



Tungsten carbide/porous carbon composite as superior support for platinum catalyst toward methanol electro-oxidation

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ABSTRACT

Tungsten carbide/porous carbon (WC/PC) composites have been successfully synthesized through a surfactant assisted evaporation-induced-assembly method, followed by a thermal treatment process. In particular, WC/PC-35-1000 composite with tungsten content of 35% synthesized at the carbonized temperature of 1000 °C, exhibited a specific surface area (S_{BET}) of 457.92 m² g⁻¹. After loading Pt nanoparticles (NPs), the obtained Pt/WC/PC-35-1000 catalyst exhibits the highest unit mass electroactivity (595.93 A g⁻¹ Pt) toward methanol electro-oxidation, which is about 2.6 times as that of the commercial Pt/C (JM) catalyst. Furthermore, the Pt/WC/PC-35-1000 catalyst displays much stronger resistance to CO poisoning and better durability toward methanol electrooxidation compared with the commercial Pt/C (JM) catalyst. The high electrocatalytic activity, strong poison-resistivity and good stability of Pt/WC/PC-35-1000 catalyst are attributed to the porous structures and high specific surface area of WC/PC support could facilitate the rapid mass transportation. Moreover, synergistic effect between WC and Pt NPs is favorable to the higher catalytic performance.

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1. Introduction

Direct methanol fuel cells (DMFCs) have received considerable attention in recent years because of the low operating temperature, high theoretical energy density, ease of handling liquid fuel, and little pollution [1,2]. Currently, Pt/C is the most commonly anodic catalyst for methanol electro-oxidation. It is well known that the properties of carbon support, including electrical conductivity, specific surface area, porosity and electrochemical stability, can greatly influence the electrocatalytic activity, durability and efficiency of Pt/C catalysts [3]. Various and novel nano-structured carbon materials, such as mesoporous carbon, nanodiamonds, carbon nanotubes (CNTs), carbon nanofibers (CNF) and graphene have been investigated as catalyst supports for DMFCs [4–9]. However, for Pt/C catalysts, electrochemical corrosion of the carbon support and the Pt poisoned by intermediates during methanol electrooxidation would lead to losses in catalytic efficiency and stability [10–12]. In order to further improve the CO poisoning tolerance and the stability of Pt catalysts, bimetallic Pt–M catalysts were developed as new catalyst materials. Among the

bimetallic Pt–M catalysts, Pt–Ru seems to be the most effective catalyst due to its electrocatalytic activity toward methanol oxidation and tolerance to the CO poisoning [13]. However, the Pt–Ru catalyst still needs high loadings of noble metals, and the dissolution of Ru causes the poor durability of catalyst, which leads to the hindrance of commercialization of DMFCs [14–17].

Recently, the carbides of transition metals, especially tungsten carbide (WC), have been regarded as promising support of DMFCs catalysts due to its Pt-like catalytic activity, excellent stability, high resistance oxidation and CO poisoning [18–21]. The addition of WC into Pt can remarkably increase the amount of adsorbed OH (OH_{ad}) at the Pt sites, thereby improving the anti-poisoning ability and stability of Pt catalyst. The activity and stability of pure WC can be further improved by constructing the WC/carbon composites [22–24]. For example, Lu et al. [25] synthesized nanostructured tungsten carbide/carbon (WC/C_x) composites by a microwave heating method. The prepared Pt/WC/C_x catalysts exhibit higher activity and stability than that of the Pt/V₂C (Pt supported on carbon black Vulcan XC-72) catalyst. Wang et al. [26] synthesized a WC/graphitic carbon nanocomposite from an in situ synthetic process. The Pt/WC/graphitic carbon catalyst exhibited a mass activity of 205.6 A g⁻¹ Pt, which was three times as that of Pt/C catalyst. Zhao et al. [27] prepared Pt catalysts supported on WC/multi-walled carbon nanotubes (MWCNT). The results showed that the synergistic effect between WC and Pt NPs, and the structural

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effect of MWCNTs could deliver to a high performance for methanol oxidation. Wang et al. [28] synthesized a WC/graphene nanocomposite by an impregnation method. The Pt/WC/graphene catalyst exhibited the higher catalytic activity and stability compared to commercial PtRu/C and Pt/C catalysts toward methanol oxidation. Additionally, porous carbon could facilitate the mass transport in the electrodes compared with other carbon materials. Hence, it is necessary to synthesize the WC and porous carbon composites (denotes as WC/PC) by a simple and economic method, which could be used as excellent support of electro-catalytic catalysts toward DMFCs.

Herein, we report a simple method for synthesis of WC/PC composites. During the synthesis, formaldehyde resin and triblock copolymer Pluronic F127 were used as the carbon source and porogen, respectively, and the tungsten hexachloride as a W source was directly introduced to the solutions containing C source and porogen. During the solvent evaporation processing, the tungsten hexachloride firstly aggregated to form a larger droplet, and then precipitated and well-dispersed in polymer films. Meanwhile, the self-assembly process between formaldehyde resin and surfactant F127 based on hydrogen bond interaction would lead to formation of mesophases consisting of triblock copolymer micelles surrounded by formaldehyde resin [29]. Then, the WC/PC composites could be obtained after carbonization in Ar ambient. The as-prepared WC/PC composites are used as supports of Pt catalysts to prepare Pt/WC/PC catalysts. The performances of Pt/WC/PC catalysts for methanol electro-oxidation are investigated via electrochemical measurements at 25 °C in acid media. For comparison, the performances Pt/PC catalyst and commercial Pt/C (JM) catalyst for methanol oxidation are investigated.

