Simple and Low-Cost Preparation Method for Highly Dispersed PtRu/C Catalysts

Bo Yang, Qingye Lu, Yang Wang, Lin Zhuang,* Juntao Lu, and Peifang Liu

Department of Chemistry, Wuhan University, Wuhan 430072, China

Jianbo Wang and Renhui Wang

Center for Electron Microscopy, Wuhan University, Wuhan 430072, China

Received April 30, 2003. Revised Manuscript Received June 26, 2003

A low-cost impregnation method was developed to prepare PtRu catalysts highly dispersed on carbon support. As clearly revealed by the HRTEM image, even with high metal loadings (up to 40 wt % Pt + 20 wt % Ru) the average particle diameter was 1.5 nm with a narrow distribution (±0.5 nm). Based on EDAX, XRD, XPS, and TGA/DTA analyses, the structure of the PtRu catalyst was deduced to be composed of PtRu alloy and amorphous ruthenium compounds, predominantly hydrous ruthenium oxide, RuO_xH_y. The PtRu catalyst thus-prepared exhibited excellent performance for methanol oxidation.

Introduction

PtRu catalyst is currently the most active anode catalyst for direct methanol fuel cells (DMFC).[1−5] Numerous works have been devoted to the preparation[6−45] and the structure−activity relationship study[46−67] of this kind of catalyst. To achieve high dispersion, PtRu

---

* To whom correspondence should be addressed. E-mail: lzhuang@whu.edu.cn.

(1) Hogarth, M.; Ralph, T. *Platinum Met. Rev.* **2002**, *46*, 146.

(2) Arico, A.; Srinivasan, S.; Antonucci, V. *Fuel Cells* **2001**, *1* (2), 1.

(3) Wasmus, S.; Kuver, A. *J. Elctroanal. Chem.* **1999**, *461*, 14.

(4) McNicol, B.; Rand, D.; Williams, K. *J. Power Sources* **1999**, *83*, 15.

(5) Lamy, C.; Leger, J.-M. In *Interfacial Electrochemistry*: Theory, Experiment, and Applications; Wieckowski, A., Ed.; Marcel Dekker: New York, 1999; Chapter 48, p 885.

(6) Antolini, E. *Mater. Chem. Phys.* **2003**, *78*, 563.

(7) Fujiwara, N.; Yasuda, K.; Ioroi, T.; Siroma, Z.; Miyazaki, Y. *Electochim. Acta* **2002**, *47*, 4079.

(8) Lasch, K.; Hayn, G.; Jorissen, L.; Garche, J.; Besenhardt, O. *J. Power Sources* **2002**, *105*, 305.

(9) Arico, A.; Monforte, G.; Modica, E.; Antonucci, P.; Antonucci, V. *Electrochem. Commun.* **2000**, *2*, 446.

(10) Wiltham, C.; Chun, W.; Valdez, T.; Narayanan, S. *Electrochem. Solid-State Lett.* **2000**, *3*, 497.

(11) Denis, M.; Gouerec, P.; Guay, D.; Dodelet, J.; Lalande, G.; Schulz, R. *J. Appl. Electrochem.* **2000**, *30*, 1243.

(12) Denis, M.; Lalande, G.; Gouerec, P.; Guay, D.; Dodelet, J.; Schulz, R. *J. Appl. Electrochem.* **1999**, *29*, 951.

(13) Pan, C.; Dassenoy, F.; Casanove, M.; Philippot, K.; Amiens, C.; Lecante, P.; Mosset, A.; Chaudret, B. *J. Phys. Chem. B* **1999**, *103*, 10098.

(14) Vogel, W.; Britz, P.; Bonnemann, H.; Rothe, J.; Horms, J. *J. Phys. Chem. B* **1997**, *101*, 11029.

(15) Schmidt, T.; Noeske, M.; Gasteiger, H.; Behm, R.; Britz, P.; Brijoux, W.; Bonnemann, H. *Langmuir* **1997**, *13*, 2591.

(16) Chu, D.; Gilman, S. *J. Electrochem. Soc.* **1996**, *143*, 1685.

