

Synthesis of ordered mesoporous carbon/tungsten carbides as a replacement of platinum-based electrocatalyst for methanol oxidation



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ABSTRACT

The mesoporous material ordered mesoporous carbon/tungsten carbide (OMC/WC) was prepared and used as electrocatalyst for methanol electro-oxidation. WC embedded OMCs was synthesized through carbothermal reactions with a blow of argon and hydrogen by employing ammonium metatungstate as a precursor. In this method, because OMC acted both as the support and the carbon sources, not only the surface area of materials is enlarged, but also the generation of deposit carbon which covers the active sites can be effectively avoided. The characterization, which carried out by X-ray diffraction, Transmission electron microscopy and N₂ adsorption–desorption measurement showed a homogeneous distribution of WC throughout the surface of the mesoporous carbon and the surface area of OMC/WCs was up to 344 m²/g. Electro-catalytic properties and mechanism of methanol oxidation on the OMC/WCs electrode has been investigated using cyclic voltammetry and *in situ* FTIR technique. The results showed that there was only one characteristic methanol oxidation peak during the whole potential scan on the OMC/WCs electrode surface, it also showed an improved CO tolerance of the WC surface. It proved that tungsten carbide had good electro-catalytic property close to that of the Pt-based materials for methanol oxidation and provided a new idea for developing electrode materials in the future.

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1. Introduction

Since Levy and Boudart theoretically conjectured that tungsten carbide (WC) display Pt-like behavior in catalytic reactions [1,2] many studies focused on WC materials acted as electrocatalyst for the direct methanol fuel cells (DMFCs) in order to replace noble metal catalyst [3–6]. Tungsten carbide has been intensively studied as a support for Pt or Ru catalyst due to [7–9] their synergistic effect and its CO tolerance [10–12]. However, it has not been reported that the WC materials have good enough electro-catalytic performance to replace PtRu as catalytic materials for DMFCs. There are two major obstacles for the application of WC materials in the fuel cell. First, the electro-catalytic activity of WC is much less than that of noble metal due to their lower surface area and deposited carbons. Particularly, the deposit carbons, which are formed when preparing WC materials, covered the electro-catalytic active sites so that the catalytic propriety of WC electrodes was difficult to reach their theoretical value. Another is the stability of WC materials in some

electrolyte. The early studies showed that W₂C was electrochemically unstable in acidic solution, immediately oxidizing to form surface W_xO_y species, while WC was stable under certain anode potentials [13]. Therefore, the implementation of WC materials as a DMFCs catalyst requires obtaining a desired stoichiometry (W:C = 1:1) material with sufficiently high specific area [14–16].

A common strategy to synthesize catalytic materials with large surface area and mesostructure is template-method. Ji et al. have reported that tungsten carbide effectually confined in the channels of SBA-15 mesoporous silica and had high specific surface area (>300 m²/g) [17]. However, The resulting carbide surface is usually contaminated by polymeric carbon which is from the pyrolysis of carbon-rich gases and then covered the electro-catalytic active sites. When carbon materials are employed as templates and carbon source, the utilization of external carbon precursor becomes unnecessary, and possible carbon deposition on the catalyst surface can be effectively avoided. It is known that ordered mesoporous carbons (OMCs) possess good electrochemical properties, and may be used as catalyst supports in fuel cells due to their appealing structural characteristics, such as periodic and uniform mesopores and large surface area. Mesoporous carbons with ordered 3D pore structures also might promote the mass transport of both reactants and by-products during fuel cell operation. For example, Ryoo synthesized highly ordered, rigid arrays of mesoporous carbon with

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uniform and tunable pore diameters (typically 6 nm inside and 9 nm outside) [18]. The resultant material supports a high dispersion of platinum nanoparticles and shows improved oxygen reduction reaction electrocatalysis, originating from a higher surface area and a highly ordered mesopore structure. Yi Wang also reported a facile soft-template synthesis of OMC/WC with a surface area of 538 m²/g. The Pt nanoparticles supported on OMC/WC demonstrated a better performance than that of the commercial PtRu@C catalyst for methanol electrooxidation.

Meanwhile, mechanism of methanol electrooxidation on WC electrode is not clearly presented. It is a public opinion that its behavior is as same as that on the platinum-based electrocatalyst. But Chen et al. demonstrated that WC's surface possesses very high electronic conductivity and catalytic-activity for the decomposition of methanol. They also discovered that CO is weakly bonded to tungsten carbides and it can be more easily removed by desorption [19–21]. It can be deduced that there is another type of mechanism of methanol electrooxidation on WC electrode. However, this supposition needs to be verified.

In this work, we designed and developed a composite of WC-embedded OMC with a large surface area and ordered mesoporous structure. We then used the as-prepared OMC/WCs as the catalyst for methanol electrooxidation reaction (MOR). It officially demonstrated, for the first time, that WC's surface plays an active role in the dissociation of methanol and produces methoxy intermediate. It is observed that the intermediates CO_{ads} on the surface of OMC/WCs electrode are easily to be desorbed and oxidized.

