

Synthesis of mesoporous tungsten carbide-supported platinum and its electrocatalytic activity for methanol oxidation

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Abstract: High activity and stability during oxidation of methanol under the relatively anode environment are two main evaluation criterias for an effective anode electrocatalyst in direct methanol fuel cell (DMFC). Mesoporous WC samples with hollow structure were prepared by gas-solid reaction at the atmosphere of CH₄/H₂ by using airflow spray dried ammonium metatungstate (AMT). The platinum supported on this material by impregnation-vapor phase deoxidation method served as a less expensive electro anode catalyst. XRD and SEM results showed that Pt particles were well dispersed on the surface of WC. The results showed that the Pt/WC-PME exhibited an attractive catalytic activity, and methanol oxidation process in Pt/WC-PME is affected by liquid-phase mass transfer. The results also indicated that the oxidation can be improved by raising temperatures.

Keywords: tungsten carbide; mesoporous; platinum; methanol oxidation

1. Introduction

In the twenty-first century, there are several obstacles for fuel cells that need to be overcome before their commercialization ^[1,2]. It is clear that new electrocatalysts for fuel cells need to be energy efficient and sustainable in addition to being economically viable ^[3]. Researchers have been perusing kindly catalyst for low temperature fuel cells such as direct methanol fuel cell (DMFC) that could improve the oxidation of methanol and the decomposition of water to produce protons, electrons, and gas-phase CO₂ for many years ^[4]. Long-term study found that a desirable electrocatalyst must remain stable under the environment at the anode. Pt-Ru alloy and PtRu/C showed high activity for electro-oxidation of methanol ^[5-8]. Although the addition of Ru improved the CO-tolerance of Pt catalyst ^[9], the problem of Ru as well as Pt is that the resource is limited. Searching for new catalyst is necessary which would help facilitate the commercialization of DMFC.

Tungsten carbide has attracted much attention over the past several decades used as electrocatalyst, hydrogenation and decomposition catalyst ^[10-14]. For so long several reports have revealed that tungsten carbide is perfect for its anti CO poisoning property, however, this pure material still discussed by low activity ^[15,16]. More efforts should be made to achieve prepare materials with special structure, high activity pure and composite material used as anode catalyst which is necessary for a compact fuel supplying system.

On the other hand, platinum is an important catalyst and a prime candidate to probe the dependence of electrocatalytic properties on particle size. Therefore, WC with special structure would be suitable for the anode environment and delivery of protons, and the addition of Pt with high activity surface area would improve the catalytic activity.

Here, more recent studies from our group were focused on synthesis and lack of qualifier structure of

WC and Pt/WC. The structure of precursors which were prepared by using airflow spray drying method was strongly preserved after carburization and nano-platinum loading procedure at the atmosphere of CH_4/H_2 and H_2 respectively. Porous structure which was considered as a suitable candidate was prepared by the evaporation of water and NH_3 . The activity of Pt/WC was investigated by cyclic voltammetry technology to discuss the application of this material as anodic electrocatalyst for DMFC.

2. Experimental

Ammonium metatungstate (AMT, $(\text{NH}_4)_2\text{W}_4\text{O}_{13} \cdot x\text{H}_2\text{O}$) was used for the synthesis of tungsten carbide. AMT was dissolved in de-ionized water and then treated by spray drying (BÜCHI Spray Dryer B-290) to produce hollow precursors. Tungsten carbide (WC) was synthesized from the precursor by gas-solid reaction at the atmosphere of CH_4/H_2 [17].

Mesoporous WC was added to the chloroplatinic acid solution ($5 \text{ mmol} \cdot \text{L}^{-1}$) and stirred in ultrasonic bath for 30 min. After that, the precipitate was impregnated in the solution for 12 hours. The precipitate was then dried in an oven at 50°C for 2 h. Then, the powder precursor was reduced under H_2 at 400°C for 2 h.

