Short communication

An electrocatalyst for methanol oxidation based on tungsten trioxide microspheres and platinum

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Abstract

Tungsten trioxide microspheres of 2–4 μm diameter have been prepared by controlled oxidation of tungsten carbide microspheres. These microspheres are characterized by XRD, SEM, and HRTEM. The microspheres are made of WO_3 nanoparticles with an average diameter of around 15 nm. Platinum supported on these WO_3 microspheres exhibits higher and stable electrocatalytic activity for methanol oxidation by a factor of around two, than commercial 20 wt.% Pt–Ru/Vulcan-XC72 carbon and 20 wt.% Pt–Ru/carbon microspheres even without Ru. The higher activity is attributed to the better tolerance to carbon monoxide of the Pt/WO_3 catalyst. These Pt/WO_3 microspheres appear to be a promising alternative anode material for direct methanol fuel cells. They replace Ru entirely and save a substantial amount of Pt in the Pt–Ru electrode that is presently employed in fluel cells.
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1. Introduction

Among the various types of fuel cell, the direct methanol fuel cell (DMFC) is suited for portable devices, or perhaps transportation applications, due to its high specific energy at low operating temperatures and the ease of handling a liquid fuel [1]. Nevertheless, it has some critical technical drawbacks that include the slow oxidation kinetics of methanol relative to those of hydrogen in a polymer electrolyte membrane fuel cell (PEMFC). The reaction occurring at the negative electrode (anode) of a DMFC is the oxidation of methanol in the presence of water to produce CO_2, electrons and protons, i.e.,

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{1}$$
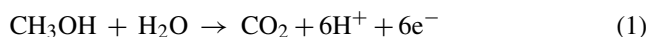
At present, the most promising anode materials for DMFCs are Pt–Ru bimetallic catalysts dispersed on carbon. This type of catalyst is favoured because of (i) its high activity for methanol oxidation and (ii) its water activation, which is critical for removal of the strongly adsorbed CO that is formed during the decomposition of methanol. In order to make up for the slow oxidation kinetics, however, high loadings (as high as 50 wt.%) of these expensive noble metals are required and this makes the DMFC expensive to produce. Further, the catalyst is still susceptible to CO poisoning [2]. Accordingly, there has been considerable research in recent years to replace noble metals for DMFC electrodes [3–5].

Platinum catalysts supported on tungsten oxide have been extensively studied [6] as active catalysts for the electrooxidation of methanol. Tungsten oxide can form a hydrogen bronze (H_xWO_3) that effectively facilitates the dehydrogenation of methanol [7,8]. Though these catalysts exhibit high performance, tungsten oxide undergoes dissolution in acid media and this reduces the electrocatalytic activity. The stability of tungsten oxide in acid media can be improved by suitably adjusting the conditions of its preparation [9].

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Carbon derived from metal carbides by selective etching of the metal component has been extensively studied in the literature [10,11]. The rigid carbide structure is used as a template for a carbon nanostructure. Because the metal is extracted layer by layer, control at the atomic level is achieved during the synthesis process. This study adopts an opposite approach, and for the first time, reports the synthesis of carbide-derived microspheres of tungsten trioxide by controlled oxidation of carbon in precursor microspheres of tungsten carbide. The synthesis and characterization of tungsten carbide microsphere have been reported elsewhere [12]. These tungsten trioxide microspheres combined with Pt display very high activity for the electrooxidation of methanol that exceeds the activities of a Pt–Ru catalyst supported on carbon microspheres and a commercial Pt–Ru catalyst with a higher metal loading. Thus, Pt/WO₃ microspheres could be a promising alternative anode material for DMFC and would replace Ru entirely and would substantially lower the amount of platinum compared with that in the present Pt–Ru electrode.