(17) Escudero, M.; Hontanon, E.; Schwartz, S.; Boutonnet, M.; Daza, L. *J. Power Sources* **2002**, *106*, 206.

(18) Dickinson, A.; Carrette, L.; Collins, J.; Friedrich, K.; Stimming, U. *Electrochim. Acta* **2002**, *47*, 3733.

(19) Boxall, D.; Deluga, G.; Kenik, E.; King, W.; Lukehart, C. *Chem. Mater.* **2001**, *13*, 891.

(20) Paulus, U.; Endruschat, U.; Feldmeyer, G.; Schmidt, T.; Bonnemann, H.; Behm, R. *J. Catal.* **2000**, *195*, 383.

(21) Bonnemann, H.; Brinkmann, R.; Britz, P.; Endruschat, U.; Mortel, R.; Paulus, U.; Feldmeyer, G.; Schmidt, T.; Gasteiger, H.; Behm, R. *J. New Mater. Electrochem. Sys.* **2000**, *3*, 199.

(22) Schmidt, T.; Noeske, M.; Gasteiger, H.; Behm, R.; Britz, P.; Bonnemann, H. *J. Electrochem. Soc.* **1998**, *145*, 925.

(23) Gotz, M.; Wendt, H. *Electrochim. Acta* **1998**, *43*, 3637.

(24) Pozio, A.; Silva, R.; De Francesco, M.; Cardellini, F.; Giorgi, L. *Electrochim. Acta* **2002**, *48*, 255.

(25) Antolini, E.; Giorgi, L.; Cardellini, F.; Passalacqua, E. *J. Solid State Electrochem.* **2001**, 5, 131.

(26) Luna, A.; Camara, G.; Paganin, V.; Ticianelli, E.; Gonzalez, E. *Electrochem. Commun.* **2000**, *2*, 222.

(27) Radmilovic, V.; Gasteriger, H.; Ross, P. *J. Catal.* **1995**, *154*, 98.

(28) Swathirajan, S.; Mikhail, Y. *J. Electrochem. Soc.* **1991**, *138*, 1321.

(29) Watanabe, M.; Uchida, M.; Motoo, S. *J. Electroanal. Chem.* **1987**, *229*, 395.

(30) Hills, C.; Mack, N.; Nuzzo, R. *J. Phys. Chem. B* **2003**, *107*, 2626.

(31) Steigerwalt, E.; Deluga, G.; Lukehart, C. *J. Phys. Chem. B* **2002**, *106*, 760.

(32) Steigerwalt, E.; Deluga, G.; Cliffel, D.; Lukehart, C. *J. Phys. Chem. B* **2001**, *105*, 8097.

(33) Che, G.; Lakeshmi, B.; Martin, C.; Fisher, E. *Langmuir* **1999**, *15*, 750.

(34) Che, G.; Lakeshmi, B.; Fisher, E.; Martin, C. *Nature* **1998**, *393*, 346.

(35) Fujiwara, N.; Shiozaki, Y.; Tanimitsu, T.; Yasuda, K.; Miyazaki, Y. *Electrochemistry* **2002**, *70*, 988.

(36) Antolini, E.; Cardellini, F. *J. Alloys Compd.* **2001**, *315*, 118.

(37) Takasu, Y.; Fujiwara, T.; Murakami, Y.; Sasaki, K.; Oguri, M.; Asaki, T.; Sugimoto, W. *J. Electrochem. Soc.* **2000**, *147*, 4421.

(38) Hills, C.; Nashner, M.; Frenkel, A.; Shapley, J.; Nuzzo, R. *Langmuir* **1999**, *15*, 690.

(39) Nashner, M.; Frenkel, A.; Somerville, D.; Hills, C.; Shapley, J.; Nuzzo, R. *J. Am. Chem. Soc.* **1998**, *120*, 8093.

(40) Nashner, M.; Frenkel, A.; Adler, D.; Shapley, J.; Nuzzo, R. *J. Am. Chem. Soc.* **1997**, *119*, 7760.

(41) Giror-Fendler, A.; Richard, D.; Gallezot, P. *Faraday Discuss.* **1991**, *92*, 69.

