



TiO₂ nanoparticles promoted Pt/C catalyst for ethanol electro-oxidation

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ABSTRACT

A simple and efficient method to enhance the activity of Pt/C catalysts for direct ethanol fuel cells (DEFCs) by ultrasonically mixing commercial Pt/C catalyst and TiO₂ nanoparticles is reported. In this novel composite anode catalyst, the as-prepared TiO₂ nanoparticles are dispersed homogeneously in the interspaces of Pt based C nanoparticles, resulting in a great deal of TiO₂-Pt-C interfaces, which greatly accelerate the ethanol electro-oxidation reaction. Cyclic voltammetry (CV), CO stripping, chronoamperometry and electrochemical impedance spectroscopy (EIS) measurements confirm that this composite catalyst structure has excellent activity and stability toward ethanol and CO electro-oxidation compared to the pure Pt/C catalyst. Particle size and content of TiO₂ are also discussed with respect to effect on catalyst performance.

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1. Introduction

Direct alcohol fuel cells (DAFCs) are very attractive nowadays as power sources for mobile and portable applications [1–3]. Consequently, oxidation of small organic molecules has been studied extensively over the past several decades. In DAFCs, ethanol has its unique advantages and proves to be a promising option as fuel due to its high energy density and environmental friendship [4]. It can be produced in large quantities from the fermentation of biomass and both ethanol and its final oxidation product, carbon dioxide, are relatively non-toxic. Platinum is generally considered to be the best monometallic catalyst for the electro-oxidation of small organic molecules. Therefore, most studies focused on platinum-based catalysts and many achievements typically in elucidating the reaction mechanism, identifying the intermediates, and enhancing the catalyst activity have been obtained [5–15]. However, the price of Pt is high and its superior catalytic activity drops severely with time when traces of carbon monoxide are present due to poisoning effect caused by CO-like species [15,16]. In recent years, efforts have been made to minimize the use of precious metal by introducing some other kinds of metal into the catalyst such as Pt-based binary (PtRu, PtSn, etc.) [17–19], ternary (PtRuNi, PtRuIr, etc.) [20,21] and quaternary (PtRuOsIr, etc.) [22], and diminish the CO poisoning effect by introducing some metal oxides into the catalyst such as CeO₂ [16], SnO₂ [23], RuO₂ [13] and ZrO₂ [24], etc. For example, Cao et al.

[13] recently reported a novel nano-composite Pt/RuO₂-H₂O/CNT catalyst which showed excellent performance compared with the benchmark PtRu/C catalyst. Scibioh et al. [25] reported a Pt-CeO₂/C anode catalyst for direct methanol fuel cells replacing Ru by CeO₂ in PtRu/C catalyst. The above referred metal oxides have received considerable attention for they all have fluorite structure whose cations can switch between +3 and +4 oxidation states and have the ability to act as an oxygen buffer [26] which is involved in promoting the CO removal from Pt during the electro-oxidation [25].

Semiconductor TiO₂ has large band gap which can also serve as oxygen buffer and is already proved an effective photocatalyst to carry out methanol oxidation under UV excitation [27]. In fact, Kamat and co-workers [27] also found that TiO₂ can improve the performance of the Pt–Ru catalyst for methanol oxidation without UV excitation, namely in darkness, by diminishing CO poisoning effects. In this paper we explored the effect of TiO₂ nanoparticles in the aspect of removing CO from Pt surface and revealed a simple and efficient method to enhance the activity of Pt/C catalysts for direct ethanol fuel cells (DEFCs) by ultrasonically mixing commercial Pt/C catalyst and TiO₂ nanoparticles. In the meanwhile, the effect of TiO₂ particle size and content on catalyst performance was investigated.

