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Ordered mesoporous tungsten carbide/carbon composites promoted Pt catalyst with high activity and stability for methanol electrooxidation

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ABSTRACT

The current anode materials used for direct methanol fuel cells (DMFCs) are expensive and not sufficiently durable for commercial development. One of the major challenges lies in the development of an inexpensive, efficient and stable anode catalyst. In the present manuscript ordered mesoporous tungsten carbide/carbon composites promoted Pt (Pt@WC/OMC) catalyst with high activity and stability for methanol electrooxidation is reported. WC/OMC nanomaterials have been synthesized by combing the hydrothermal reaction and the hard-template method and they have been platinized by a pulse microwave assisted polyol technique. The combination of high surface area, ordered mesopores, the synergistic effect and CO-tolerant ability of WC and well dispersed Pt nanoparticles provide Pt@WC/OMC with high activity, desirable stability, and CO-tolerance toward methanol electrooxidation. Compared with the commercial PtRu@C (40 wt.% Pt, 20 wt.% Ru) catalyst, Pt@WC/OMC demonstrates longer stability as well as higher specific mass activity for methanol electrooxidation by a factor of 1.1 (per mg Pt) and 1.7 (per mg noble metal). Experimental results have proved that Pt@WC/OMC is a promising anode catalyst for DMFCs applications.

1. Introduction

Direct methanol fuel cells (DMFCs) have been attractive as a new, clean alternative power source for portable electronic devices. This is due to their high energy density, near room temperature operation, longer-lasting power compared with a rechargeable battery, instantaneous recharging by simply replacing the disposable fuel cartridge, non-toxic disposal, and light weight [1,2]. Currently, there still exist many challenges for commercializing DMFCs, including the undesirable activity, kinetics, durability and high cost of Pt-based catalysts. Consequently, to break through these major bottlenecks, it is vital to identify and develop highly efficient, durable and inexpensive catalysts. Today, PtRu based electrocatalysts are the most widely adopted and well recognized as the best anode materials in DMFCs due to their reliable methanol electrooxidation performance. However, their low specific mass activity and thereby their high cost [3], high sensitivity to CO [4], and instability [5–9] are their main drawbacks that make PtRu-based electrocatalysts unsatisfactory for practical DMFCs applications. Moreover, Ru is susceptible to leach out from PtRu catalysts [10–14], which not only continuously deteriorates the anode activity [11], but also leads to about 40–200 mV decrease in the cell performance caused by "Ru crossover" [13]. The dissolved Ru at the anode can permeate through the electrolyte membrane to the cathode and can be re-deposited on the cathode catalyst [12]. Hence, new type Ru-free, more efficient and more stable electrocatalysts for methanol electrooxidation are still highly desirable.

Tungsten carbides have been widely used in machines due to their superior hardness, high melting point, good resistance to fracture, wear, oxidation and corrosion [15,16]. Recently, tungsten carbides have attracted much attention because of their similar catalytic activity to that of Pt group metals [17,18], possessing desirable stability in both acidic and alkaline solutions [19–25], as well as high tolerance to both CO and H_2S poison [26,27]. Moreover,

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synergetic effects on Pt's activity to methanol electrooxidation have also been reported [28–31]. Among tungsten carbides, WC is found to be more stable than W_2C in an electrochemical environment. W_2C can be immediately oxidized to W_xO_y species, while WC is stable at the anode potential below 0.6 V (*vs.* NHE) [22,23].

Since the discovery of ordered mesoporous solids of the MCM-41 type and related materials in the early 1990s [32], ordered mesoporous materials have become a research focus and have been widely used in catalysis. This is due to their relatively large pores which facilitate mass transfer and the very high surface area which allows a high concentration of active sites per mass of material [33]. Through soft-template and hard template method, various self-supported ordered mesoporous materials with variable composites have been synthesized. Unfortunately, these two methods are difficult for the preparation of ordered mesoporous self-supported metal carbides. This is due to the lack of proper precursors for so-gel process in soft-template method and very possible collapse of the mesoporous regularity in the conversion of metal precursor to carbide in the hard-template method [34]. Until now, to our best knowledge, there is no report about the synthesis of self-supported ordered mesoporous transition carbides. Considering also the inherent property of high density of WC and the necessary high temperature synthesis conditions for WC formation, ordered mesoporous WC is difficult to be synthesized. One of the feasible ways is to evenly load WC on carbon materials or to functionalize carbon with WC in order to obtain WC/carbon composites, which have exhibited excellent performance in DMFCs [28–31].

In the present work, ordered mesoporous tungsten carbide/carbon (WC/OMC) composite was synthesized by combing the hydrothermal reaction and hard template method. In this process, ammonium metagungstate (AMT) was used as tungsten precursor, glucose as the carbon source and the ordered mesoporous silica (SBA-15) as the hard template. Thereafter, Pt nanoparticles were deposited on the as-prepared OMC/WC, leading to Pt@WC/OMC electrocatalyst for methanol electrooxidation, exhibiting high activity, desirable CO tolerance and good stability.

