

Preparation of Pt/CeO₂-ZrO₂/carbon nanotubes hybrid catalysts for methanol electrooxidation

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Received 15 April 2013; accepted 20 June 2013

Pt/CeO₂-ZrO₂/multi-walled carbon nanotubes composites have been synthesized for the application of catalyst in direct methanol fuel cells. The introduction of CeO₂-ZrO₂, which has high surface area and oxygen storage capacity, can eliminate the toxic gases at low temperature. Electrocatalytic activity and stability of Pt/CeO₂-ZrO₂/MWCNT catalysts for methanol oxidation have been investigated with cyclic voltammetric and chronoamperometric techniques. Electrochemical measurements demonstrate that the Pt/CeO₂-ZrO₂/MWCNT catalysts exhibit superior electrocatalytic activities as compared with Pt/CeO₂/MWCNT and Pt/MWCNT catalysts. The peak current density of Pt/CeO₂-ZrO₂/MWCNT catalysts for methanol electrooxidation is 3.9 times as high as that of Pt/MWCNT catalysts. The outstanding performance is likely to be due to the co-catalytic effect of CeO₂-ZrO₂ and the deposition manner of Pt nanoparticles.

Keywords: Catalysts, Electrocatalysts, Electrooxidation, Fuel cells, Methanol electrooxidation, Electrochemical deposition, Platinum, Ceria, Zirconia, Carbon nanotubes

Considerable efforts have been made to develop different kinds of green energies to power portable devices such as cell phones and computers. Direct methanol fuel cell (DMFC) has recently emerged as one of the most promising candidates and has been widely studied due to its high energy density and ease of handling a liquid fuel¹. In the standard DMFC device, liquid methanol is oxidized to carbon dioxide at the anode². Pt-based anode electrocatalysts exhibit excellent performance in catalyzing the dehydrogenation of methanol. However, it is well-recognized that different intermediate chemisorbed species such as HCHO, HCOOH and CO are produced during the electrochemical oxidation reaction of methanol, which block the catalytic active sites of Pt catalyst, and hence inhibit the oxidation reaction^{3,4}. Significant efforts have been dedicated to

overcome the disadvantage of Pt catalysts. For example, several different platinum-based alloys, such as the bicomponent catalysts Pt-Ru⁵, Pt-Sn⁶ and the tricomponent catalysts Pt-Ru-X (X = W, Cu, Au, Ni, Fe)^{7,8}, have been proposed as novel catalysts for DMFC application. In addition, mixed oxides, which are known as excellent catalysts for CO oxidation, have also been employed as the alternative materials based on so-called bifunctional mechanism⁹.

In our work, Pt/CeO₂-ZrO₂/MWCNT catalysts have been designed for application in DMFC. CeO₂-ZrO₂ solid solutions, which display high activity and good stability, have been reported to exhibit high oxygen storage capacity (OSC)¹⁰. They also exhibit high activity for eliminating toxic gases such as CO at low temperature¹¹. CeO₂-ZrO₂ is expected to provide oxygen to promote the oxidation of intermediates (CO) produced during the electrochemical oxidation reaction of methanol. MWCNTs have been extensively applied as electrode materials and good supports for the dispersion of noble metal. Pt and Pt-based electrocatalysts supported on the MWCNTs exhibit high electrocatalytic activity in methanol oxidation due to their large surface area on the supports¹².

The formation of Pt/CeO₂-ZrO₂/MWCNT catalysts, if properly developed, would improve the CO tolerance performance, and thus promote the practical application of DMFC. In our previous work, the stable CeO₂-ZrO₂ solid solutions with remarkable properties such as high surface area and high OSC have been successfully synthesized via a sonochemical method¹³. Therefore, we have proposed the synthesis of CeO₂-ZrO₂/MWCNT composites by sonochemical method for supports of Pt catalysts. And Pt nanoparticles were electrochemically deposited on the surface of CeO₂-ZrO₂/MWCNT composites. The as-prepared Pt/CeO₂-ZrO₂/MWCNT catalysts were investigated in detail as catalyst for methanol electrooxidation.