The crystal phase, morphology and chemical components of the sample were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) respectively. XRD were carried out on a Thermo ARL SCINTAG X'TRA at room temperature, by Cu K α 1 radiation source ($k=1.541 \text{ nm}$) under a voltage of 45 kV and a current of 40 mA . The XRD patterns were recorded with a step size of 0.04° from 15° to 80° at a speed of $2.4^\circ/\text{min}$. SEM was performed with a Hitachi S-4700 II equipped with energy dispersive X-ray spectroscopy (EDS, Cambridge).

The electrocatalytic activity of the sample was collected by the approach of powder microelectrode (PME). Electrochemical studies were performed in a three-electrode electrochemical cell composed of

reference electrode (saturated calomel electrode (SCE), counter electrode (platinum gauze, 99.99% purity, $\sim 1 \text{ cm}^2$ surface area) and working electrode (powder microelectrode (diameter $60 \mu\text{m}$)). Autolab PGSTAT 30 was used to determine the electrochemical experiments. All potentials reported here were referred to the SCE. All peak currents reported here were subtracted from the background currents. The solution was deaerated with N_2 for 30 min.

3. Results and discussion

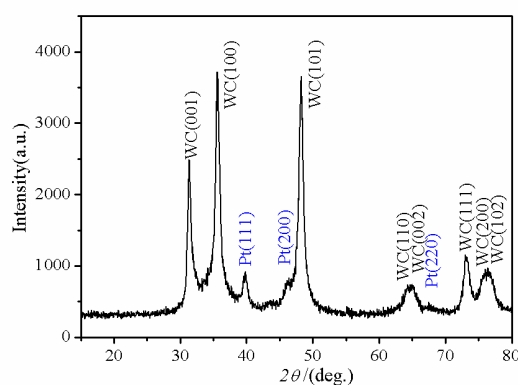


Figure 1. XRD patterns of Pt/WC samples

XRD analysis was used to determine the phases of the pure WC and Pt/WC. The XRD pattern in Figure 1 presents the XRD patterns of the as-prepared Pt/WC samples. The Pt phase showed that Pt particles had been adsorbed on the WC successfully.

Table 1 Chemistry element of Pt/WC by EDS

Element	Atom %	Element Wt %
C	52.96	6.82
W	43.27	85.30
Pt	7.88	16.20

The EDS analysis was also testified at the presence of Pt which was showed at Table 1. The ratios of W, C and Pt atoms are 43.27 %, 52.96 % and 7.88 % respectively. The ratio of carbon and tungsten atoms is 1.22 with the existence of a small amount of free carbon.

Figure 2 shows SEM micrographs of AMT, WC and Pt/WC samples obtained at a magnification of 2500 and 20000 \times (inset). The mesoporous WC sample shows a surface morphology resembling that of the precursor.

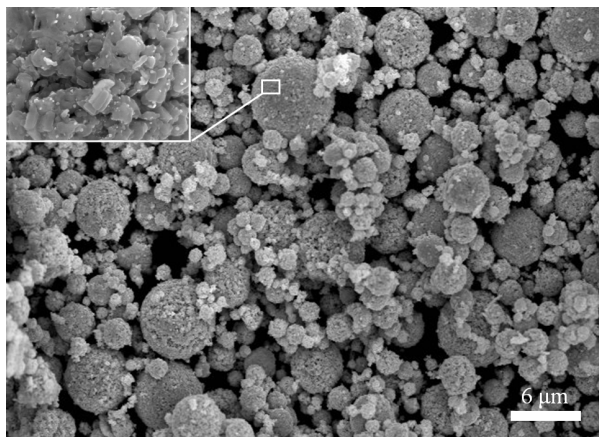


Figure 2. SEM images of the Pt/WC sample (2500 \times , inset: 20000 \times)

In addition, due to the slow decomposition carburization process, the range of pore sizes of WC was less than 200 nm (inset). The highly dispersed Pt sample was adsorbed on the WC with particle sizes ranging from 5 to 15 nm.

