The origin of the high performance of tungsten carbides/carbon nanotubes supported Pt catalysts for methanol electrooxidation

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1. Introduction

Catalysts are the key materials in the polymer electrolyte membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs) [1]. Pt is still the most commonly used catalyst for both anode and cathode in PEMFCs and DMFCs. However, the high cost and limited resources of Pt hinder fuel cell commercialization. Therefore, the development of the new alternative catalysts to reduce or replace expensive Pt is necessary [2–4]. Another serious problem is that Pt is readily poisoned by the CO-like species produced during the alcohol oxidation even at ppm level [5–8]. In this effort to solve the problem of CO poisoning, PtRu/C catalyst has been recognized as the best CO-tolerant catalyst due to the bi-functional mechanism [9,10]. The combination of Pt with an oxophilic element is essential since this allows for the activation of water at low potential. This step provides oxygenated species that are necessary to oxidize some of the intermediates produced during the reaction and avoids poisoning of the catalyst surface.

In the searching of the stable supports for catalysts, tungsten carbide (WC) has been evaluated to be a promising candidate [11–13]. In electrocatalysis, tungsten carbides have been mainly used as the electrocatalyst supports for methanol oxidation [14–16], oxygen reduction [11,17], nitrophenol oxidation [18,19] and hydrogen evolution [20,21]. It has been proved that WC is not only stable in acidic solutions [22–24], but also highly tolerant to both carbon monoxide and bisulfide [25–27]. However, the mechanism of the high performance of the alcohol oxidation on the metal loaded on WC-based supporting materials is unclear so far. In this work, Pt supported on the WC modified MWCNT (PtWC/MWCNT) catalysts were prepared by the method of combining the organic colloidal and intermittent microwave heating (IMH) technique [11,12,17,28]. The origin of the high performance of the PtWC/MWCNT catalysts for methanol electrooxidation was studied via electrochemical measurements including the CO stripping test along with the comparison with PtRu/C and Pt/C catalysts.

2. Experimental

2.1. The preparation of PtWC/MWCNT catalysts

Tungsten powders (1.0 g) were dissolved in 25 ml mixture of 10 ml 30v/v% H2O2, 5 ml 2-propanol and 10 ml distilled–deionized water. The multiwalled carbon nanotubes (MWCNTs, Shenzhen Nanoharbor Co., China) (0.5 g) were then added into the mixture after stirring 24 h to make uniformly dispersed ink. The dried ink was heated in a homemade program-controlled microwave oven (2000 W, 2.45 GHz) with a heating procedure of 5 s on and 5 s pause for ten times. The well-dispersed powders were used as the precursor of WC and mixed with 0.1 g iron powders. The
mixture in the alumina crucible was continuously heating treated in the microwave oven for another 10 min to form WC on MWCNTs (WC/MWCNT).

Pt supported on WC/MWCNT catalysts was prepared as follows. The WC/MWCNT powders (300 mg) were dispersed into the well-mixed solution of H2PtCl6 solution (9 ml, 7.45 mg ml−1), sodium citrate (229 mg) and ethylene glycol (EG, 20 ml). The pH of the mixture was adjusted to 10 by 5 wt% NaOH/EG solution. The mixture was then added into 50 ml autoclave and heated at 140 °C for 6 h. After the mixture was cooled down to room temperature, the pH of the mixture was re-adjusted to 4 by 2 mol dm−3 HNO3 solution. The mixture was filtered and washed by alcohol and water for several times after sonification for 15 min. The dried powders were further treated by IMH with a heating procedure of 5 s on and 5 s pause for five times.

2.2. The characterization of the catalysts

Electrochemical measurements were performed on IM6e electrochemical workstation (Zahner-Electrik, Germany) and VoltaLab 80 Electrochemical Laboratory (Radiometer Analytical, France). A standard three-electrode cell with separate anode and cathode compartments was used. A Pt foil and saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. A glassy carbon (0.196 cm2) covered by catalyst was used as working electrode. For electrode preparation, 10 mg of 20 wt% PtWC/MWCNT, 4 mg of 50 wt% Pt/C (Columbian Chemicals, Inc., USA) and 3.3 mg of 60 wt% PtRu/C (Johnson Matthey, Inc.) were respectively dispersed in a suspension containing 1 ml of ethanol and 5 wt% Nafion (DuPont, USA) (ethanol:Nafion = 20:1) under ultrasonic stirring to form the catalyst inks. The catalyst ink (10 μl) was then deposited on the surface of the glassy carbon rod and dried at 80 °C for 30 min. The total Pt loadings were controlled at 10 μg.

The CO stripping experiments were performed in a 0.5 mol dm−3 H2SO4 solution. Along with the continuous CO bubbling for 15 min, the anode electrode was controlled at −0.14 V vs. SCE for CO adsorption. The solution was then purged with N2 for 30 min to remove the dissolved CO before the stripping test.