2. Experimental

Tungsten carbide (W₂C) microspheres were synthesized by heating composites composed of resorcinol-formaldehyde polymer as a carbon precursor and ammonium metatungstate salt (AMT) as a tungsten precursor [12]. In a typical synthesis, a mixture containing AMT, resorcinol, formaldehyde and water was mixed in a molar ratio of 4.0×10^{-4}: 1.1×10^{-2}:2.2×10^{-2}:1.1 and refluxed at 367 K for 24 h. The resulting gel was dried at room temperature and heated at 1173 K for 1 h in an argon flow and for 2 h in a hydrogen flow (68.2 μmol s⁻¹). The hydrogen treatment served to remove the free carbon deposited on the tungsten carbide surface [13]. The carbon microsphere was prepared in the same way, but without the AMT salt. The carbon in the tungsten carbide microspheres is selectively removed by calcining tungsten carbide at 773 K in an oxygen atmosphere for 3 h to obtain WO₃ microspheres. Platinum particles are supported on the WO₃ microspheres and the carbon microspheres by the conventional borohydride reduction method in neutral media [14]. The platinum content in each sample was analyzed by means of ICP (calibrated with a standard solution of Pt) after extracting platinum with aqua regia.

Powder X-ray diffraction (XRD) measurements were conducted with a Mac Science M18XHF diffractometer with Cu Kα radiation. The BET surface area and pore-size distribution were calculated from nitrogen adsorption/desorption at 77 K in a constant volume adsorption apparatus (Micrometrics ASAP2012). The morphology of the sample was examined by scanning electron microscopy (SEM) using a Hitachi S-4200 instrument and a Jeol 2001 high resolution transmission electron microscope (HRTEM).

The working electrodes for the electrochemical measurements were fabricated by dispersing the platinum-supported

catalysts in 1 ml of distilled water and 10 μL of 5 wt.% Nafion. The dispersion was ultrasonicated for 15 min. A given amount of the suspension was placed on the glassy carbon and the water was slowly evaporated. A further 10 μL of 5 wt.% Nafion was added to the coating and the solvent was slowly evaporated. Platinum foil and Ag/AgCl/3M NaCl were used as the counter and the reference electrodes, respectively. A solution of 1 M H₂SO₄ and 1 M CH₃OH was used for the electrochemical studies using Princeton Applied Research (PAR) voltammetry.

3. Results and discussion

Typical XRD patterns for the W₂C and WO₃ microspheres are shown in Fig. 1. The reflections of W₂C microspheres indicate that W₂C (hcp) is the major phase together with a trace of WC$_{1-x}$ (fcc) as the minor phase. There are no XRD
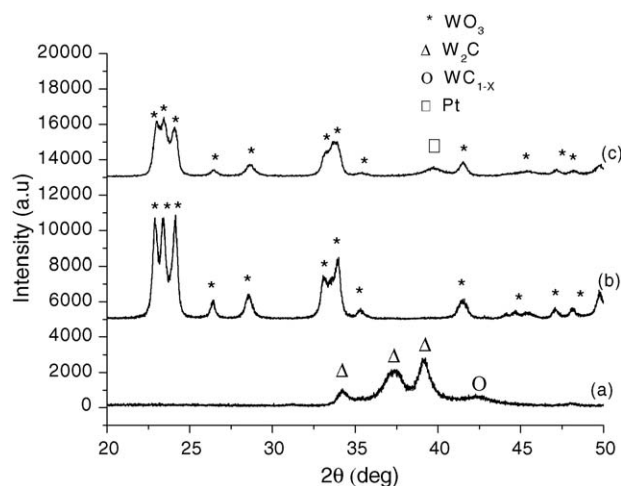