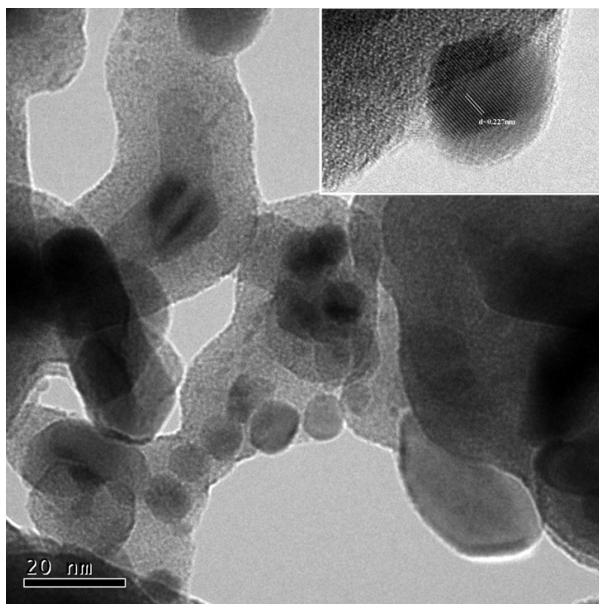


Figure 3. HRTEM images of the Pt/WC sample

Figure 3 represents HRTEM images of the Pt/WC samples. Pt particles prepared by the

impregnation-vapor phase deoxidation method show high dispersion in Figure a. The average size of the particles is 5~15 nm which is basically the same as the previous result which was tested by the SEM images. Pt nano-particles can be seen in the inset of Figure 3. The distance between the two adjacent stripes is 0.227 nm, which is almost the same as 0.2265 nm that is the d-value of Pt (111) with a face-centered cubic lattice [18]. A slight change of band with small-width which was based on relatively gentle had high density of states to be highest catalytic performance. Pt (111) has shows higher catalytic activity for its high density of states. Therefore, main goal of catalyst preparation is how to promote the growth of Pt (111) and enhance the absorption capacity of Pt (111) on WC.

In order to compare the performance of Pt/WC with platinum, CVs were tested as shown in Figure 4. WC at the C/W ratio of 1.22 displays low activity towards ethanol oxidation.

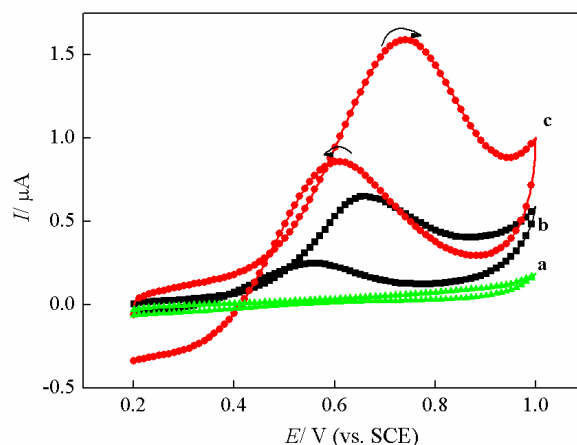
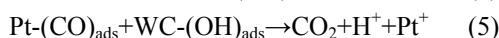
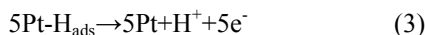
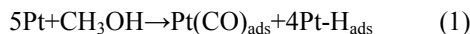


Figure 4. Cyclic voltammograms of different electrodes in 1mol·L⁻¹ H₂SO₄+1mol·L⁻¹ CH₃OH at scan rate of 100 mV/s (a) WC; (b) 16.2 wt.% Pt/WC; (c) Pt

By contrast, 16.2 wt.% Pt supported on WC microspheres has reveals an effective current performance. The peak potential of methanol oxidation on Pt/WC shifts negatively by 90 mV than that of the plane Pt electrode (0.65 V for Pt/WC, 0.74 V for Pt). This means that the methanol oxidation can take place at a lower potential on Pt/WC.