2. Experimental

2.1. Synthesis of WC/OMC and ordered mesoporous carbon (OMC)

WC/OMC sample was prepared by combing the hydrothermal reaction and the hard template method with ammonium metagungstate (AMT) as tungsten precursor, glucose as the carbon source and the ordered mesoporous silica (SBA-15) as the hard template, respectively. The preparation procedure is shown in Fig. 1 and described in details as follows. In a flask, 0.736 g AMT and 1.982 g glucose were dissolved in distilled water and mixed with 1.000 g SBA-15 under stirring for several hours. Subsequently, the above mixture was transferred into an autoclave for reaction at 180 °C for 12 h. After reaction, the solution mixture was poured into a disk and then dried at 90 °C for 12 h in order to remove the solvent. Then the as-prepared product was carbonized at 900 °C for 3 h in N_2 and H_2 mixed atmosphere ($V_{N_2}/V_{H_2} = 3/1$). The heating rate was controlled to be 5 °C min^{-1}. The resulting sample was washed in HF solution (40 wt.%) under stirring to remove SBA-15 hard template, and then filtered, washed, and dried at 90 °C for 12 h in a vacuum oven. The final product was defined as WC/OMC.

For comparison, the ordered mesoporous carbon (OMC) was also prepared by the hard template method [35]. The SBA-15 (1.000 g) was added into the solution obtained by dissolving 1.250 g sucrose and 0.150 g H_2SO_4 in 5.0 mL H_2O. The mixture was reacted at 100 °C for 6 h and then at 160 °C for another 6 h. After the first drying composites were grinded, the second heating process was performed with additional precursor solution (0.800 g sucrose and 0.080 g H_2SO_4 in 5.0 mL H_2O). After that, the sample was heated to 900 °C at a heating rate of 5 °C min^{-1}, and kept at 900 °C for 3 h in N_2 atmosphere. Finally, the carbon/SBA-15 composites were washed using HF solution (40 wt.%) for removing SBA-15 to obtain OMC.

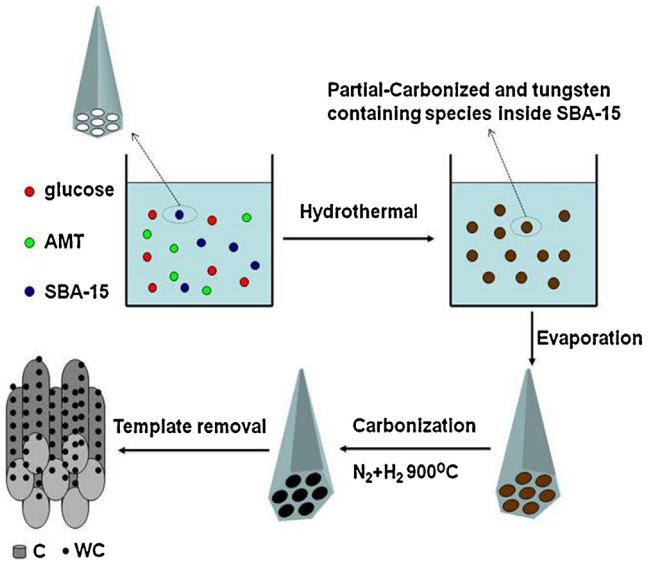

Fig. 1. Synthetic process of ordered mesoporous tungsten carbide/carbon composites with SBA-15 as a hard-template, ammonium metatungstate salt (AMT) as the tungsten precursor, and glucose as the carbon source, respectively, by combing a hydrothermal reaction and a hard template method.

2.2. Preparation of electrocatalysts

The Pt@WC/OMC and Pt@OMC catalysts with a Pt loading of 20 wt.% were prepared by a pulse-microwave assisted polyol method [36,37]. The as-prepared WC/OMC or OMC as the supporting materials was well mixed with ethylene glycol (EG) in an ultrasonic bath and then an appropriate amount of $H_2PtCl_6{\cdot}6H_2O$ dissolved in EG was added into the mixture. After the pH value of the above mixture was adjusted to more than 10 by the dropwise addition of 1.0 mol L^{-1} NaOH/EG solution, a well-dispersed slurry was obtained with magnetic stirring for another 1 h. Thereafter, the slurry was microwave-heated in the pulse form of 10 s-ON/10 s-OFF for several times. After reaction, 1.0 mol L^{-1} HCl solution was added to accelerate the deposition process. Finally, the resulting sample was filtered, washed with copious hot water (≥80 °C) until no chloride anion was detected by 1.0 mol L^{-1} $AgNO_3$ solution in the filtrate and then dried at 90 °C overnight in a vacuum oven.

2.3. Characterization of electrocatalysts

2.3.1. Physico-chemical characterization

The low-angle and wide-angle X-ray diffraction (XRD) patterns were recorded on a D-MAX 2200 VPC diffractometer using Cu K_α radiation (30 kV, 30 mA). N_2 adsorption measurements were carried out using a Micromeritics ASAP 2010 analyzer at 77 K. The BET surface area (S_{BET}) and the mesopore volume (V_{mes}) were determined by BET theory and Barrett–Joyner–Halenda (BJH) method, respectively. The transmission electron microscopy (TEM) investigations were performed on a JEOL TEM-2010(HR) operating at 120 kV. Scanning electron microscopy (SEM) and element mapping were performed using Quatnta 400F thermal field emission environmental SEM.