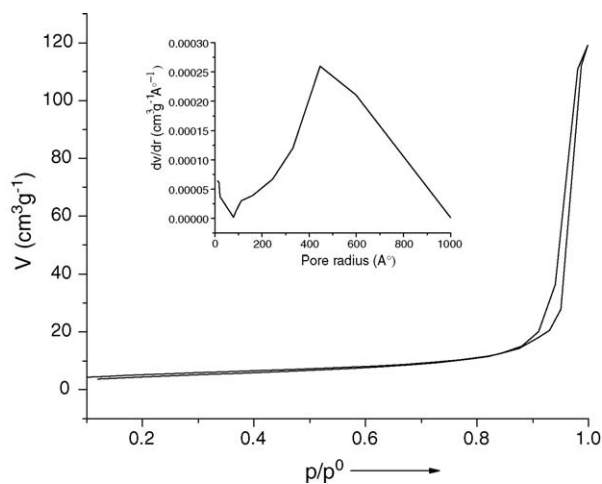Fig. 1. XRD patterns of (a) W₂C microspheres, (b) WO₃ microsphere, (c) Pt/WO₃ microspheres.

Fig. 2. Nitrogen adsorption/desorption isotherms on WO₃ microspheres. Inset shows BJH pore-size distribution calculated from analysis of desorption branch of each isotherms.

peaks that correspond to tungsten trioxide, metallic tungsten, or carbon materials. A typical XRD pattern for WO_3 prepared by oxidation of this carbide is shown in Fig. 1b. All of the reflection peaks can be indexed to pure monoclinic WO_3 (JCPDS card no. 43-1035). The XRD pattern of Pt-loaded WO_3 microspheres is given in Fig. 1c. The average crystallite size as estimated by application of the Debye-Scherer equation is 6.5, 15, 12 nm for Pt, WO_3, W_2C respectively.

The nitrogen adsorption/desorption isotherms for WO_3 microspheres are presented in Fig. 2. The isotherms are iden-tified as Type II, which is characteristic of macroporous materials. The pore-size distribution, as calculated from the desorption isotherm, shows a large number of pores of around 45 nm. The large pore-size is attributed to the inter-particle spaces between WO_3 nanoparticles of ~15 nm in diameter. The BET surface area of the WO_3 microspheres is about $18 \, m^2 \, g^{-1}$.