(42) McNicol, B.; Short, R. *J. Electroanal. Chem.* **1977**, *81*, 249.

(43) Machida, K.; Fukuoka, A.; Ichikawa, M.; Enyo, M. *J. Electrochem. Soc.* **1991**, *138*, 1958.

(44) Kenedy, B.; Smith, A. *J. Electroanal. Chem.* **1990**, *293*, 103.

(45) Goodenough, J.; Hamnett, A.; Kennedy, B.; Manoharan, H.; Weeks, S. *J. Electroanal. Chem.* **1988**, *240*, 133.

(46) Rolison, D. *Science* **2003**, *299*, 1698.

(47) Long, J.; Stroud, R.; Swider-Lyons, K.; Rolison, D. *J. Phys. Chem. B* **2000**, *104*, 9772.

(48) Rolison, D.; Hagans, P.; Swider, K.; Long, J. *Langmuir* **1999**, *15*, 774.

(49) Koper, M.; Shubina, T.; Santen, R. *J. Phys. Chem. B* **2002**, *106*, 686.

(50) Arico, A.; Antonucci, P.; Modica, E.; Baglio, V.; Kim, H.; Antonucci, V. *Electrochim. Acta* **2002**, *47*, 3723.

10.1021/cm034306r CCC: $25.00

catalyst is usually supported on a high-surface-area carbon support such as Vulcan XC-72. Among the preparation methods reported in the literature for carbon-supported PtRu catalysts (PtRu/C),[17−45] colloidal chemistry methods are the most adopted routes.[20−29] The colloidal methods usually include the following common steps: (1) preparation of PtRu-containing colloids, e.g., organometallic colloids[20−23] or metal oxide colloids,[24−29] (2) deposition of the colloids onto the carbon support, and (3) chemical reduction of the mixture. Although highly dispersed PtRu catalysts can be attained, these methods are relatively high in cost and low in efficiency.[2] These methods are somewhat complex in general. Especially, repeated filtering and washing are often required for the nanoscaled particles,[23−29] but these procedures are time-consuming and easily cause loss of noble metals.

Another widely adopted category of methods for preparing PtRu/C is based on an impregnation process.[30−42] An obvious advantage of these methods is they eliminate the need for filtering and washing procedures and are suitable for large-scale production.[4] However, it has been said that these methods are not able to obtain high dispersions for high metal loadings,[2] especially when chlorine-containing precursors, e.g., H_2PtCl_6 and $RuCl_3$, were used directly.[4,36,37] In fact, the structure and the activity of PtRu/C are very sensitive to the preparation conditions. Recently, we found that under appropriate conditions highly dispersed PtRu/C with metal loadings as high as 60 wt % can still be obtained by impregnation method, even using chlorine-containing precursors. Furthermore, some structure parameters such as particle size, alloyed degree, and hydrous level, were found to be tunable in our procedures. In this paper, emphases will be put on the preparation and the characterization of the catalyst. Detailed studies of the structure−activity relationship will be reported elsewhere.

Hydrous ruthenium oxide, $RuO_2 \cdot xH_2O$ or RuO_xH_y, is a well-known anode catalyst in the chloralkali industry[68] and an excellent energy-storage material for supercapacitor.[69−71] Recently, it was found that the presence of RuO_xH_y in PtRu catalyst greatly promoted the electrocatalysis of methanol oxidation.[46−48] The benefits of RuO_xH_y are attributed to its electrons and protons conductibility and the innate possession of a surface OH group,[68,47,48,72] which is the key species in the methanol oxidation mechanism.[1−3,73−75] Using hydrous PtRu as the anode catalyst seems to be a new trend in developing high-performance DMFCs.[46−48,76,77] Therefore, efforts were made in this work to obtain RuO_xH_y-rich catalyst instead of bimetallic PtRu alloy which was emphasized in the most relevant papers, especially those that are relatively old.

