Heterogeneous Catalysis

DOI: 10.1002/ange.200501272

Tungsten Carbide Microspheres as a Noble-Metal-Economic Electrocatalyst for Methanol Oxidation**

*Raman Ganesan and Jae Sung Lee**

Among various fuel cells, the direct methanol fuel cell (DMFC) is suited for portable devices or transportation applications owing to its high energy density at low operating temperatures and the ease of handling a liquid fuel.[1] However, the DMFC has some critical technical drawbacks including the slow oxidation kinetics of methanol relative to hydrogen in the polymer-electrolyte membrane fuel cell (PEMFC). The reaction occurring at the anode of the DMFC is the oxidation of methanol in the presence of water to produce CO_2, electrons, and protons [Eq. (1)].

$$CH_3OH + H_2O \rightarrow CO_2 + 6\,H^+ + 6\,e^- \quad (1)$$

Currently the most promising anode materials for the DMFC are Pt–Ru bimetallic catalysts dispersed on carbon. This catalyst is favored because of its high activity for methanol oxidation and for water activation, which is critical for the removal of strongly adsorbed CO formed during the decomposition of methanol. However, it still requires high loadings of these expensive noble metals, which makes the cost of DMFC prohibitively high. Further, this catalyst system is susceptible to CO poisoning.[2] Thus, in recent years there has been considerable interest in replacing noble metals in DMFC electrodes.[3]

Tungsten carbides have been studied extensively because of their interesting chemical and physical properties.[4] The carbides of Groups 4–6 (Ti–Cr groups) show catalytic properties similar to those of platinum group metals.[5,6] There have been several attempts to utilize tungsten carbide as an electrocatalyst because of its platinum-like catalytic behavior, its stability in acid solutions at anodic potentials, and its resistance to CO poisoning.[7] But when used for an anodic material under DMFC conditions, tungsten carbide alone showed low electrocatalytic activity although it showed resistance to CO poisoning.[8] Recent surface-science studies have demonstrated that the activity of tungsten carbide film or carbon-modified W(111) or W(110) single-crystal surfaces could be promoted by adding submonolayer coverages of platinum.[9] Herein we report for the first time the synthesis of W_2C microspheres with high surface areas and chemisorption capacity. The material when combined with platinum showed very high activity for the electrooxidation of methanol exceeding that of a commercial Pt–Ru catalyst with a higher metal loading. Thus Pt/W_2C microspheres could be a promising alternative anodic material for DMFC replacing ruthenium entirely and saving substantial amount of platinum from the current Pt–Ru electrodes. In addition, inorganic spheres have tailored properties, low densities, higher surface areas, and unique optical and surface properties, which are desired for applications as catalysts, sensors, and fillers.[10]

We synthesized W_2C microspheres by heating mixtures of resorcinol–formaldehyde polymer (a carbon precursor) and ammonium metatungstate salt (AMT) (a tungsten precursor). In a typical synthesis, a mixture containing AMT, resorcinol, formaldehyde, and water was mixed in a molar ratio of 8.1×10^{-4}:1.1×10^{-2}:2.2×10^{-2}:1.1 and heated under reflux at 367 K for 24 h. The resulting gel was dried at room temperature then heated at 1173 K for 1 h in an argon flow and 2 h in a hydrogen flow (100 mL min^{-1}). The H_2 treatment was to remove the free carbon deposited on the W_2C surface.[11] The carbon microsphere was prepared in the same way without AMT salt.

The typical X-ray diffraction (XRD) pattern of the resulting W_2C microspheres is shown in Figure 1. The reflections of the microsphere correspond to W_2C (hexagonal-close packed (hcp)) as the major phase and to WC (hcp) and WC_{1-x} (face-centered cubic (fcc)) as minor phases. The formation of tungsten–carbide phases depends on heating rate, temperature, and especially, the amount of carbon present in the sample.[11–13] To study this phase variation, the amount of AMT was varied from 4.1×10^{-4} mol to 16×10^{-4} mol in the polymer while keeping all others factors constant. A phase transition was observed from W_2C (with minor amount of WC_{1-x}) to pure WC (no other phases were present) as the amount of AMT increased. But at higher amounts of AMT, the surface area decreased and the spherical structure