Microscopic images of the W_2C and WO_3 microspheres are shown in Fig. 3. Both microspheres have uniform mor-phology with diameters of 2–4 μm. The carbon microspheres
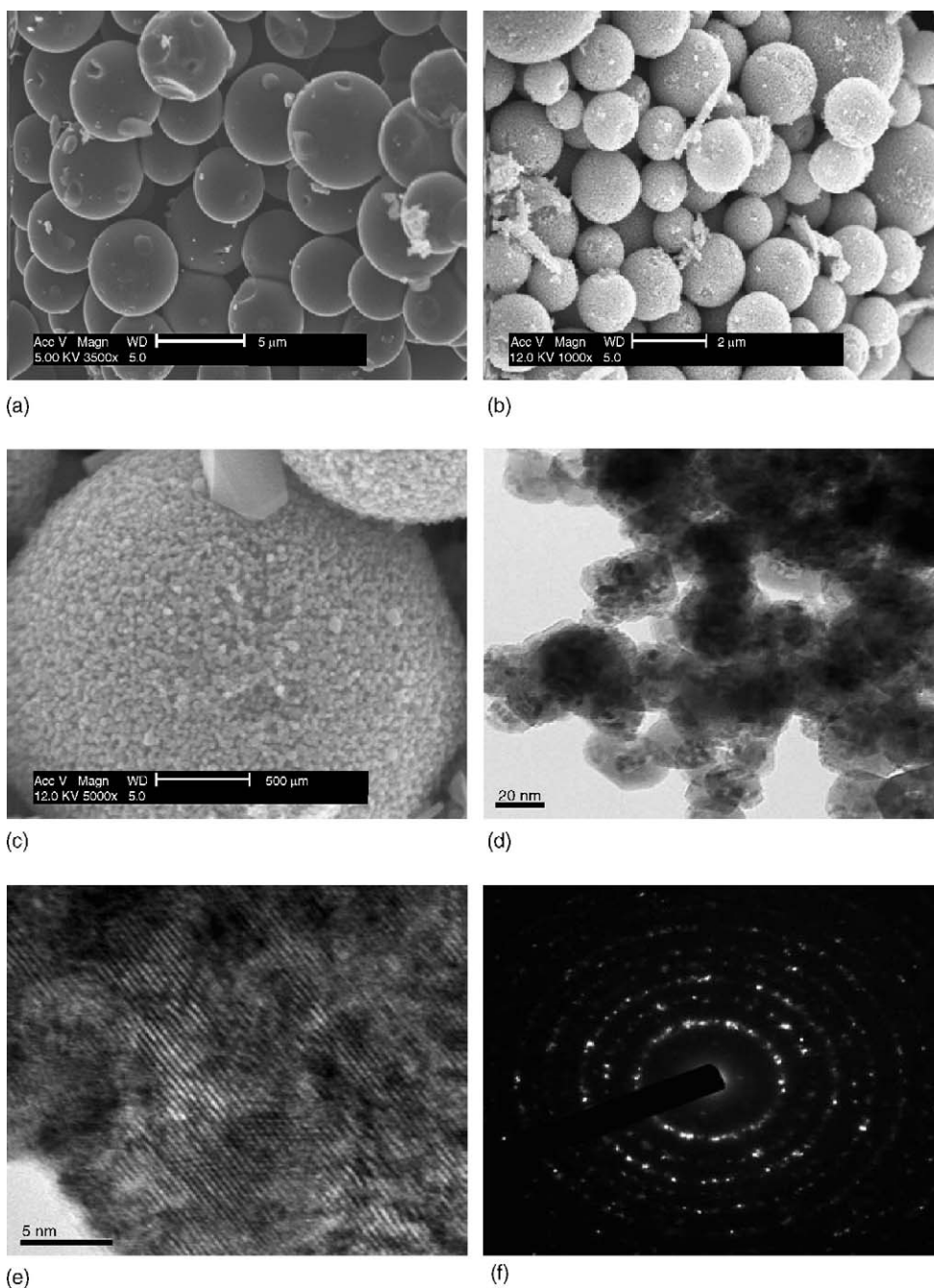

Fig. 3. (a) SEM image of W_2C micosphere, (b) SEM image of WO_3 microspheres, (c) SEM image of WO_3 microspheres (higher magnification), (d) HRTEM image of WO_3, microsphere, (e) Lattice image of WO_3 microspheres, (f) SAED pattern of WO_3 microspheres.
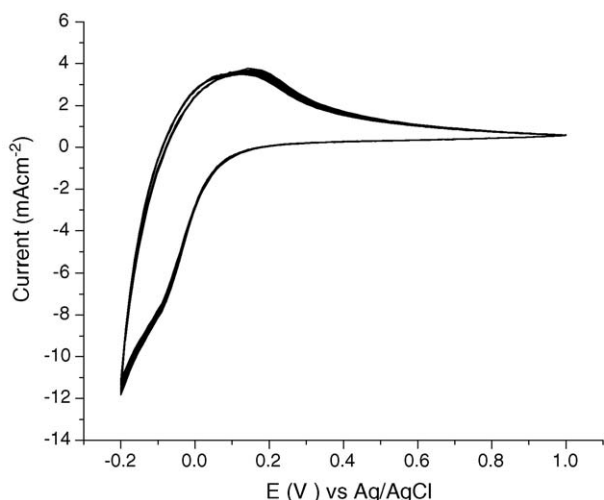
Fig. 4. Cyclic voltammaogram for WO_3 microspheres in 1 M H_2SO_4 at scan rate of 50 mV s^{-1} at 298 K.

