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Short communication

An opposite change rule in carbon nanotubes supported platinum catalyst for methanol oxidation and oxygen reduction reactions

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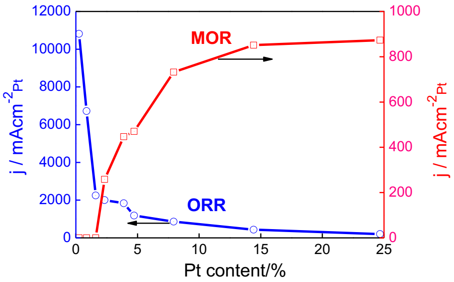
HIGHLIGHTS

- A series of carbon nanotubes supported Pt (Pt/CNTs) with same size of Pt are prepared.
- Oxygen reduction (ORR) and methanol oxidation (MOR) reactions are studied contrastively.
- Pt/CNTs show an opposite change rule for ORR and MOR along the different Pt loadings.
- The proton transfer is the key factor to determine the MOR activity.
- The reasons for the intrinsic difference between for ORR and MOR are revealed.

GRAPHICAL ABSTRACT



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ABSTRACT

The electrocatalytic performances of carbon nanotubes supported platinum (Pt/CNTs) with different Pt loadings for oxygen reduction reaction (ORR) and methanol oxidation (MOR) are studied contrastively. Pt/CNTs showed an opposite change rule along different Pt loadings for ORR and MOR, which is discussed based on the charge transportation and mass transfer. The results show that at low Pt loading, proton conduction is the key factor, which determines the MOR activity; at high Pt loading, mass transfer is crucial, which decides the ORR activity of Pt/CNT catalysts. The viewpoint proposed in this paper can guide the design and preparation of Pt based catalysts for the commercialization of direct methanol fuel cells.

1. Introduction

Direct methanol fuel cells (DMFCs), as a clear and efficient electrochemical energy conversion system, have received much attention with a wide range of potential application. In the recent twenty years, although tremendous efforts have been devoted to develop the alternative catalysts due to the Pt scarcity and cost, generally speaking, in acidic medium, Pt and Pt-based catalysts are still the most practical oxygen-reduction reaction (ORR) and methanol-oxidation reaction (MOR) catalysts at the current stage of technology [1,2]. Besides the scarcity and the cost, another drawback with Pt-based catalyst for DMFC is the methanol diffusion across the membrane to cathode, which causes significant deterioration of cathode performance due to the mixed potential caused by the two simultaneous reactions of ORR and MOR at the cathode.

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Because Pt possesses good catalytic activity for ORR and MOR, it seems impossible for Pt based catalyst to eliminate this drawback. However, in our recent work, we found an interesting phenomenon [3]. The carbon nanotube supported Pt catalyst (Pt/CNT) showed high activity for ORR but had hardly activity for MOR when the Pt loading was lower than 1 wt%, which means that Pt catalyst has selectivity for ORR and MOR when designed rationally. This inspired us to acquire deeper insights into the reasons for Pt showing such intrinsic difference for MOR and ORR, which is very crucial for the design of Pt-based catalyst for the commercialization of DMFC.

In this work, a series of Pt/CNT catalysts with different Pt loadings were prepared. Their morphologies and activities for ORR and MOR were investigated. The reasons for the intrinsic difference between for ORR and MOR were revealed.

2. Experimental

CNTs were provided by Shenzhen Nanotech Port Co., Ltd. Before use, it was treated by a well-known acid oxidation method to introduce oxygenous groups for the subsequent immobilization of Pt. Pt/CNTs catalyst was prepared as follows [4]. Treated CNTs were added to ethylene glycol under constant stirring for 10 min. Then appropriate amounts of H_2PtCl_6 and KOH were added with constant stirring. The slurry was refluxed at 140 °C for 2 h to ensure the complete reduction of Pt (IV). The solid product was rinsed repeatedly with deionized water, and dried in vacuum at 70 °C for 12 h. For comparison, 5% RuO_2/CNTs were prepared [4], and then Pt was deposited on RuO_2/CNTs with the same procedure as Pt/CNTs to obtain Pt/RuO_2/CNTs (1 wt% Pt). The as-prepared Pt/CNTs (14.4 wt% Pt) were diluted homogeneously with the above treated CNTs to obtain Pt/CNTs-D (1 wt% Pt).

Electro-Probe Microanalyzer (EPMA, EPMA-1600, Shimadzu Corporation) was used to determine the content of Ru and Pt in the catalyst. High resolution transmission microscopy (HTEM, JOEL, JEM-2010HT) was used to characterize the morphology of the catalysts.