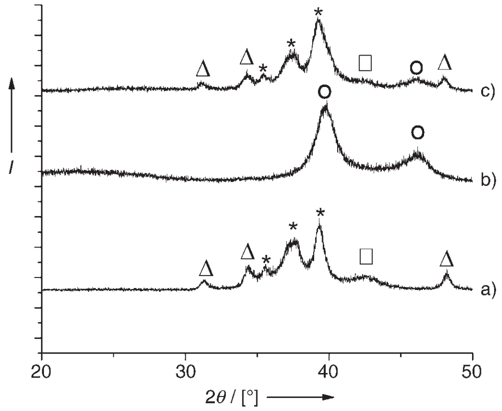

Figure 1. XRD patterns of a) W_2C microsphere, b) Pt–Ru/C- microsphere, and c) Pt/W_2C-microsphere. * W_2C, △ WC, □ WC_{1-x}, O Pt.

---

[*] Dr. R. Ganesan, Prof. J. S. Lee
Department of Chemical Engineering
Pohang University of Science and Technology
San 31 Hyoja-Dong, Pohang, 790-784 (Republic of Korea)
Fax: (+82) 542-795-528
E-mail: jlee@postech.ac.kr

[**] This work has been supported by National Research Laboratory program, National R&D Project for Nano Science and Technology, Bioplus Ltd and Hydrogen R&D Center.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

collapsed into bulk particles. The optimized molar ratio for the spherical structure with a high surface area was the composition specified above. Under these optimized conditions, we observed W_2C as the major phase with WC_{1-x} and WC as minor phases. There were no XRD peaks corresponding to tungsten trioxide, metallic tungsten, and carbon materials. Tungsten trioxide should be present as an amorphous phase because we observed the phase by X-ray photoelectron spectroscopy (XPS). The XRD pattern of carbon microspheres prepared without the tungsten salt AMT indicated an amorphous nature and showed no peaks.

The BET surface area of the W_2C microspheres was about 176 $m^2 g^{-1}$ (compared to 635 $m^2 g^{-1}$ for carbon microspheres). The CO uptake was calculated from temperature-programmed desorption (TPD) (see Supporting Information) by referring the area under the CO mass signal (28) to the known quantity of CO used. The CO uptake value (956 $\mu mol\, g^{-1}$) indicates that the number of CO molecules taken up corresponds to 18.7% of the total number of tungsten atoms in the sample. To our knowledge, these surface area and CO uptake values are the highest reported for tungsten carbide.[12,13] Carbon microspheres prepared without the tungsten salt AMT, and the commercial WC (Alfa-JM) did not chemisorb CO molecules. XPS of the W_{4f} doublet ($4f_{5/2}$ and $4f_{7/2}$) showed peaks at 31.6 eV and 32.5 eV, arising from the presence of tungsten carbide (see Supporting Information).[14] Peaks observed at higher binding energies indicate that a part of the tungsten is present as an oxide, which probably arises from surface oxidation of W_2C in air after preparation.[15]

The microscopic images of carbon and W_2C microspheres are shown in Figure 2. Both microspheres showed uniform morphology with diameters of 2–4 μm. The carbon microspheres appear to act as a template for the formation of W_2C microspheres. The W_2C microspheres were also observed under a high-resolution transmission electron microscope (HRTEM). As shown in Figure 2c, the microsphere appears to be a collection of W_2C nanoparticles wrapped with a carbon-rich skin. The surface was fairly rough (Figure 2d). The microspheres must be porous to give the high BET surface area of 176 $m^2 g^{-1}$. Furthermore, application of the Debye–Scherrer equation to the XRD peaks shown in Figure 1 gives a W_2C crystal size of approximately 12 nm. Energy dispersive X-ray spectroscopy (EDX) analysis of the W_2C microspheres showed that the surface was composed of tungsten, carbon, and oxygen and gave a composition of $WCO_{0.06}$ (see Supporting Information). There is a 100% excess of carbon over the stoichiometry of the observed main phase of W_2C. Thus, it appears that the microsphere is a composite material made of W_2C particles and carbon.