Table 1
Electrocatalytic activity of various catalysts for methanol oxidation in 1 M H_2SO_4–1 M CH_3OH

Catalyst	Specific activity at 0.75 V (mA cm^{-2})	Mass activity at 0.75 V (mA mg-Pt^{-1})
WO_3	0.0	0.0
7.5 wt.% Pt/WO_3	131	584
20% Pt–Ru/carbon microsphere	87	280
20% Pt–Ru/VulcanXC-72R Commercial E-Teck catalyst	114	307

(not shown) also displays the same morphology. Thus, the carbide structure acts as a template for the formation of WO_3 microspheres. At higher magnification, it is seen that each sphere is made up of very tiny nanospherical particles (see Fig. 3c). The HRTEM images provide further insight into the structure of the WO_3 nanoparticles in the microspheres. As shown in Fig. 3d, the microsphere is made up of tiny nanospheres with an average size of ~15 nm. This is consistent with the particle size determined from the XRD line-broadening displayed in Fig. 1b. The lattice structure of WO_3 can be seen clearly in Fig. 3e. The lattice fringes are about 0.33 nm, which corresponds to the interplanar spacing of (2 0 0) planes of monoclinic WO_3 (JCPDS card no. 43-1035). The selected area electron diffraction pattern in (Fig. 3f) indicates that WO_3 is well crystallized and exhibits well-resolved ring patterns that are made up of many spots. Finally, EDX analysis of the WO_3 microspheres demonstrated that the material was composed of W and O with a composition of $WO_{1.8}$.

Cyclic voltammetry was employed to study the stability of tungsten trioxide microspheres in sulfuric acid medium. Tungsten trioxide shows a broad anodic current peak at 0.1 V. The peak is due to the formation of tungsten bronzes by hydrogen intercalation in the tungsten trioxide [15,16]. There is no decrease in peak current even after 50 cycles (see Fig. 4). This indicates that the tungsten trioxide microspheres are stable and do not undergo any dissolution in acid medium. This is a highly desirable attribute of the WO_3 microspheres prepared in this study for application as an electrocatalyst. The platinum particles are deposited on the WO_3 microspheres by the conventional borohydride reduction method [14]. The average particle size of the Pt is calculated from XRD analysis (Fig. 1) by using the Debye-Scherer equation and is about 6.5 nm, whereas Pt in 20 wt.% Pt–Ru/carbon microspheres has a size of about 14 nm. This difference in size influences the electrochemical activity towards oxidation of methanol (Table 1 and Fig. 5). The WO_3 microspheres without Pt dis-

play no activity. By contrast, 7.5 wt.% Pt supported on WO_3 microspheres has a higher current density (taken at 0.75 V, after the voltammogram became stabilized) than Pt–Ru supported on carbon microspheres or 20 wt.% Pt–Ru/VulcanXC-72R (the commercial E-Teck catalyst). The onset potential of methanol oxidation on Pt/WO_3 is found to be at 0.2 V, which is 100 mV more negative than that for Pt–Ru/C and the commercial 20% Pt–Ru/C E-Teck catalyst. The peak potential of methanol oxidation on Pt/WO_3 is also shifted by 50 mV more negative than that of the commercial E-Teck catalyst (0.75 V for Pt/WO_3, 0.80 V for commercial E-Teck catalyst). This suggests that methanol oxidation can take place at a lower potential on Pt/WO_3. The difference between the peak potentials for the forward and the backward sweeps is smaller (80 mV) on Pt/WO_3 than on the commercial E-Teck catalyst (270 mv) and on Pt–Ru/C (210 mV). This indicates that Pt/WO_3 catalyst has greater tolerance towards CO [17]. The mass activity (mA mg^{-1} of Pt taken at 0.75 V after voltammogram is stabilized) of Pt supported on WO_3 microspheres is higher by a factor of 2.1 and 1.9 than that of the Pt–Ru/carbon microspheres and the commercial E-Teck catalyst, respectively. This clearly shows that Pt dispersed on
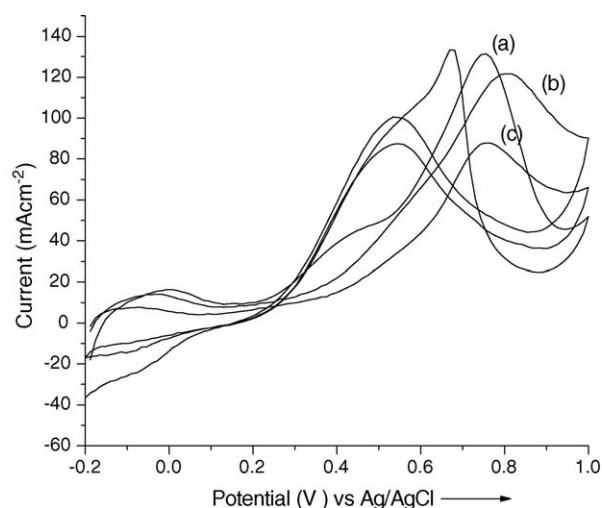