3. Result and discussion

Fig. 1 shows the cyclic voltammograms (CVs) of the methanol oxidation on Pt/C, PtRu/C and PtWC/MWCNT catalysts before and after 1000 cycles. It can be found that the PtRu/C catalyst gave the lowest onset potential due to the bi-functional effect. However, the PtWC/MWCNT catalyst gave the highest peak current density (Fig. 1a). The CV curves for the same samples after 1000 cycles are shown in Fig. 1b. It is clear that the peak current densities were reduced for methanol oxidation on three catalysts. However, the reduction in the activity for methanol oxidation on PtWC/MWCNT catalyst was slower compared to other two catalysts. The insets in Fig. 1a and Fig. 1b show the cyclic voltammograms on corresponding catalysts in background solution. It show that the active surface areas are Pt/C < PtRu/C < PtWC/MWCNT which further confirmed the structure effect of the MWCNT. Fig. 1c compares the normalized activity of three catalysts at different cycling numbers. The significance is that the onset potential for methanol oxidation on PtWC/MWCNT catalyst is almost the same before and after 1000 cycles. It is worth noticing that the onset potential of the methanol oxidation on PtRu/C catalyst moved to more positive position after 1000 cycles, indicating the changing in the catalytic property.

The origin of the onset potential shifting of the methanol oxidation on PtRu/C catalyst was investigated by CO stripping examination. Fig. 2 shows the CO stripping results performed on Pt/C, PtRu/
noticing that the peak potential for CO oxidation on PtWC/MWCNT catalyst is over 0.1 V more negative than that of on Pt/C catalyst. This means that the Pt loaded on WC/MWCNT can reduce the overpotential for CO oxidation. The importance is obvious since the poisoning-tolerance and performance of the direct alcohol fuel cells could be improved by using such anode catalyst even the mechanism is unclear at this stage.

Fig. 2. (a) CO stripping data on Pt/C, PtRu/C and PtWC/MWCNT in 0.5 mol dm$^{-3}$ H$_2$SO$_4$ at scan rate of 20 mV s$^{-1}$. Peak potentials for CO stripping on, (b) PtRu/C electrode and (c) PtWC/MWCNT electrode after 200, 400, 800 and 3200 cycles in 1 mol dm$^{-3}$ methanol + 0.5 mol dm$^{-3}$ H$_2$SO$_4$ solution at scan rate of 20 mV s$^{-1}$. The insets are the plots of the peak potentials for CO oxidation varying with potential cycling.

Fig. 3. The current sweep curves of methanol oxidation (a) on Pt/C, PtRu/C and PtWC/MWCNT catalysts, (b) on PtRu/C catalyst before and after 800 times potential cycling and (c) on PtWC/MWCNT catalyst before and after 800 times potential cycling in 1.0 mol dm$^{-3}$ methanol + 0.5 mol dm$^{-3}$ H$_2$SO$_4$ at scan rate of 50 $\mu$A s$^{-1}$. The potential for CO oxidation. The importance is obvious since the poisoning-tolerance and performance of the direct alcohol fuel cells could be improved by using such anode catalyst even the mechanism is unclear at this stage.

Fig. 2b and c show the CO stripping results on PtRu/C and PtWC/MWCNT before and after different potential cycles. The peak potential for CO oxidation on PtRu/C is gradually moved to more
positive direction with increasing the cycling number. It is possible that Ru suffers from the dissolution during the potential cycling. One of the evidences is that two peaks appeared on PtRu/C after 200 cycles. The potential of the second peak was very close to the potential on Pt/C. This means that some of the Pt atoms exposed to the solution due to the dissolution of adjacent Ru atoms to show Pt/C behavior. However, the PtWC/MWCNT catalyst showed extremely high stability against the potential cycling. The peak potential for CO oxidation was hardly changed after several thousands cycles. The results indicated that the presence of WC enhances the CO-tolerance for the catalyst which is favorable as anode catalyst for direct alcohol fuel cells.

The CO poisoning-resistance of the Pt/C, PtRu/C and PtWC/MWCNT catalysts were measured by a linear current sweeping. Fig. 3a shows the current sweeping curves of methanol oxidation on Pt/C, PtRu/C and PtWC/MWCNT catalysts. The potential oscillation is a typical phenomenon on Pt/C due to the poisoning by CO. This means that some of the Pt atoms exposed to the solution due to the dissolution of adjacent Ru atoms to show Pt/C behavior. However, the PtWC/MWCNT catalyst showed extremely high stability against the potential cycling. The peak potential for CO oxidation was hardly changed after several thousands cycles. The results indicated that the presence of WC enhances the CO-tolerance for the catalyst which is favorable as anode catalyst for direct alcohol fuel cells.

4. Conclusion

The PtWC/MWCNT catalysts were synthesized by organic colloidal and IMH methods. The origin of the high performance of PtWC/MWCNT for methanol electrooxidation was studied via electrochemical measurements including the CO stripping test. The PtWC/MWCNT catalyst showed a lower and stable onset potential and higher activity for methanol oxidation. It is realized that the high performance is probably due to the synergistic effect between Pt nanoparticles and WC and the structure effect of the MWCNTs [30]. The CO stripping test further evidenced that the CO oxidation on PtWC/MWCNT catalyst has lower overpotential compared to the Pt/C catalyst which is consistent with the lower onset potential for methanol oxidation. The reduction in the overpotential for the oxidation of CO-like species results in the shift of the onset potential for methanol oxidation.

Acknowledgements


References


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