Platinum particles were supported on these W_2C and Pt–Ru particles on carbon microspheres by the conventional borohydride reduction method.[16] The HRTEM images (Figure 2e,f) show that the platinum particles are finely dispersed on W_2C microspheres but Ru–Pt alloy particles form large aggregates on carbon microspheres. The average platinum particle size is around 6 nm on W_2C, which is in good agreement with the value calculated from XRD (Figure 1) using the Debye–Scherrer equation (6 nm for 7.5 wt% Pt on W_2C, 14 nm for 15 wt% Pt on W_2C, and 14 nm for 20 wt% Pt–Ru on carbon microspheres).

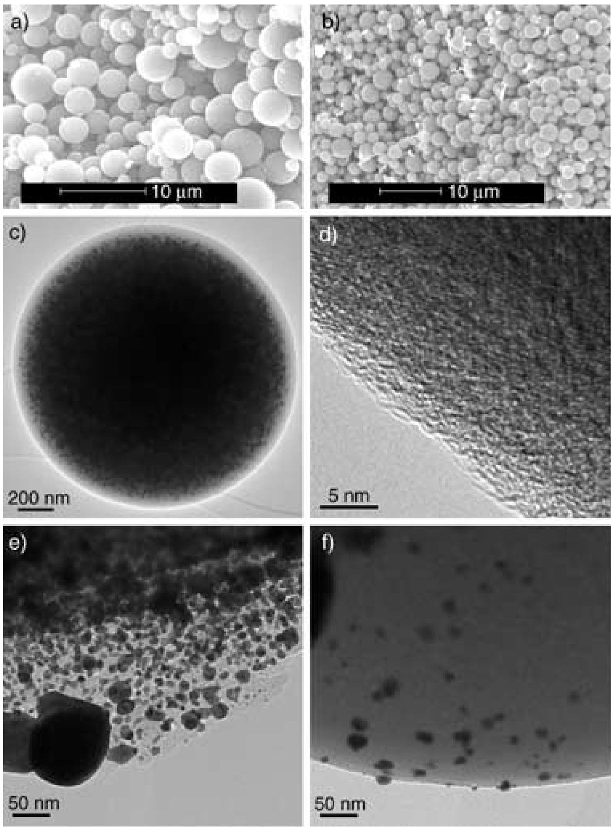

Figure 2. a) SEM image of carbon microspheres, b) SEM image of W_2C microspheres, c) HRTEM image of a W_2C microsphere, d) HRTEM image of the surface of a W_2C microsphere, e) HRTEM image of a Pt–Ru/carbon microsphere, f) HRTEM image of a Pt(7.5wt%)/W_2C microsphere.

By using hydrogen adsorption–desorption methods in conjunction with cyclic voltammetry the electrochemical surface area (ESA) of platinum supported on various catalysts was measured. As shown in Table 1, the ESA of platinum supported on W_2C is several-times higher than those of Pt–Ru supported on carbon microspheres and commercial (E-Teck) 20% Pt–Ru(1:1 atomic ratio)/Vulcan XC-72R carbon. This result indicates that the platinum particles were better dispersed on the W_2C spheres than on the other

Table 1: Electrocatalytic activity of various catalysts for methanol oxidation.

Catalyst	ESA[a] [$m^2 g^{-1}$ Pt]	Specific activity[b]	Mass activity[c]
W_2C	0.0	0.0	0.0
7.5 wt% Pt/W_2C	327	156	728
15 wt% Pt/W_2C	189	224	560
11 wt%Pt–9 wt%Ru/Carbon microsphere	58	87	280
13 wt%Pt–7 wt%Ru/VulcanXC-72R[d]	71	114	307

