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Short communication

Investigation of PdSn nanometals alloy supported on spherical TiO_2 for methanol electro-oxidation

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ABSTRACT

A novel PdSn/TiO_2 electrocatalyst for methanol oxidation is fabricated by the surface reductive deposition method using spherical TiO_2 nanoparticles as support. The structural and electrochemical properties of the PdSn/TiO_2 catalysts are characterized by X-ray diffraction, transmission electron microscopy and electrochemical analysis. Under appropriate composition and uniform dispersion of PdSn alloy nanoparticles on the surface of the TiO_2, the new catalyst has shown promising electrocatalytic activity for methanol oxidation reaction (MOR) and anti-poisoning ability. The MOR mechanism of the PdSn/TiO_2 catalyst mainly results from the photocatalytic process of composite TiO_2 material that has high catalytic activity without ultraviolet light illumination. The PdSn/TiO_2 catalyst might become a promising candidate for direct methanol fuel cell.

1. Introduction

The direct methanol fuel cell (DMFC) is one of the most promising portable power sources for mobile electronic devices. DMFCs offer advantages such as relatively high specific energy, convenient storage of fuel, and low operating temperature [1,2]. Among the critical components of DMFC, the anode electrocatalyst is crucial for its performance [3]. Platinum is a well-known electrocatalyst for the methanol oxidation reaction (MOR) at room or moderate temperature. However, pure platinum behaves poorly because it can be easily poisoned by absorbing CO or CO-like species [4,5]. To overcome such a disadvantage, other platinum-based catalysts have been widely investigated by employing a secondary metal to assist the complete oxidation of methanol to CO_2, through the electronic effect, bifunctional mechanism, and geometric effect [4,6]. Among these known binary catalysts, PtRu is a widely employed electrocatalyst for DMFC, having the highest activity toward MOR [7–10], however its price is high (in part due to high loading of PtRu), and it does not retain activity for long-term application (due to Ru dissolution). PtSn is another extensively studied catalyst, and its activity is comparable to that of PtRu, however its disadvantages are similar to that of PtRu [11–13].

Recently, the application of TiO_2 and TiO_2 composite materials, either in single form as support or in combination with PtRu, has shown its promise for improving the activity of catalysts and reducing the loading of noble metal Pt and/or PtRu in fuel cell operation. TiO_2-based materials have unique advantages including low cost, commercial availability, and stability in water [14–16]. Chen et al. [17], Tian et al. [18] and Kim et al. [19] reported that the presence of TiO_2 could enhance the dispersion of the electrocatalyst particles on carbon carrier and help the PtRu catalyst to better electro-oxidize the methanol. Kamat et al. [20] also found that TiO_2 could improve the performance of the Pt–Ru catalyst for methanol oxidation without ultraviolet (UV) excitation, namely in darkness, by diminishing CO poisoning effects. However, the loading of Pt or PtRu in these catalysts was still high, and study of using non-Pt material (such as the combination of Pd, Ni, Sn and Ag with TiO_2) for methanol oxidation is still lacking.

In this paper, a novel non-Pt electrocatalyst (PdSn/TiO_2) for methanol oxidation was fabricated by using spherical TiO_2 nanoparticles as support. The PdSn/TiO_2 catalyst was synthesized by the surface reductive deposition method. The structural and electrochemical properties of the PdSn/TiO_2 catalysts were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and electrochemical analysis. It is shown that the MOR mechanism and high performance of the PdSn/TiO_2 catalyst is mainly attributed to the photocatalytic process of the TiO_2 composite material that has high catalytic activity without UV light illumination.

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2. Experimental

2.1. Preparation of spherical TiO_2 nanoparticle

The TiO_2 nanopowder was prepared by sol–gel method, where surfactant (PEG600 or CTAB) was added in the precursor solution, forming sol and gel under continual stirring. The gel was dried at 80 °C in a vacuum chamber after several days, and the spherical TiO_2 nanoparticles were obtained after calcination at 550 °C for 3.5 h.