The difference between the peak potentials for the forward and the backward sweeps is smaller (40 mV) on Pt/WC than on the plane Pt electrode. This suggests that Pt/WC catalyst has greater tolerance towards CO [19]. Therefore, Pt/WC showed potential capability of ethanol oxidation in DMFC. This indicates that adsorption structures of dissociated methanol on the platinum surface are $(\text{CH}_x\text{O})_{\text{ads}} (x=1\sim3)$ [20,21], which would be decomposed by high surface area WC [22]. Mesoporous WC would promote to active oxygen species ($-\text{OH}_{\text{ads}}$) as oxidants catalysts transform carbon monoxide (CO_{ads}) into carbon dioxide to reduce the impact of poisoning of the catalyst. The behavior of WC is very important to the material which would catalyze oxidation of ethanol for its high surface area and high adsorption ability of active oxygen species.

Consequently, the electrochemical activity during the methanol oxidation reaction on Pt/WC could be described by equation 1-6. The role of tungsten carbide in the oxidation of ethanol can be explained by reaction (2), (4) and (5) in the following way:



The overall reaction can be expressed as:

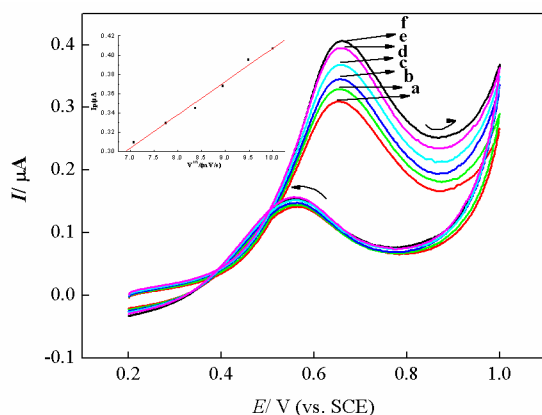
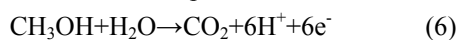


Figure 5. Cyclic voltammograms of Pt/WC-PME in $1\text{ mol}\cdot\text{L}^{-1}\text{CH}_3\text{OH} + 1\text{ mol}\cdot\text{L}^{-1}\text{H}_2\text{SO}_4$ at different scan rate: (a)50; (b)60; (c)70; (d)80; (e)90; (f)100 $\text{mV}\cdot\text{s}^{-1}$

In order to study the controllable process of methanol oxidation, the influence of scan rate has been discussed. Figure 5 shows the peak of oxidation mounting from $0.309\text{ }\mu\text{A}$ to $0.406\text{ }\mu\text{A}$ with the increasing of scanning speed. In order to research control characteristics of the electrode, linear relations between I_p and $v^{1/2}$ was fitted. The fitting line was showed on the inset of Figure 5. According to the result of linear relationship, methanol oxidation process in Pt/WC-PME is affected by liquid-phase mass transfer [23]. We believe that WC as a hollow mesoporous material has potential to improve the diffusion coefficient of electrode.

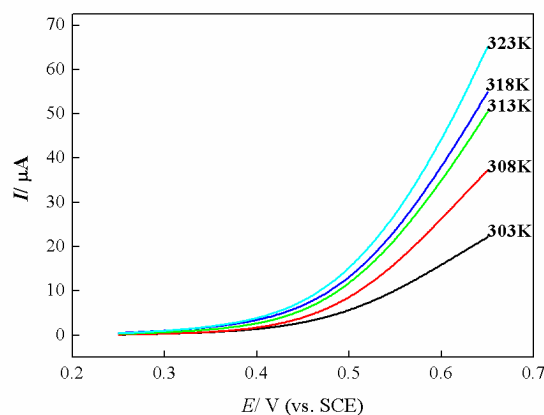


Figure 6. Linear sweep voltammetry in $1\text{ mol/L CH}_3\text{OH} + 1\text{ mol/L H}_2\text{SO}_4$ solution by Pt/WC-PME at different temperature

Figure 6 showed the quasi-steady-state polarization curves of methanol on the Pt/WC-PME at different temperature. It depicted that the polarization currents increased with increasing of temperature. These increasing electrochemical properties seemed to originate from the enhanced diffusion and adsorption on the electrode.

As mentioned above, these phenomena indicated that the transfer of the molecules can be improved by raising temperatures, which could finally promote the progress of methanol oxidation reaction.