[a] Electrochemical surface area. [b] At 0.75 V [$mA\,cm^{-2}$]. [c] At 0.75 V [$mA\,mg^{-1}$ Pt]. [d] Commercial E-Teck catalyst

supports. This dispersion is reflected in the electrochemical activity towards the oxidation of methanol (Table 1 and Figure S4 in Supporting Information). The W_2C microspheres alone without platinum showed no activity. In contrast, both 7.5 wt% and 15 wt% Pt supported on W_2C microspheres show higher current density (taken at 0.75 V, after the cycle was stabilized) than Pt–Ru supported on carbon microspheres and a commercial 20% Pt–Ru E-Teck catalyst. The mass activity of platinum ($mA\,mg^{-1}$ of Pt taken at 0.75 V) supported on W_2C microspheres (7.5 wt% Pt) is higher by factors of 2.6 and 2.4 than those of Pt–Ru/carbon microspheres and the commercial E-Teck catalyst, respectively (that is, a lower amount of platinum is required to generate the same current. The mass activity of Pt/W_2C was greater for the lower platinum-loading electrocatalyst (7.5 wt% Pt versus 15 wt% Pt). These results clearly shows that platinum dispersed on W_2C microspheres provides much better utilization of platinum than in the Pt–Ru/carbon catalysts and that ruthenium could be entirely replaced.

There are several reasons why Pt/W_2C-microsphere catalyst performs better than the commercial catalyst even with the smaller platinum loadings and in the absence of ruthenium. The first is the ability of W_2C to stabilize the high dispersion of platinum relative to carbon supports as discussed above. Second, in the presence of platinum, W_2C is active in the electrochemical methanol oxidation and water decomposition as discussed by Chen and co-workers.[9] The formation of hydroxy groups from water activation is essential for the removal of metal-poisoning CO from the surface. This converion is the main role played by ruthenium in conventional Pt–Ru catalysts and this role can be played by W_2C. Finally, W_2C shows high CO resistance. The CO desorption temperature for pure platinum is 460 K.[17] It decreases to 420 K (Figure S1 in Supporting Information), when the platinum is supported on W_2C. This feature would decrease the poisoning of the catalyst surface by CO and increase the activity for electrooxidation of methanol.

The stability of the Pt/W_2C-microsphere catalyst was tested by repeating electrochemical reaction cycles in a 1 M H_2SO_4/1 M CH_3OH solution. As shown in Figure 3, the specific activity as represented by the area of cyclovoltammogram increased initially, but stabilized after around 30 cycles. We believe that surface oxygen species formed on the catalyst are removed during this transient period. Once a steady state is established, there was no sign of deactivation during 100 consecutive reaction cycles.

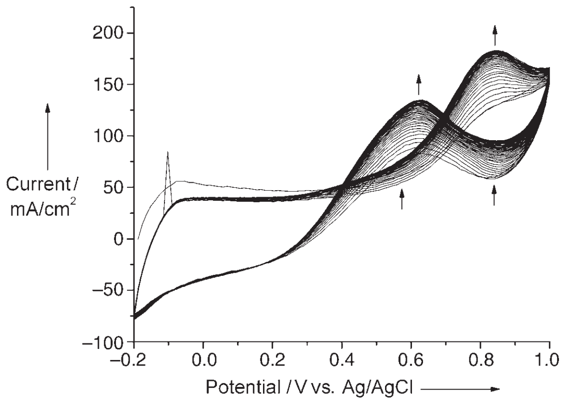

Figure 3. Cyclic voltammogram of 7.5% Pt/W_2C-microsphere in a 1 M H_2SO_4/1 M CH_3OH solution at a scan rate of 50 $mV\,s^{-1}$ at 298 K, arrows indicate changes with increasing numbers of scans.

In summary we have for the first time synthesized and characterized W_2C microspheres by a polymer method. A new ruthenium-free electrocatalyst composed of platinum supported on these microspheres shows higher activity for electrochemical oxidation of methanol than a commercial Pt–Ru/C catalyst by a factor of 2.4 (per mass of Pt). This activity could be further increased with optimization of the platinum-loading technique to deposit platinum particles smaller than 6 nm. Since the catalyst is also stable in electrochemical environment, it could become a noble-metal-economic electrocatalyst for DMFC and has the potential to replace current Pt–Ru catalysts.

Experimental Section

Before TPD experiments, the catalysts were activated at 473 K in hydrogen for 1 h. After cooling to room temperature the CO chemisorption was carried out at room temperature for 1 h. Finally CO was desorbed by heating from room temperature to 573 K in He flow.