2.2. Preparation of $PdSn/TiO_2$ electrocatalysts

The $PdSn/TiO_2$ electrocatalysts were prepared by the surface reductive deposition method. Spherical TiO_2 nanoparticles were firstly dispersed in deionized water, and then stir mixed with appropriate volume of $PdCl_2$ solution (0.01 mol L^{-1}) and $SnCl_2 \cdot 2H_2O$ solution (0.01 mol L^{-1}). The atomic ratio between Pd and Sn was adjusted as 1:1, 2:1, and 3:1, respectively, in different samples. Next, the solution was adjusted to pH 10.8 with $NH_3 \cdot H_2O$. After a homogeneous suspension was formed, 2 wt% KBH_4 was added to the mixture under steady stirring. The resulted precipitate was collected by filtration, washed several times with deionized water and dried at 70 °C in a vacuum. The $PdSn/TiO_2$ catalyst was confirmed with a 3 wt % PdSn loading.

2.3. Physicochemical characterization

XRD pattern of the sample was collected in the range 20–80^0 using a Rigaku D/max-rB X-ray diffractometer (CuKα radiation, $\lambda = 1.5406$ Å), operated at 40 kV and 100 mA. The surface morphologies and particles were observed by TEM (JEOL JEM-1203).

2.4. Electrochemical characterization

The electrochemical measurements were performed on a CHI 660C workstation (American CHI instrument). The electrochemical cell consisted of a tri-electrode system with platinum wire as counter, a saturated calomel electrode as reference, and a modified carbon paste electrode (CPE) as working electrode, respectively. The preparation of CPE was based on a previous report [21]. The $PdSn/TiO_2$ catalyst of 5 mg was mixed completely with paraffin of 30 μL and some VulcanXC-72 in the evaporating dish, followed by evaporation of the water under vacuum. The mixture was finally packed into an electrode cavity of Teflon (3-mm diameter, 5-mm depth). Electrical contact to the paste was established by placing a copper rod into the back of the mixture. The polished and modified electrode was used as the working electrode. The cyclic voltammograms and chronoamperograms were conducted in the solution of 1 mol L^{-1} H_2SO_4 and 1 mol L^{-1} methanol, 2 mol L^{-1} methanol and 4 mol L^{-1} methanol, respectively, at room temperature with the purge of N_2 at a scan rate of 50 mV s^{-1},100 mV s^{-1} and 200 mV s^{-1}. For comparison purpose, the reference commercial catalyst of 20 wt% PtRu/C was acquired from E-TEK.

3. Results and discussion

Fig. 1 shows the XRD pattern of the TiO_2 and $PdSn/TiO_2$ catalysts with different Pd to Sn atomic ratios. The XRD patterns of $PdSn/TiO_2$ in Fig. 1 exhibit characteristic reflections, arising from not only the anatase but also the rutile structure of TiO_2. The peaks located at 2θ values of about 25.4°, 37.8°, 48.2° and 54.4° were the (101), (004), (200) and (204) diffraction peaks of the anatase TiO_2, and the peaks located at 2θ values of about 27.5° and 36.2° were the (110) and (101) diffraction peaks of the rutile TiO_2. Indeed, pure TiO_2 and $PdSn/TiO_2$ catalysts with anatase and rutile structures could make them having higher catalytic activity than that of only anatase or rutile structure [22,23]. Compared with the pure TiO_2, the characteristic peak of anatase and rutile in the $PdSn/TiO_2$ catalyst with different Pd to Sn atomic ratio shifted from 25.7° and 27.8° to about 25.4 and 27.5°, indicating that the deposition of PdSn alloy nanoparticles on the surface of spherical TiO_2 influenced its structure and catalytic activity. Two characteristic peaks corresponding to (111) and (200) planes of the face-centered cubic (fcc) crystalline of Pd can be observed in Fig. 1. The corresponding 2θ values located at 39.96° and 46.3° were shifted shorter as compared to the 2θ values of 40.1° and 46.4° for pure Pd fcc. The corresponding 2θ values located at 26.5°, 33.8° and 51.9° associated with the (111),(101) and (201) diffraction peak of Sn were exactly the same as that of pure Sn fcc structure, implying that the PdSn alloy nanoparticles had single-phase-disordered structures, and the lattice constants were enlarged because of the Sn substitution in Pd fcc-center. The average size of the pure TiO_2 particles, and that of $PdSn/TiO_2$ catalysts with the Pd to Sn atomic ratio of 1:1, 2:1 and 3:1, was about 24.6 nm, 25.4 nm, 26.8 nm, and 27.5 nm, respectively (estimated by the Debye–Scherrer equation [24]). The rise of the particle size of $PdSn/TiO_2$ would decrease the contacting area with methanol and reduce the catalytic activity of the $PdSn/TiO_2$ catalyst.