Experimental

The multi-walled carbon nanotubes (MWCNTs) (purity >95%) were prepared by the chemical vapor deposition method. These MWCNTs were 1-2 μ m in length with diameter of 20-40 nm. Raw MWCNTs

were purified by oxidation with nitric acid at 140 °C for 4 h. A facile, low-temperature solution approach with ultrasound was employed to generate CeO₂-ZrO₂/MWCNT composites. In a typical synthesis route, purified MWCNTs (1 g) was dispersed into deionized water (50 mL), and added to 50 mL of aqueous solution containing (NH₄)₂Ce(NO₃)₆ (0.1096 g) and Zr(NO₃)₄·5H₂O (0.0858 g). Then, polyethylene glycol (PEG) 600 was added to the above solution until its content (w/w) was up to 2%. Dilute aqueous ammonia (2.6 M) was added dropwise to the aforementioned mixture with vigorous stirring until precipitation was complete (pH = 9). Subsequently, 5 mL of NaOH solution (0.3 M) was added for mineralization and the colloidal precipitate was exposed to high-intensity ultrasound irradiation under ambient air for 2 h with a pulse of 5 s on and 5 s off. The temperature was kept under 323 K throughout the reaction with a cooling system. After cooling to room temperature, the precipitate was centrifuged, washed several times with deionized water and absolute ethanol in sequence to remove the surfactant. The obtained CeO₂-ZrO₂/MWCNT composite was characterized by powder X-ray diffraction (XRD, Cu - K α radiation, λ = 1.5418 Å), field emission scanning electronic microscope (FESEM, JEOL model JSM-6700F) with an energy dispersive spectroscopy (EDS) probe for the analysis of composition and transmission electron microscopy (TEM, JEOL model JEM-1200EX).

The electrochemical deposition of platinum nanoparticles on the surface of CeO₂-ZrO₂/MWCNT was performed on the electrochemical workstation (CHI660a, Shanghai Chenhua, China) using a conventional three-electrode system at 25 °C. A platinum wire was employed as the counter electrode, Ag/AgCl electrode was used as the reference electrode and the modified glassy carbon electrode (GCE) was employed as the working electrode. All potential values were referenced to Ag/AgCl.

The working electrode was prepared as follows: About 2 mg support material such as CeO₂-ZrO₂/MWCNT, CeO₂/MWCNT and MWCNT composites was dispersed in 1 mL chitosan (CHIT, 1 mg mL⁻¹) solution with sonication treatment to get a highly dispersed colloidal solution. CeO₂-ZrO₂/MWCNT solution (8 μ L) was cast on GC electrodes, and then dried in air at room temperature.

Before the electrochemical deposition of platinum, the obtained GC electrode was swept for 40 cycles in

the potential range of -0.2 - 0.9 V in 0.5 M H₂SO₄ solution at a scan rate of 50 mV s⁻¹ to get the activated electrode. Then the electrochemical deposition of platinum on the activated electrode was performed for different cycles in a bath containing 2.5 mM H₂PtCl₆ and 0.5 M H₂SO₄. The potential ranged from -0.2 to 0.9 V at a sweep rate of 50 mV s⁻¹. After 20, 30 and 50 cycles of electrodeposition, the Pt loading in Pt/CeO₂-ZrO₂/MWCNT hybrid catalysts were 14, 17, 20 wt %, respectively.

Cyclic voltammetry (CV) and chronoamperometric measurements were employed to study electrocatalytic properties of the catalysts. All electrochemical experiments were performed in the CHI660A three-electrode cell. Hydrogen adsorption cyclic voltammograms were recorded in 0.5 M H₂SO₄ solution. The electrochemical active surface (EAS) of platinum for the catalysts was estimated from the area of the hydrogen adsorption region. The electrocatalysis activity of the catalysts was measured with cyclic voltammetry in a bath containing 0.5 M H₂SO₄ and 1 M CH₃OH, with the potential ranging from -0.3-1.0 V at a scan rate of 50 mV s⁻¹. Chronoamperometric measurements for the catalysts were made for 3000 s at a fixed voltage of 0.6 V in a mixture solution of 0.5 M H₂SO₄ and 1 M CH₃OH.