2. Experimental

Ordered mesoporous carbon (OMC) was prepared following the method previously established by Ryoo et al. [18]. The tungsten modified OMC was prepared through carbothermal reactions by employing ammonium metatungstate hydrate (AMT) as a precursor for tungsten carbide. Briefly, OMC (~0.2 g) was added into 10.0 g ethanol under stirring for 2 h and then was slowly mixed with AMT (~0.27 g) was dissolved in ethanol aqueous solution (1:1, mass ratio). Next, the mixture was kept stirring at room temperature 1–2 days until the ethanol volatilized completely, followed by drying at 80 °C for 5 h. The as-prepared product was then thermally reduced in a tubular furnace under H₂/Ar. By controlling temperature of H₂ thermal reduction treatment, different compositions of OMC/WCs were obtained. The sample was cooled in Ar and then ground to fine powder for use as an electrocatalytic material.

The morphology, crystal phase and structure of the sample were characterized by X-ray diffraction (XRD, Thermo ARL SCINTAG X'TRA), transmission electron microscopy (TEM, Tecnai G2 F30 FEI Inc., Holland) and the energy-dispersive X-ray (EDX), respectively. Powder X-ray diffraction patterns were collected using an X'Pert Pro diffractometer at room temperature with a Cu K α radiation source. TEM was performed under a voltage of 200 kV and a current of 103 mA. The specific surface area was determined from the nitrogen adsorption isotherm at 77 K treated according to the Brunauer–Emmett–Teller (BET) by Barrett–Joyner–Halenda (BJH) model (micromeritics ASAP2020MC).

Electrochemical measurement of catalysts to methanol oxidation was evaluated by an EG&G 273A potentiostat. *In situ* FTIR spectroscopic experiments were carried out on Nicolet 670 FTIR spectrometer equipped with a MCT-A detector cooled with liquid nitrogen. The spectroelectrochemical cell was provided with a CaF₂ disk window (diameter 32 mm and thickness 2 mm). The conventional three-electrode cell consisting of a glassy carbon electrode with an area of 0.1256 cm² as the working electrode, platinum sheet (1 cm × 1 cm) as the counter electrode, and a saturated

calomel electrode (SCE) as the reference electrode was used. All the electrochemical measurements were carried out in a mixed aqueous solution of 0.5 M H₂SO₄ and 4.0 M CH₃OH. The catalyst ink was prepared by dispersing 5 mg of catalyst in 0.8 ml deionized water, 1.2 ml 2-propanol and 50 μ l Nafion solutions (5 wt% Aldrich). The mixture was ultrasonicated for 30 min, then 10 μ l of the suspension was dropped onto the pre-cleaned glassy carbon electrode and the solvent was slowly evaporated. Electrolytes were bubbled with N₂ for 30 min before and throughout the test to remove trapped air. All potentials in this paper are reported Vs. SCE.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of OMC and the formation process of crystal phases of the mesoporous OMC/WCs at different carburization temperatures. The formation of WC underwent the transition from W to W₂C, and finally converting to WC as the main phase with a long reaction time (3 h). It was noted that the more WC phase formed by carbothermal reduction on carbon supports under the lower temperature, while WC was more stable under certain anode potentials. As shown in Fig. 1, in the case of OMC, the respective diffraction peaks at 22.5° and 43.5° correspond to a mesoporous carbon framework. A pure tungsten phase is generated initially at 700 °C under H₂/Ar, followed by the formation of a W₂C-dominated phase at 800 °C. Since W₂C is thermally unstable, the further increase of both calcination temperature and time favors the conversion of W₂C to WC, resulting in a WC-dominated phase at 900 °C. The tungsten species-modified mesoporous carbons were denoted as W-C, W₂C-C and WC-C, respectively. Upon the formation of tungsten species after H₂/Ar thermal reduction treatment, little changes on pore size distributions were observed. The results suggested that the basic mesoporous structure of carbon was maintained during the formation of tungsten carbides species. In the small-angle range (inset), it can be noted that OMC has an intense diffraction peak (1 0 0) and two resolved peaks (1 1 0) and (2 0 0), indicating the formation of a highly ordered 2D hexagonal (*p6mm*) mesostructure. Meanwhile, only a diffraction peak could be clearly seen on the OMC/WCs, which can be indexed as a (1 0 0) reflection of a hexagonal mesostructure.

The TEM images of OMC and OMC/WCs are shown in Fig. 2. It showed that the tungsten carbides particles were well dispersed

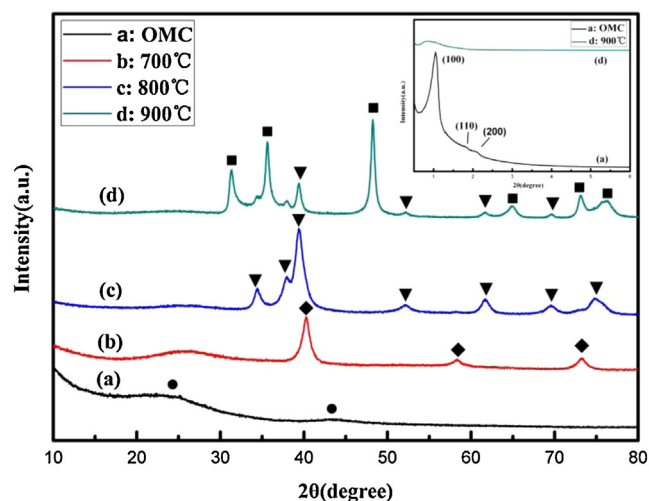


Fig. 1. Small-angle (inset) and large-angle XRD patterns of (a) OMC and the products OMC/AMT carburized at a temperature of (b) 700, (c) 800, (d) 900 °C with H₂/Ar for 3 h: (●) C, (◆) W, (▼) W₂C, (■) WC.

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