Fig. 5. Cyclic voltammaogram of (a) 7.5 wt.% Pt/WO_3 microspheres, (b) 20 wt.% Pt–Ru (1:1)/Vulcan XC-72 (commercial E-Teck catalyst), (c) 20 wt.% Pt–Ru (1:1)/carbon microsphere in 1 M H_2SO_4–1M CH_3OH solution at scan rate of 50 mV s^{-1} at 298 K.
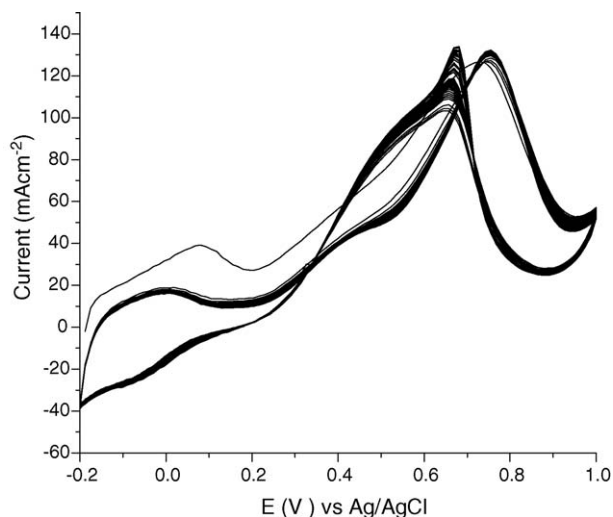
Fig. 6. Cyclic voltammogram of 7.5 wt.% Pt/WO$_3$-microspheres in a 1 M H$_2$SO$_4$–1 M CH$_3$OH solution at a scan rate of 50 mV s^{-1} at 298 K.

WO$_3$ microspheres provides much better utilization of Pt and that Ru could be entirely replaced.

The stability of the Pt/WO$_3$-microsphere catalyst was tested by repeating electrochemical reaction cycles in a 1 M H$_2$SO$_4$–1 M CH$_3$OH solution. As shown in Fig. 6, the specific activity, as represented by the area of voltammogram, increases initially, but becomes stabilized after about 15 cycles. Once a steady-state is established, there is no sign of deactivation during 100 consecutive reaction cycles.

4. Conclusions

Tungsten carbide-derived WO$_3$ microphares have been synthesized and characterized. An electrocatalyst composed of Pt supported on these microspheres display higher activity for electrochemical oxidation of methanol than a commercial Pt–Ru/C catalyst by a factor of 1.9 (per mass of Pt) even without Ru. The onset potential and peak potential of methanol oxidation on Pt/WO$_3$ is shifted by 100 and 50 mV more negative than that of a commercial E-Teck catalyst. This is probably due to better CO tolerance of the catalyst. The activ-

ity can be further increased by optimization of the Pt-loading technique to deposit Pt particles with a size smaller than 6 nm. Since the catalyst is also stable in an electrochemical environment, it could become a noble-metal-thrifty electrocatalyst for DMFCs with good prospects to replace present Pt–Ru catalysts.

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