The working electrodes for the electrochemical measurements were fabricated by dispersing the platinum supported catalysts in 1 mL of distilled water and 5 wt% Nafion (10μL). The dispersion was ultrasonicated for 15 min. A known amount of suspension was added on to the glassy carbon and the solvent was slowly evaporated. 5 wt% Nafion (10μL) was added onto the coatings and the solvent was slowly evaporated. Pt foil and Ag/AgCl/3 M NaCl were used as counter and reference electrodes, respectively. A solution of 1M H_2SO_4/1M CH_3OH was used for electrochemical studies using Princeton Applied Research (PAR) voltammetry.

Received: April 12, 2005
Revised: May 18, 2005

Keywords: carbides · fuel cells · heterogeneous catalysis · platinum · tungsten

---

[1] M. Winter, R. J. Brodd, *Chem. Rev.* **2004**, *104*, 4245.
[2] H. Zhang, Y. Wang, E. R. Fachini, C. R. Cabrera, *Electrochem. Solid-State Lett.* **1999**, *2*, 437.
[3] a) H. C. Yu, K. Z. Fung, Tz. C. Guo, W. L. Chang, *Electrochim. Acta* **2004**, *50*, 807; b) V. Raghuveer, B. Viswanathan, *Fuel* **2002**, *81*, 17; c) V. Raghuveer, K. R. Thampi, J. M. Bonard, N. Xanthopoulos, H. J. Mathieu, B. Viswanathan, *Solid State Ionics* **2001**, *140*, 263.
[4] a) J. S. Lee, S. Locatelli, S. T. Oyama, M. Boudart, *J. Catal.* **1990**, *125*, 157; b) J. S. Lee, S. T. Oyama, M. Boudart, *J. Catal.* **1987**, *106*, 125; c) R. B. Levy, M. Boudart, *Science* **1973**, *181*, 547.
[5] a) M. A. A. Merino, F. C. Marin, J. L. G. Fierro, C. M. Castilla, *J. Catal.* **2003**, *192*, 363; b) J. S. Lee, M. Boudart, *Catal. Lett.* **1993**, *20*, 97; c) S. Li, J. S. Lee, *J. Catal.* **1998**, *173*, 134; d) S. Li, J. S. Lee, *J. Catal.* **1998**, *178*, 119; e) J. S. Lee, M. Boudart, *Catal. Lett.* **1991**, *8*, 107; f) J. S. Lee, L. Volpe, F. H. Ribeiro, M. Boudart, *J. Catal.* **1988**, *112*, 44; g) J. S. Lee, M. Boudart, *Appl. Catal.* **1985**, *19*, 207.
[6] a) M. J. Ledoux, C. P. Huu, J. Guille, H. Dunlop, *J. Catal.* **1992**, *134*, 383; b) M. J. Ledoux, C. P. Huu, *Catal. Today* **1992**, *15*, 263; c) C. P. Huu, M. J. Ledoux, J. Guille, *J. Catal.* **1993**, *143*, 249;