2. Experimental

2.1. Chemicals

All chemicals were used as received without further purification. Poly (ethylene oxide)-poly (propylene oxide)-poly (ethylene oxide) triblock copolymer Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆, $M_w = 12,600$) was bought from Aldrich, and the tungsten hexachloride (WCl₆, used as tungsten source) was bought from Aladdin Chemical Company. Phenol, formaldehyde solution (37 wt%), sodium hydroxide and ethanol were analytical reagents. Deionized water was used in all the experiments.

2.2. Preparation of WC/PC

In a typical synthesis, resol solution was prepared by a modified method [30]. Firstly, 0.40 g of phenol was melted in a flask and mixed with 10 mL of 0.1 M NaOH aqueous solution under stirring. Then 1.4 mL of 37 wt% formaldehyde was added into the above solution. After the clear mixture reacted under stirring at 75 °C for 2 h, the phenolic resin solution was obtained. Next, 0.75 g of F127 powders were dissolved in ethanol under stirring and then was mixed with the above as-prepared resol solution. After that, 0.15 g of tungsten hexachloride (WCl₆) powders were added into the present mixture under stirring to obtain a homogeneous mixture. Finally, it was transferred to a dish and evaporated at room temperature for 12 h, followed by heating at 100 °C for 24 h to prepare the precursor. The WC/PC composite was obtained after the precursor was carbonized at 1000 °C for 4 h with a heating ramp rate of 2 °C/min under highly pure Ar flow. The prepared materials were defined WC/PC-*x*-*y*, where *x* is the content of tungsten and *y* is the carbonization temperature. Thermogravimetric (TG) method was used to measure the amount of tungsten in the resultant products. Based on the analyses of TG curves, the content of tungsten in the resultant sample was about 35 wt%, and

the carbonization temperature was 1000 °C, thus the product was denoted as WC/PC-35-1000. To investigate the influence of different carbonization temperatures on the performances of the resultant materials, samples with different carbonization temperatures of WC/PC-35-900, WC/PC-35-1000 and WC/PC-35-1100, were also studied. For the same purpose, the samples synthesized with the different content of tungsten were also prepared, such as WC/PC-8-1000, and WC/PC-65-1000. The pure porous carbon (denoted as PC) at the carbonization temperature of 1000 °C and the tungsten carbide and carbon (denoted as WC/C-35-1000) for comparison were also prepared. Their preparation procedure was exactly the same as that of the WC/PC-35-1000, except that the addition of WCl₆ or F127 bypassed, respectively. The sample codes and the corresponding experimental parameters are showed in Table S1.

2.3. Synthesis of Pt/WC/PC catalyst

10 wt% of platinum particles were loaded on WC/PC composite was prepared by a borohydride reduction method in alkaline media. In a typical procedure, 0.4 g WC/PC composite and 0.117 g H₂PtCl₆·6H₂O dissolved in a certain quality of deionized water were placed in a flask. Then the pH value was adjusted to 8 by NaOH solution. After the suspension was sonicated for 10 min, the NaBH₄ solution were dropwise added to the above solution. The resulting Pt/WC/PC suspension was filtered, washed, and dried at 100 °C. In addition, 10 wt% Pt supported on the PC materials (denoted as Pt/PC catalyst) and 10 wt% Pt supported on the WC/C-35-1000 composite (denoted as Pt/WC/C-35-1000 catalyst) were also prepared according to the same procedure. For comparisons, 10 wt% Pt and 20 wt% Pt supported on the commercial carbon black [Johnson Matthey, labeled Pt/C (JM, 10 wt% Pt) catalyst and Pt/C (JM, 20 wt% Pt) catalyst, respectively], were also used.

2.4. Characterizations

X-ray diffraction (XRD) patterns were obtained with a Rigaku D/max-III B diffractometer by using Cu-Kα ($\lambda = 1.5406 \text{ \AA}$) radiation. The accelerating voltage and the applied current were 40 kV and 20 mA, respectively. Raman spectra with a Jobin Yvon HR 800 micro-Raman spectrometer at 457.9 nm. Thermogravimetric analysis was carried out by using an SDTQ600 instrument. Nitrogen adsorption-desorption isotherm and pore-size distributions were obtained using a Tristar 3000 nitrogen adsorption apparatus. TEM analysis was performed on a Fei Tecnica G2-STWIN electron microscope with an acceleration voltage of 200 kV. XPS studies were carried out with a Kratos-AXIS UL TRA DLD instrument by using an Al-Kα radiation source.

2.5. Electrochemical measurements

Electrochemical measurements were performed with a BAS100B electrochemical workstation. The conventional three-electrode cell consisting of a glassy carbon (GC) electrode with an area of 0.1256 cm² as working electrode, Pt plate as a counter-electrode, and saturated calomel electrode (SCE) as a reference electrode was used. The catalyst (5 mg) and 5 wt% Nafion solutions (50 μL) were dispersed in 2-propanol (100 μL). After the catalyst ink had been mixed uniformly by using ultrasound, the ink (5 μL) was dropped onto the GC electrode and left to dry. Cyclic voltammetry (CV) measurements were carried out in mixed solutions of 1.0 M H₂SO₄ and 1.0 M CH₃OH between -0.2 and 1.0 V at a scan rate of 50 mV s⁻¹. For CO-stripping tests, the electrode was first CO-saturated in 1.0 M H₂SO₄ solution for 15 min. Then, the high pure N₂ was bubbled into the solution for 20 min to remove dissolved CO in the solution. The CO-stripping was

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