Electrochemical measurements were carried out at room temperature in a three-electrode cell connected to computer-controlled Autolab PGSTAT30 electrochemical analyzer (Eco Chemie B. V., Utrecht, Netherlands). The preparation of electrodes was described in our previous paper in detail [5]. A glass carbon electrode coated with 0.02 mg catalyst was used as the working electrode. An Ag/AgCl electrode and a Pt electrode were used as reference and counter electrodes, respectively. Cyclic voltammogram (CV) curves for ORR were recorded in 1 M O_2-saturated $HClO_4$ solution with a scan rate of 100 mV s^{-1}. The MOR activity was measured also by CV in 1 M CH_3OH with 1 M $HClO_4$ as electrolyte at 25 °C with a scan rate of 100 mV s^{-1}. For the electrochemical active surface area (EAS) measurement, the CV curve of pre-adsorbed CO electro-oxidation was recorded from −220 to 900 mV versus Ag/AgCl [6].

3. Results and discussion

Fig. 1 shows the HTEM images and particle size distributions of Pt/CNTs with different Pt loadings. It can be seen that the density of Pt nanoparticles on the surface of CNTs increased with the Pt loading increasing. While the size of Pt nanoparticles changed little ranging from 3.41 to 3.68 nm for Pt loadings from 0.87 wt% to 14.42 wt%, indicating the effect of particle size on activity may be excluded.

The electrocatalytic activities of ORR and MOR of the Pt/CNTs with different Pt loadings were tested by CV. The transformation CVs based on mass of Pt loaded on electrode for ORR and MOR were shown in Figs. 2 and 3, respectively. It was proven that CNTs performed no ORR activity without Pt deposition in acidic medium [3]. Fig. 2 shows the 0.26%-Pt/CNT catalyst possessed outstanding ORR peak current of 5.1 A mg^{-1}_{Pt}, which is five times as much as that of Pt nanoparticles with a diameter of 3 nm that had the maximum mass activity reported by Perez-Alonso et al. [7]. However, from Fig. 3, it can be seen that Pt/CNT catalysts with Pt loadings of 0.26 wt% and 0.87 wt% showed no MOR activity. The MOR activity began to appear and increase when the Pt loading was larger than 2.33 wt% and then became stable with the Pt loading further increasing. For clarity, the relationship between the electrocatalytic activities of ORR and MOR and the Pt loadings were shown in Fig. 4. From Fig. 4, it can be seen that the variation of curves based on the mass-specific activity agrees well with that of based on EAS-specific

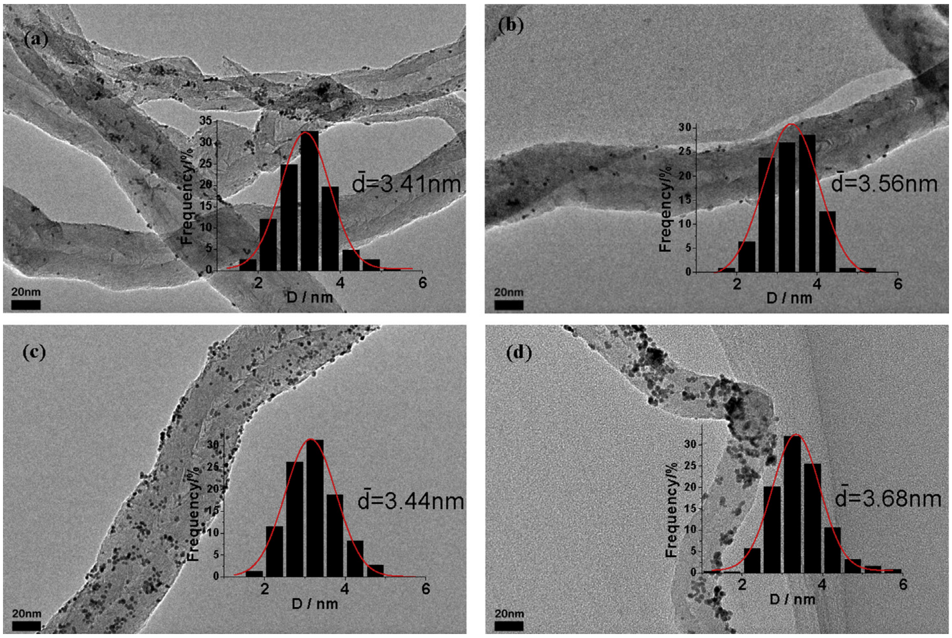

Fig. 1. TEM photos of Pt/CNTs with different Pt loadings: (a) 0.87%, (b) 1.61%, (c) 4.73% and (d) 14.42%.