2. Experimental

2.1. Synthesis and characteristics

All the reagents used in this study are of analytical grade if not specified. For the synthesis of TiO₂ nanoparticles, K₂C₂O₄ solution was added drop-wise with constant stirring into the tetrabutyl

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titanate solution maintaining a pH value of 10. The resultant precipitation was filtrated and washed with deionized water and ethanol repeatedly, and then dried at 80 °C for 12 h. This precipitation and KNO_3 were mixed efficiently in a mortar at a molar ratio of 1:3. The mixture was calcined at 500 °C for 3 h, and then cooled to ambient temperature. The product was immersed in deionized water, washed and filtered repeatedly to remove the residual fluxes. Finally, the product was dried at 120 °C to obtain the TiO_2 nanoparticles (denoted as as-prepared TiO_2) with the BET surface area of 136.8 m^2/g . Degussa P25 TiO_2 nanoparticles of 80% anatase and 20% rutile with high purity (denoted as P25) were used as commercially received with the BET surface area of 54.2 m^2/g . The morphologies of the TiO_2 nanoparticles, Pt/C catalyst and Pt/C + TiO_2 composite catalyst were examined by transmission electron microscope (TEM, JEOL model JEM-1200EX) and scanning electron microscope (SEM, LEO1530) in which EDS analysis was used to analyze the element distribution in the catalyst architecture. The structure of TiO_2 nanoparticles was examined by X-ray diffraction (XRD) analysis using the Rigaku X-ray diffractometer with Cu $\text{K}\alpha$ -source. The 2θ angular region between 20° and 80° was explored at a scan rate of 6° min^{-1} with step of 0.02°.

2.2. Working electrode preparation

The Pt/C catalyst ink was prepared by mixing the Pt/C catalyst (E-Tek, 20 wt.% Pt) with perfluorsulfonic acid solution (5 wt.%, Nafion®, DuPont), ethylene glycol (EG) and deionized water ultrasonically. For the case of Pt/C + TiO_2 catalyst ink, TiO_2 nanoparticles were first dispersed in deionized water ultrasonically, and then mixed with Pt/C, Nafion®, and EG ultrasonically. The resulting slurries were spread onto gold patches of ca. 1.0 cm^2 (1 cm × 1 cm). Then the electrodes were dried at 80 °C in air with the catalyst loadings of about 0.1 mg Pt/ cm^2 .

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a three-electrode cell using a Solartron SI1287/1255B workstation at 25 °C. A saturated calomel electrode (SCE) and Pt gauze were used as reference and counter electrodes, respectively. All electrode potentials in this paper were referred to the SCE. A solution of 1 M ethanol + 1 M HClO_4 was used as electrolyte. Several activation scans were performed until reproducible voltammograms were obtained. Cyclic voltammograms (CV) were recorded from -0.2 to 1.0 V at a scan rate of 50 mV/s. The oxidation of pre-adsorbed CO was measured by CO stripping voltammetry in 1 M HClO_4 solution at a scan rate of 10 mV/s. All the currents in this paper are specific currents (i) normalized to mass of Pt. The experimental error in voltage measurements during CV test in this work was within 5 mV. Electrochemical impedance spectroscopy (EIS) was carried out for the Pt/C, Pt/C + 20 wt.% TiO_2 , and Pt/C + 20 wt.%P25 catalysts at 0.45 V in a solution of 1 M ethanol + 1 M HClO_4 with a frequency range from 1 MHz to 0.5 Hz.

3. Results and discussion

3.1. Morphological characterization and proposed mechanism

Fig. 1 shows the XRD pattern of as-prepared TiO_2 nanoparticles and all the sharp peaks can be indexed to the anatase TiO_2 which means that the structure of the as-prepared TiO_2 nanoparticles is uniformly anatase.