d) M. J. Ledoux, P. D. Gallo, C. P. Huu, A. P. E. York, *Catal. Today* **1996**, *27*, 145; e) M. J. Ledoux, C. P. Huu, R. R. Chianelli, *Curr. Opin. Solid State Mater. Sci.* **1996**, *1*, 96; f) F. Eunier, P. Delporte, B. Heinrich, C. Bouchy, C. Crouzet, C. P. Huu, P. Panissod, J. J. Lerou, L. P. Mills, M. J. Ledoux, *J. Catal.* **1997**, *169*, 33; g) C. P. Huu, C. Bouchy, T. Dintzer, G. Ehret, C. Estournes, M. J. Ledoux, *Appl. Catal. A* **1999**, *180*, 385; h) M. J. Ledoux, F. Meunier, B. Heinrich, C. P. Huu, M. E. Harlin, A. I. Krause, *Appl. Catal. A* **1999**, *181*, 157; i) N. Keller, C. P. Huu, G. Ehret, V. Keller, M. J. Ledoux, *Carbon* **2003**, *41*, 2131; j) D. Mordenti, D. Brodzki, G. Djega-Mariadassou, *J. Solid State Chem.* **1998**, *141*, 114; k) S. H. Kim, G. Bugli, G. Djega-Mariadassou, *J. Solid State Chem.* **1999**, *142*, 100; l) T. Becue, J. M. Manoli, C. Potvin, R. J. Davis, G. Djega-Mariadassou, *J. Catal.* **1999**, *186*, 110; m) J. S. Choi, G. Bugli, G. Djega-Mariadassou, *J. Catal.* **2000**, *193*, 238; n) A. Szymanska, M. S. Lewandowski, C. Sayag, G. Djega-Mariadassou, *J. Catal.* **2003**, *218*, 24; o) J. Y. Piquemal, C. Potvin, J. M. Manoli, G. Djega-Mariadassou, *Catal. Lett.* **2004**, *92*, 189; p) A. Otarba, G. Adamski, W. Piskorz, Z. Sojka, C. Sayag, G. Djega-Mariadassou, *J. Phys. Chem. B* **2004**, *108*, 2885; q) F. H. Ribeiro, B. Dalla, A. Ralph M. Boudart, J. Baumgartner, E. Iglesia, *J. Catal.* **1991**, *130*, 86; r) F. H. Ribeiro, M. Boudart, B. Dalla, A. Ralph, E. Iglesia, *J. Catal.* **1991**, *130*, 498; s) E. Iglesia, J. E. Baumgartner, F. H. Ribeiro, M. Boudart, *J. Catal.* **1991**, *131*, 523; t) E. Iglesia, F. Ribeiro, M. Boudart, J. E. Baumgartner, *Catal. Today* **1992**, *15*, 307; u) E. Iglesia, F. H. Ribeiro, M. Boudart, J. E. Baumgartner, *Catal. Today* **1992**, *15*, 455.

[7] a) C. J. Barnett, G. T. Burstein, A. R. J. Kucernak, K. R. Williams, *Electrochim. Acta* **1997**, *42*, 2381; b) S. Bodoardo, M. Maja, N. Penazzi, F. E. G. Henn, *Electrochim. Acta* **1997**, *42*, 2603.

[8] a) M. B. Zellner, J. G. Chen, *Catal. Today* **2005**, *99*, 299; b) D. R. McIntyre, G. T. Burstein, A. Vossen, *J. Power Sources* **2002**, *107*, 67.

[9] H. H. Wu, J. G. Chen, *J. Vac. Sci. Technol. A* **2003**, *21*, 148.

[10] a) D. E. Bergbreiter, *Angew. Chem.* **1999**, *111*, 3044; *Angew. Chem. Int. Ed.* **1999**, *38*, 2870; b) X. M. Sun, Y. D. Li, *Angew. Chem.* **2004**, *116*, 607; *Angew. Chem. Int. Ed.* **2004**, *43*, 597; c) X. L. Li, T. J. Lu, X. M. Sun, Y. D. Li, *Inorg. Chem.* **2004**, *43*, 5442.

[11] F. H. Ribeiro, R. A. D. Betta, G. J. Guskey, M. Boudart, *Chem. Mater.* **1991**, *3*, 805.

[12] S. Ramanathan, S. T. Oyama, *J. Phys. Chem.* **1995**, *99*, 16365.

[13] L. Volpe, M. Boudart, *J. Solid State Chem.* **1985**, *59*, 348.

[14] A. Katrib, F. Hemming, L. Hilaire, P. Wehrer, G. Maire, *J. Electron Spectrosc. Relat. Phenom.* **1994**, *68*, 589.

[15] S. Wanner, L. Hilaire, P. Wehrer, J. P. Hindermann, G. Maire, *Appl. Catal. A* **2000**, *203*, 55.

[16] P. R. Van Rhennen, M. J. McKelvy, W. S. Glaunsingers, *J. Solid State Chem.* **1987**, *67*, 151.

[17] a) G. Ertl, M. Neuman, K. M. Streit, *Surf. Sci.* **1977**, *64*, 393; b) A. Crossley, D. A. King, *Surf. Sci.* **1977**, *68*, 528.