Experimental Section

Catalyst Preparation. H_2PtCl_6 and $RuCl_3$ were directly used as the precursors and were dissolved in alcohol or water. High-surface-area carbon black, e.g., Vulcan XC-72 (Carbot), was preheated at 110 °C in air and then poured into the warm precursor solution. The weight ratio of Pt−Ru−C was controlled according to the targeted metal loading. After ultrasonic blending for 30 min, the suspension was heated under magnetic stirring to let the solvent evaporate till a smooth thick slurry resulted which had an apparent volume over 10 times larger than that of the raw carbon powder. The slurry was left overnight for drying then further dried at 110 °C in an oven. The resulting agglomerates were ground in an agate mortar and then placed in a glazed ceramic boat and heated in a tube furnace at 120 °C under flowing H_2 for 2 h. Finally, the powder material was cooled to room temperature in argon atmosphere.

Catalysts with different metal loadings were prepared in the above-described manner and high dispersion was reached for all samples. For a concise demonstration of our method, this paper reports mainly the results of high loading (40 wt % Pt + 20 wt % Ru) samples, for which high dispersion is generally considered more difficult to obtain than for low loadings.

Catalyst Characterizations. High-resolution transmission electron microscopy (HRTEM) examination and energy-dispersive analysis by X-rays (EDAX) were performed on a JEOL JEM-2010FEF ultrahigh-resolution transmission electron microscope working at 200 kV accelerating voltage. The ultimate spatial resolution of the instrument was 0.19 nm. Specimens were prepared by ultrasonically suspending the catalyst powders in ethanol, applying the suspension onto a celloidin-covered holey Cu grid, and drying it in air.

Powder X-ray diffraction (XRD) pattern for the catalyst was obtained on a Shimadzu XRD-6000 X-ray diffractometer using Cu Kα radiation source operating at 40 kV and 30 mA. The peak profile of the (220) reflection of Pt face-centered cubic

---

(51) Jusys, Z.; Kaiser, J.; Behm, R. *Electrochim. Acta* **2002**, *47*, 3693.

(52) Takasu, Y.; Itaya, H.; Iwazaki, T.; Miyoshi, R.; Ohnuma, T.; Sugimoto, W.; Murakami, Y. *Chem. Commun.* **2001**, 341.

(53) O'Grady, W.; Hagans, P.; Pandya, K.; Maricle, D. *Langmuir* **2001**, *17*, 3047.

(54) Iwasita, T.; Hoster, H.; John-Anacker, A.; Lin, W.; Vielstich, W. *Langmuir* **2000**, *16*, 522.

(55) Antolini, E.; Cardellini, F.; Giorgi, L.; Passalacqua, E. *J. Mater. Sci. Lett.* **2000**, *19*, 2099.

(56) Arico, A.; Creti, P.; Modica, E.; Monforte, G.; Baglio, V.; Antonucci, V. *Electrochim. Acta* **2000**, *45*, 4319.

(57) Dinh, H.; Ren, X.; Garzon, F.; Zelenay, P.; Gottesfeld, S. *J. Electroanal. Chem.* **2000**, *491*, 222.

(58) Crown, A.; Kim, H.; Lu, G.; Moraes, I.; Rice, C.; Wieckowski, A. *J. New Mater. Electrochem. Sys.* **2000**, *3*, 275.

(59) Lin, S.; Hsiao, T.; Chang, J.; Lin, A. *J. Phys. Chem. B* **1999**, *103*, 97.

(60) McBreen, J.; Mukerjee, S. In *Interfacial Electrochemistry*; Wieckowski, A., Ed.; Marcel Dekker: New York, 1999; Chapter 49, p 895.

(61) Chrzanowski, W.; Wieckowski, A. In *Interfacial Electrochemistry*; Wieckowski, A., Ed.; Marcel Dekker: New York, 1999; Chapter 51, p 937.

(62) Chrzanowski, W.; Wieckowski, A. *Langmuir* **1998**, *14*, 1967.

(63) Arico, A.; Creti, P.; Kim, H.; Mantegna, R.; Giordano, N.; Antonucci, V. *J. Electrochem. Soc.* **1996**, *143*, 3950.

(64) Aberdam, D.; Durand, R.; Faure, R.; Gloaguen, F.; Hazemann, J.; Herrero, E.; Kabbabi, A.; Ulrich, O. *J. Electroanal. Chem.* **1995**, *398*, 43.

(65) