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Ethanol electro-oxidation on catalysts with TiO_2 coated carbon nanotubes as support

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Abstract

Pt–TiO_2/CNTs electrocatalysts for direct ethanol fuel cells (DEFCs) were prepared by sol–gel and ethylene glycol reduction method. XRD and TEM showed that the size of the Pt particles on TiO_2/CNTs is 3.5–4 nm and with narrow particle size distribution. HRTEM revealed that a thin layer of uniform amorphous TiO_2 on CNTs was formed and the faces of the Pt crystal on Pt–TiO_2/CNTs catalysts were quite ‘‘rough’’ and ‘‘rounded’’ and some grain bounders and/or twins also appeared. The electrochemical studies using cyclic voltammetry (CV), chronoamperometry and CO stripping voltammetry indicate that Pt–TiO_2/CNTs catalysts have higher electro-catalytic activity and CO-tolerance for ethanol oxidation than Pt/C (20 wt% Pt, E-TEK) and Pt/CNTs catalyst in acid. The Pt/TiO_2 molar ratio was also optimized and proved that 1:1 was the best Pt/TiO_2 molar ratio.

Keywords: Pt–TiO_2/CNTs; Electrocatalyst; Ethanol electro-oxidation; Direct ethanol fuel cells

1. Introduction

The low kinetic of electro-oxidation of alcohol is still the main obstacle for the commercialization of direct alcohol fuel cells (DAFC) [1–5]. Recently some papers have reported that the addition of oxide is efficient to improve catalytic activity of platinum and its CO-tolerance for alcohol electro-oxidation. Qiu [6,7] and Vatistas et al. [8] have found that RuO_2 can enhance the catalyst activity in acid solution for methanol electro-oxidation. Olivi [9] and Xin [10] have reported, respectively, that the addition of SnO_2 can promote the catalyst activity for methanol and ethanol oxidation. ZrO_2 [11], CeO_2 [12] and MgO [13] were also studied and found they can improve the catalytic activity and CO-tolerance in alkaline solution for ethanol electro-oxidation, but it is well known that alkaline aqueous solutions are not stable for DAFC owing to the carbonation, and the Nafion membrane, which is very popular to use in DAFC, can only be used in acid. So it is better to find a new catalyst that not only can enhance the catalytic activity and CO-tolerance for ethanol electro-oxidation, but also can be used in acid.

TiO_2, as one of the semi conductive oxide, has been widely studied for its special photoelectric properties. In addition, TiO_2 is very stable in acidic solution and it has been reported that TiO_2 electrode as the support of Pt [14,15] or PtRu [16] has high catalytic activity and CO-tolerance for alcohol electro-oxidation because the interaction between Pt and TiO_2. Herein, we prepared TiO_2 coated carbon nanotubes (TiO_2/CNTs) by a sol–gel method, and used them as catalyst support of platinum. The electrochemical activity for ethanol oxidation and CO-tolerance were investigated by using cyclic voltammetry (CV), chronoamperometry and CO stripping voltammetry at 25 °C in acid solutions.

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2. Experimental

2.1. Preparation and characterization of Pt–TiO_2/CNTs catalyst

TiO_2/CNTs catalyst was prepared using tetrabutyl titanate as precursors. First, tetrabutyl titanate was dissolved in ethanol with agitating to get a 10% solution, and then the solution was slowly dropped into acetic acid solution (which contained 10% acetic acid and 56% ethanol)to get the sol, diluted to 5% by adding the ethanol. The CNTs (MWNTs were used) were put into the diluted sol, agitating for 20 min, dried at 80 °C in an oil bath and then calcined at 600 °C for 2 h to get TiO_2/CNTs. Pt–TiO_2/CNTs catalysts were prepared by reducing of chloroplatinic acid with ethylene glycol on TiO_2/CNTs powders. The amount of tetrabutyl titanate was controlled by the Pt/TiO_2 molar ratio in the final catalyst. The nominal loading of Pt in the catalyst was 20 wt%.

The morphology of the catalyst was observed by TEM (JEM-1200EX) at 100 kV for conventional and HRTEM (JEM-2010) equipped with an energy-dispersive X-ray detector (EDX) for high resolution imagine. X-ray diffraction (XRD) analysis was performed using the Rigaku X-ray diffractometer with Cu Kα-source. The 2θ angular regions between 20° and 90° were explored at a scan rate of $6°\ \text{min}^{-1}$ with step of 0.02°. The elemental composition of the catalyst was investigated by energy-dispersive X-ray (OXFORD INCA 300) attached to scanning microscope (JSM-6301F).

