocatalytic activities of these particles [35]. The metal nanoparticles obtained from the presently existing preparation methods are inevitably coordinated with oxygen at their outermost perimeter although the majority of the surface atoms are in the 0-valence metallic form [35,36]. The presence of these oxidized species on the surface of nanoparticles was stated to decrease the activities of these catalysts [35]. However, due to the lack of a means to effectively control the fraction of oxidized species, this effect has not been experimentally demonstrated previously. We recently demonstrated that the fraction of oxygen coordinated metal atoms at the surface could be greatly decreased when the PtRu/PS-MWCNTs were treated with a H_2 plasma. These plasma treated PtRu/PS-MWCNTs were reported to exhibit increased electrochemically active surface areas (EASA), improved electrocatalytic activities toward ethanol oxidation and enhanced tolerance to carbonaceous species [37]. This indicates that the H_2 plasma treatment is an potential way to improve the electrocatalytic properties of PtRu nanoparticles.

As two of important types of PEMFCs, DMFCs and DFAFCs have received particular attention in recent years, due to their superior properties of high-energy conversion efficiency, low-pollutant emission, low operating temperature, and simplicity of handling and processing of liquid fuel [38–40]. To be practically viable, it is generally required that the catalysts used for DMFCs and DFAFCs possess high activities and tolerance to carbonaceous species. In this work, we demonstrate that the plasma treatment used to reduce oxygen coordinated metal atoms at the nanoparticle surface can also greatly increase the electrocatalytic activity of PtRu/PS-MWCNTs toward methanol and formic acid oxidation. These plasma treated PtRu/PS-MWCNTs are found to exhibit increased EASA, improved activity and stability toward the electrocatalytic oxidation of methanol and formic acid, and enhanced tolerance to carbonaceous species relative to the sample untreated with the H_2 plasma. The electrochemical impedance spectroscopy (EIS) studies suggest that the H_2 plasma treated PtRu/PS-MWCNTs have lower charge transfer resistance for methanol and formic acid oxidation. In addition, the influence of the Pt:Ru atomic ratios of PtRu nanoparticles on the catalytic activities of the H_2 plasma treated PtRu/PS-MWCNTs are investigated. It shows that the catalysts with a Pt:Ru atomic ratio close to 1:1 show superior properties than those with other Pt:Ru atomic ratios, such as much higher catalytic activity and long term stability in the electrooxidation of methanol and formic acid at room temperature and better tolerance to carbonaceous species.

2. Results and discussion

2.1. Characterization of PtRu/PS-MWCNTs electrocatalysts

The MWCNTs used in the present work are synthesized by a chemical vapor deposition (CVD) technology using Ni–Fe nanoparticles as catalysts, as reported in our previous work [33,34]. These MWCNTs are then purified to remove carbon nanoparticles and carbonaceous impurities. To create appropriate surface for the deposition of metal nanoparticles, the purified MWCNTs are functionalized via a plasma treatment in a N_2 environment, as described in Section 4. The plasma treatment has been identified as a relatively mild surface functionalization approach, which can effectively protect MWCNTs from the structural destructions possibly caused by the other functionalization methods [33,34]. The functionalized MWCNTs are terminated with –COOH, –OH and a trace amount of $-NH_2$ which endow them with a hydrophilic surface, facilitating their dispersion in an aqueous solution and the subsequent uniform growth of metal nanoparticles on their surface [33,34].

The synthesis of PtRu metal alloys is conducted by a reported method with HCHO as the reducing agent [27]. The growth of the metal nanoparticles onto the plasma treated MWCNTs depends on the strong binding interactions between the metal nanoparticles and the surface functional groups. The average size and the Pt:Ru atomic ratio of the PtRu nanoparticles on the PS-MWCNTs can be well controlled by the reaction parameters, such as reaction time and amounts of the Pt and Ru precursors added into the reaction mixture prior to the metal reduction, respectively. In the present work, three different PtRu nanoparticles with an average size of 1.4 nm and the respective Pt:Ru atomic ratios of 38:62, 47:53, and 60:40 (determined by an energy-dispersive X-ray (EDX) spectroscopic analysis as shown in Fig. S1) are fabricated. Fig. 1 shows a typical TEM image of PtRu/PS-MWCNTs with the Pt:Ru atomic ratio of 47:53. Clearly, the PtRu nanoparticles supported on the PS-MWCNTs have relatively narrow size distributions, with an average particle of 1.4 nm (as demonstrated from the size distribution histogram of PtRu nanoparticles shown in Fig. 1c) and no free nanoparticles observed.

The alloy structure of the PtRu nanoparticles can be demonstrated from the XRD analysis. As shown in Fig. 2, the XRD pattern of the PtRu/PS-MWCNTs with the Pt:Ru atomic ratio of 47:53 before the H_2 plasma treatment shows a combination of diffraction peaks from MWCNTs and materials with a face-centred cubic (fcc) structure, without any other diffraction peaks observed that could be assigned to metal Ru nanoparticles which usually exist with a hexagonal structure [19]. The assignments of the diffraction peaks are shown in Fig. 2. The peak around $2\theta = 26^\circ$ is assigned to the