Fig. 2(a) and (b) shows the TEM images of as-prepared TiO_2 nanoparticles and Pt/C (E-Tek, 20 wt.% Pt) catalyst, respectively. The carbon nanoparticles have an average size of about 30 nm while TiO_2 nanoparticles have an average size of about 10 nm. Fig. 2(c)

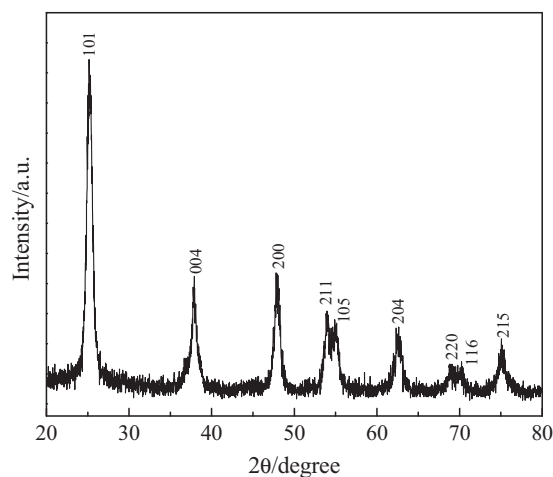


Fig. 1. XRD pattern of as-prepared TiO_2 nanoparticles.

shows the SEM image of the as-prepared catalyst architecture of Pt/C + 20 wt.% TiO_2 , with the inset showing the enlarged part. In order to reveal the actual architecture of catalyst in the electrode, the SEM sample was made through the same procedure as the working electrode preparation except that the resulting slurry was spread onto the SEM supporter. Fig. 2 (d) and (e) shows the element distribution positions of Ti (from TiO_2) and Pt (from Pt/C) for the selected position in Fig. 2 (c) by EDS. It can be seen that the distribution of elements Pt and Ti is homogeneous in the catalyst architecture which means that Pt/C nanoparticles and TiO_2 nanoparticles can be dispersed evenly in the catalyst system by ultrasonically mixing. This can result in a great deal of TiO_2 -Pt-C interfaces and may promote the electro-oxidation of adsorbed CO species on Pt surface, as demonstrated in Fig. 2(f).

Fig. 2(f) shows the schematic diagram of structure of Pt/C + TiO_2 catalyst. The right part shows the mechanism of CO oxidation at the interfaces of TiO_2 /Pt. Kamat et al. [27] have proved that TiO_2 improves the performance of the Pt-Ru catalyst in darkness, indicating possible surface area improvement or diminished poisoning effects. In our experiments, there is no obvious improvement of surface area of Pt through adding TiO_2 . The electrochemically active surface (EAS) of Pt is 58.5 m^2/g and 61.2 m^2/g before and after adding TiO_2 . An EAS improvement of 4.6% may not account for more than a 50% improvement of ethanol oxidation current from 412.3 mA/mg Pt to 647.6 mA/mg Pt before and after adding TiO_2 as shown in Fig. 3(a). Data in Fig. 3(a) will be discussed in more detail later. It is well known that in fuel cells some oxides such as SnO_2 [28], RuO_2 [13], TiO_2 [29] can promote the CO removal and improve the catalyst activity by supplying active oxygen species. This encourages us to investigate the relationship between the big improvement of ethanol oxidation current and the TiO_2 -accelerated oxidation of CO species. Detailed intermediates and sub-products (such as acetaldehyde and acetic acid) are not discussed here since reaction mechanism of ethanol electro-oxidation involves several steps and products from Ethanol oxidation still remain a great challenge [30].

3.2. Cyclic voltammetry and chronoamperometry analysis

Fig. 3(a) shows CV curves of ethanol electro-oxidation on Pt/C catalyst and Pt/C + 20 wt.% TiO_2 catalyst, while Fig. 3(b) shows the stability of Pt/C + 20 wt.% TiO_2 catalyst for ethanol electro-oxidation. It can be seen from Fig. 3(a) that ethanol oxidation on Pt/C + 20 wt.% TiO_2 catalyst has higher electro-catalytic current than on Pt/C catalyst over the whole scanning voltage range. Correspondingly, the peak current of ethanol oxidation on

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