2.2. Electrochemical assessment of catalysts and determination of ethanol oxidation activity

The catalysts slurry was casted onto a gold electrode (1 cm in diameter) to determine their ethanol oxidation activity. The catalyst slurry was prepared by mixing the calalysts with distilled water and Nafion (20% Nafion and 80% ethylene glycol) solution under sonicate for 20 min. After casting, the catalysts were air-dried for 60 min at 80 °C.

Electrochemical measurements were carried out in a three-electrode cell with Solartron workstation at room temperature. The gold electrode (1 cm in diameter) coated with catalyst ink was used as working electrode. 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 1.0 M perchloric acid or 1.0 M ethanol + 1.0 M perchloric acid was used as electrolyte. All the reagents used were of analytical grade. The cyclic voltammetry data for ethanol electro-oxidation were recorded in the potential range of −0.2 to 1.0 V *vs.* SCE with a scan rate of $50\ \text{mV s}^{-1}$ and the chronoamperometric curves were recorded at 0.45 V for 3600 s.

The CO stripping voltammetry was measured in the potential range of −0.2 to 1.0 V with a scan rate of $10\ \text{mV s}^{-1}$. Before CO is adsorbed at 0.1 V, the catalyst was cycled in N_2-saturated solution (the content of N_2 in the used gas is 99.999%) until a well-established cyclic voltammogram was observed. After forming a saturated CO adlayer (holding at 0.1 V for 20 min in CO-saturated solution), the electrolyte was purged with N_2 (20 min) again to remove the dissolved CO from the electrolyte solution. If there were no special indication, the testing result for Pt–TiO_2/catalyst is 1:1 molar ratios of Pt and TiO_2.

3. Results and discussion

3.1. Structure and morphology

Fig. 1a and b shows the TEM images of Pt supported on TiO_2/CNTs. Mean particle size of prepared Pt was estimated to be 3.5–4 nm with narrow particle size distribution. The characteristic XRD peaks of platinum in Fig. 2d can be indexed as the face-centered cubic phase and the particle size calculated from Pt (220) using Scherrer formula after background subtraction is about 3.7 nm, which is agreed well with the results of TEM observation. Comparing the XRD patterns of Pt/CNTs, Pt–TiO_2/CNTs, it is easy to find that there is no any shift in the diffraction peaks of platinum indicating that the addition of TiO_2 has no effect on the crystalline lattice of platinum in Pt–TiO_2/CNTs catalysts. It can also be found that there is no diffraction peak of TiO_2 in the XRD patterns of TiO_2/CNTs and Pt–TiO_2/CNTs, which means that the prepared TiO_2 is amorphous. This can be confirmed from high-resolution electron microscopy (HRTEM) and energy-dispersive X-ray (EDX) analyses. In Fig. 3a, a layer of uniform amorphous TiO_2 on CNTs can be clearly seen and the thickness of the TiO_2 is about 4–5 nm. The EDX analyses carried out on the amorphous layer proved the presence of TiO_2. The HRTEM image, depicted in Fig. 3b, reveals that although the basic shape of Pt particles on TiO_2/CNTs is face-centered cubic (as described in Fig. 2), the faces of the crystal are quite "rough" and "rounded", and some defects, such as grain bounders and/or twins have also appeared on the surface of Pt–TiO_2/CNTs catalysts. From the above analysis, it appears that the uniform amorphous TiO_2 layer and irregular surfaces of nano-platinum particles may play an important role in synergetic interaction between Pt and TiO_2.

3.2. Ethanol electro-oxidation

The typical cyclic voltammogram curves for ethanol electro-oxidation on Pt/CNTs, Pt–TiO_2CNTs were shown in Fig. 4, where CV curves of Pt/C (20 wt% Pt, E-TEK) were also presented for comparison. It can be seen that ethanol oxidation began at approximately 0.51 V for Pt–TiO_2/CNTs and reached its current peak at about 0.8 V. On the reverse sweep, re-oxidation of ethanol began at approximately 0.78 V and reached a peak current density at around 0.68 V, after which strongly bonded surface inter-