Results and discussion

The TEM image of CeO₂-ZrO₂/MWCNT composites is shown in Fig. 1a. It can be observed that CeO₂-ZrO₂ nanoparticles are well dispersed on the MWCNTs support, and only a few particles are aggregated together. The powder XRD patterns of CeO₂-ZrO₂/MWCNT are shown in Fig. 1b. The XRD patterns indicate that the structure of CeO₂-ZrO₂ is Fm-3m fluorite structure with the corresponding diffraction peaks of (111), (200), (220) and (311). Figure 1c demonstrates the EDS analysis of CeO₂-ZrO₂/MWCNT composites shown in Fig. 1a. The presence of elements Ce, Zr, O and C can be clearly observed, and the atomic ratio of Ce:Zr is 1:1 according to the EDS results.

The electrochemically active surface area (EAS) of Pt particles for Pt/CeO₂-ZrO₂/MWCNT catalysts was estimated by the hydrogen adsorption plot. The cyclic voltammograms of Pt/CeO₂-ZrO₂/MWCNT catalysts with different Pt loading of 14, 17, 20 wt % were recorded in 0.5 M H₂SO₄ without methanol (Fig. 2). As is shown in Fig. 2, the hydrogen adsorption-desorption peaks, H_{A1} and H_{D1}, are assigned to the Pt(110) crystal plane, and the hydrogen adsorption-desorption peaks,

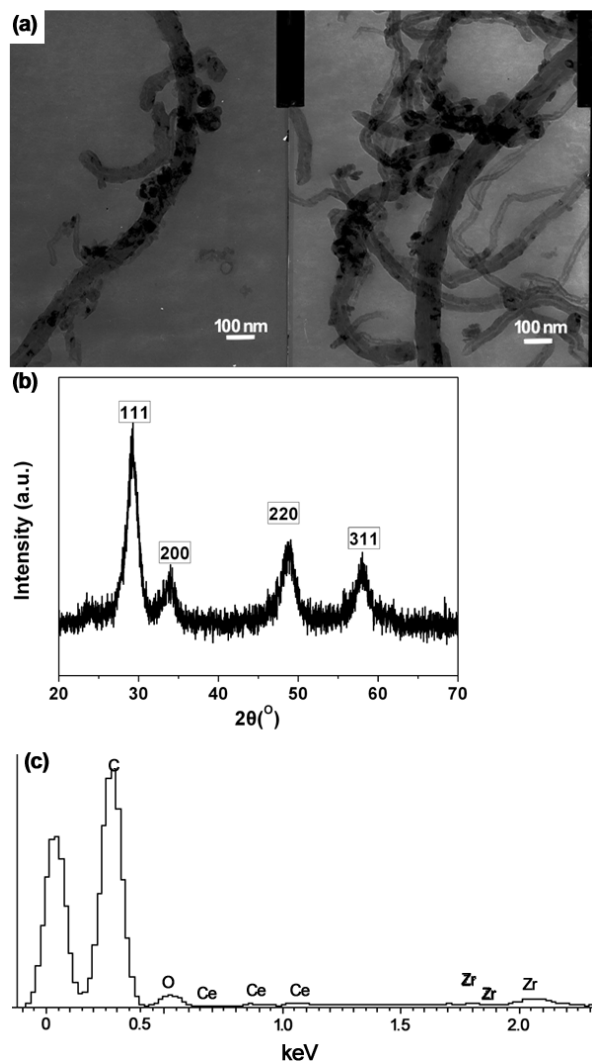


Fig. 1 – (a) TEM images of CeO₂-ZrO₂/MWCNT, (b) XRD patterns of CeO₂-ZrO₂/MWCNT, and, (c) EDS of CeO₂-ZrO₂/MWCNT.

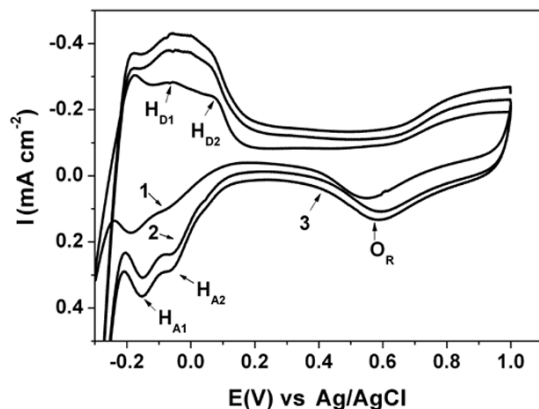


Fig. 2 – Cyclic voltammograms of Pt particles for Pt/CeO₂-ZrO₂/MWCNT catalysts in 0.5 M H₂SO₄ with varying Pt loadings. [Pt loading (wt %) = 1, 14; 2, 17; 3, 20].

H_{A2} and H_{D2}, are assigned to the Pt(100) crystal plane¹⁴. These features are in accordance with the typical voltammetric profile of Pt surfaces¹⁵. The significant hydrogen adsorption shows that CeO₂-ZrO₂ does not block the catalytic sites of Pt. This is probably due to our synthetic route, wherein we prepared the CeO₂-ZrO₂/MWCNT composites first, and then the Pt nanoparticles were electrochemically deposited on its surface. This route ensured that Pt nanoparticles were on the outermost part of the Pt/CeO₂-ZrO₂/MWCNT catalysts. Hence, the active sites of Pt were not blocked by CeO₂-ZrO₂. In Fig. 2, there also exists a peak O_R associated with the reduction of platinum oxide, which is another evidence for the presence of Pt particles. The above evidences demonstrate that Pt particles have been successfully deposited on the surface of CeO₂-ZrO₂/MWCNT and the Pt nanoparticles possess good catalytic activities. The electrochemically active surface (EAS) areas of Pt particles can be calculated from the CV curves by the following equation¹⁶,

$$EAS(m^2 / (gPt)) = \frac{Q_H}{0.21 \times 10^{-3} C \times M_{Pt}}$$

where Q_H is the amount of charge exchanged during the hydrogen atom electro-adsorption and M_{Pt} is the platinum loading (mg cm⁻²) on the working electrode. The EAS areas of Pt particles for Pt/CeO₂-ZrO₂/MWCNT catalysts with different Pt loading of 14, 17, 20 wt% are 19.9, 24.5 and 27.7 m² g⁻¹, respectively.

The catalytic properties of Pt/CeO₂-ZrO₂/MWCNT and Pt/MWCNT catalysts with 20 wt % Pt loading were characterized by cyclic voltammetry. In an earlier work, the rare earth oxide CeO₂ has been studied as co-catalyst with Pt for the electrooxidation of methanol¹⁷. For comparison, the Pt/CeO₂/MWCNT catalysts with 20 wt % Pt loading were prepared and tested by the same method. Figure 3a presents the CVs obtained in a 0.5 M H₂SO₄ and 1 M CH₃OH solution. The potential was swept in the range from -0.3-1.0 V at a scan rate of 50 mV s⁻¹. As is shown in Fig. 3a, there is a well defined oxidation peak for the oxidation of methanol at about 730 mV in the positive direction sweep. In the negative direction sweep, an oxidation peak appears at about 500 mV. This peak is due to the electrooxidation of the surface-absorbed and incompletely oxidized intermediates generated during the oxidation of methanol. The peak current density of Pt/CeO₂-

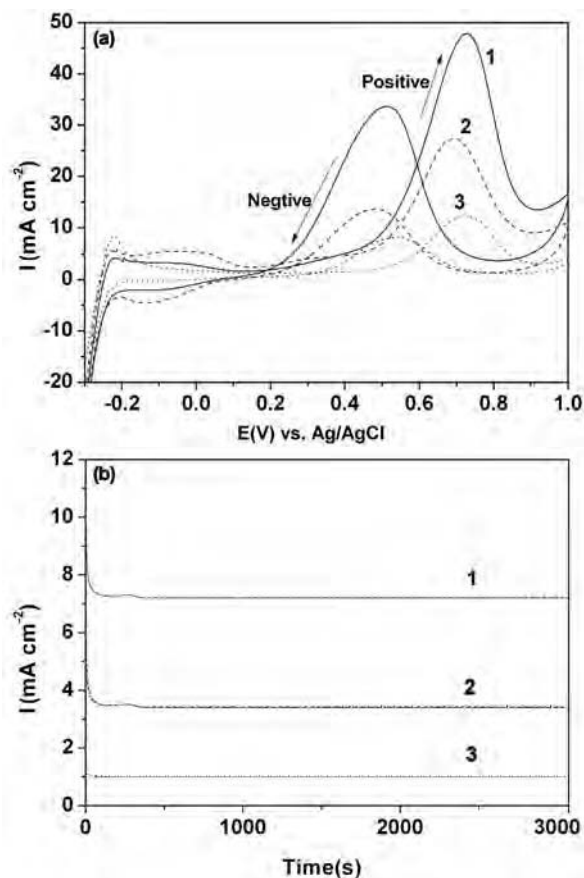


Fig. 3 – (a) Cyclic voltammograms of (1) Pt/CeO₂-ZrO₂/MWCNT, (2) Pt/CeO₂/MWCNT and (3) Pt/MWCNT catalysts in 0.5 M H₂SO₄ and 1 M CH₃OH solution at a scan rate of 50 mV s⁻¹, (b) Chronoamperometric curves for (1) Pt/CeO₂-ZrO₂/MWCNT, (2) Pt/CeO₂/MWCNT and (3) Pt/MWCNT catalysts in 0.5 M H₂SO₄ and 1 M CH₃OH solution at 0.6 V for 3000 s.

ZrO₂/MWCNT catalysts reaches 47.9 mA cm⁻² during the forward scan. The corresponding peak current density is 27.4 and 12.3 mA cm⁻² for Pt/CeO₂/MWCNT and Pt/MWCNT catalysts, respectively. The peak current density of Pt/CeO₂-ZrO₂/MWCNT catalysts is about 3.9 times as that of Pt/MWCNT catalysts. However, there is no distinct difference between the H region areas of the three different electrodes. CeO₂-ZrO₂ and CeO₂ can thus be employed as co-catalyst, which would promote the electrooxidation of methanol with the same electrochemical active surface of platinum. The excellent catalytic performance of Pt/CeO₂-ZrO₂/MWCNT catalysts is attributed to the higher oxygen storage capacity of CeO₂-ZrO₂, which has been reported in literature^{10,13}.

The electrocatalytic activity and stability of Pt/CeO₂-ZrO₂/MWCNT, Pt/CeO₂/MWCNT and

Pt/MWCNT catalysts were measured by chronoamperometric technique. As is shown in Fig. 3b, all the three curves exhibit typical current density-time associated with methanol oxidation. The current density of Pt/CeO₂-ZrO₂/MWCNT catalysts declines relatively slowly and maintains a near stable value after about 3000 S. The current density, maintained for Pt/CeO₂-ZrO₂/MWCNT catalysts, is evidently the highest in these three samples, which indicates the superior catalytic performance of these catalysts. This agrees well with the results of cyclic voltammetry. Pt/CeO₂-ZrO₂/MWCNT catalysts display the best long-term performance amongst these three catalysts.

In the present study, the application of Pt/CeO₂-ZrO₂/MWCNT catalysts, synthesized with the electrochemical technique, in direct methanol fuel cells was investigated for the first time. In the hybrid catalyst, CeO₂-ZrO₂ acted as a co-catalyst which could promote the electrooxidation of surface-absorbed intermediates generated during the electrochemical oxidation of methanol. Pt/CeO₂-ZrO₂/MWCNT catalysts exhibited better catalytic activities and long-term stability for methanol oxidation, which is attributed to the high OSC and good catalytic activity for CO oxidation of CeO₂-ZrO₂. These results suggest that Pt/CeO₂-ZrO₂/MWCNT hybrid composites prepared with this method is a promising and inexpensive candidate for methanol oxidation anode catalyst.

Acknowledgement

This work was financially supported by the National Natural Science Foundation of China (21003079), Research Award Fund for Outstanding Middle-Aged and Young Scientist of Shandong Province (BS2011CL020), Natural Science Foundation of Shandong Province (ZR2011BM018) and Qingdao Project of Science and Technology (12-1-4-3-(20)-jch).

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