4. Conclusions

Novel WC was synthesized by the carburizing of AMT which by using airflow spray dried. Hollow ball

structure was well copied from the precursor to WC sample, also mesoporous was created when the carburize processing in the atmosphere of CH_4/H_2 . Nano-Pt with particle size of 5~15 nm on mesoporous hollow WC has been synthesized by impregnation-vapor phase deoxidation method. This material with high-performance catalytic composite showed high stability and can be applied as an electrocatalyst. In addition, this catalyst represents synergy of Pt and WC, and methanol oxidation can take place at a lower potential on Pt/WC. High activity of methanol oxidation and Pt poisoning by CO can be prevented more effectively than signal-Pt.

References

- [1] Stevens D. A., Zhang S., Chen Z., Dahn J. R., *Carbon*, 2003, 41, 2769.
- [2] Williams M. C., *Fuel Cells*, 2001, 1, 87.
- [3] Costamagna P., Srinivasan S., *J. Power Sources*, 2001, 102, 242.
- [4] Li J. L., Mao Z. Q., *Battery Bimonthly* (Chinese), 2001, 31, 36.
- [5] Rojas S., García-García F. J., Jaras S., Martínez-Huerta M. V., García-Fierro J. L., Boutonnet M., *Applied Catalysis A: General*, 2005, 285, 24.
- [6] Cahen S., Furdin G., Maréche J. F., Albinia A., *Carbon*, 2008, 46, 511.
- [7] Bonnemant H., Brinkmann R., Britz P., Endruschat U., Mortel R., Paulus U. A., Feldmeyer G. J., Schmidt T. J., Gasteiger H. A., Behm R. J., *J. New Mat. Electrochem Syst.*, 2000, 3, 199.
- [8] Antolini E., *Mater. Chem. Phys.*, 2003, 78, 563.
- [9] Papageorgopoulos D. C., Keijzer M., Bruijn F. A., *Electrochim Acta*, 2002, 48, 197.
- [10] Vértés G., Horányi G., Szakács S., *J. Chem. Soc., Perkin Trans. II*, 1973, 1400.
- [11] Horányi G., Vértés G., *J. Chem. Soc., Perkin Trans. II*, 1975, 827.
- [12] Hudson M. J., Peckett J. W., Harris P. J. F., *Ind. Eng. Chem. Res.*, 2005, 44, 5575.
- [13] Hu L. H., Ji S. F., Xiao T. C., Guo C. X., Wu P. Y., Nie P. Y., *J. Phys. Chem. B*, 2007, 111, 3559.
- [14] York A. P. E., Claridge J. B., Brungs A. J., Tsang S. C., *Chem. Commun.* 1997, 9, 39.
- [15] Harald B., *Nature*, 1970, 227, 483.
- [16] Levy R. B., Boudart M., *Science*, 1973, 181, 547.
- [17] Ma C., Sheng J. F., Brandon N., Zhang C., Li G. H., *Int. J. Hydrogen Energy*, 2007, 32, 2824.
- [18] Kobayashi Y., Horie M., Nagao D., Ando Y., Miyazaki T., Konno M., *Materials Letters*, 2006, 60, 2046.
- [19] Rajesh B., Ravindranathan Thampi K., Bonard J. M., Xanthopoulos N., Mathieu H. J., Viswanathan B., *J. Phys. Chem. B*, 2003, 107, 2701.
- [20] Hwu H. H., Chen J. G., Kourtakis K., Gerry Lavin J., *J. Phys. Chem. B*, 2001, 105, 10037.
- [21] Lee J., Eickes C., Eiswirth M., Ertl G., *Electrochim. Acta*, 2002, 47, 2297.
- [22] Hwu H. H., Polizzotti B. D., Chen J. G., *J. Phys. Chem. B*, 2001, 105, 10045.
- [23] Bard A. J., Faulkner L. R., *Electrochemical Methods, Fundamentals and Applications*, 1st ed., John Wiley & Sons, New York, 1980, p. 215.