Fig. 2 shows TEM images of the $PdSn/TiO_2$ catalyst, where the overall size of the particles ranged from 20 to 30 nm and the particles exhibited fine spherical feature with some PdSn alloy particles about 1–2 nm dispersed on the surface. The spherical feature of TiO_2 would make it be of large surface area and preferable to the dispersion of PdSn alloy particle, improving the catalytic activity of $PdSn/TiO_2$. The PdSn nanoparticles dispersed more uniformly on the surface of the $PdSn/TiO_2$ catalyst, when the Pd to Sn ratio is 1:1 and 3:1 than that of 2:1. The $PdSn/TiO_2$ catalyst with the Pd to Sn ratio of 2:1 had some aggregation, resulting in the small rise of particle size, the decrease of contacting area with methanol and reducing the catalytic activity. The TEM results are consistent with that of XRD catalysis.

The electrochemical oxidation of 1 M H_2SO_4 and 2 M CH_3OH solution was used to test the catalytic activity of $PdSn/TiO_2$catalysts. Fig. 3a shows the cyclic voltammograms for methanol electro-oxidation of $PdSn/TiO_2$ and TiO_2 at a scan rate of 100 mV s^{-1}. In Fig. 3a, on the scan to positive potentials from −0.2 V to 1.2 V, the onset of 0.42 V and a large methanol oxidation peak was observed at 0.734 V, 0.706 V and 0.719 V, respectively, for the Pd to Sn ratio of 1:1, 2:1 and 3:1. No oxidation peak of intermediates such as CO or CO-like species could be found, implying that the $PdSn/TiO_2$ catalysts had good anti-poisoning ability for methanol oxidation. No current peaks of methanol oxidation corresponded TiO_2 was observed in Fig. 3a, which means that the pure TiO_2 had no electrocatalytic activity for methanol oxidation. It was obvious that the deposition of PdSn on the surface of spherical TiO_2 nanoparticles gives rise to the activity in methanol oxidation of the $PdSn/TiO_2$ catalyst.

Compared with the cyclic voltammograms for methanol electro-oxidation of the commercial PtRu/C catalyst in Fig. 3b (whose methanol oxidation peak potential is about 0.7 V), the methanol oxidation peak potential of the current $PdSn/TiO_2$ catalyst was higher. The better catalytic activity of the $PdSn/TiO_2$ is consistent with our previous study [25] and literature [19,26,27]. Among the three samples investigated, the catalytic activity of the catalyst with the Pd to Sn ratio of 1:1 was the highest while the catalytic activity of the catalyst with the Pd to Sn ratio of 2:1 was the lowest whose particle size was neither the biggest nor the smallest, suggesting that appropriate composition of PdSn on the surface of spherical TiO_2 nanoparticles would be preferable to improve its catalytic activity for methanol oxidation. In other words, the dispersion and composition of PdSn on the surface of TiO_2 is the key for $PdSn/TiO_2$ (and the size of the nanoparticle is relatively less important).

Cyclic voltammograms of $PdSn/TiO_2$ catalysts with the PdSn atomic ratio of 1:1 in 1 M H_2SO_4 and different methanol concentration of 1 M, 2 M, 4 M at a scan rate of 100 mV s^{-1} were presented in Fig. 4. When the methanol concentration increased from1 M to 4 M, the methanol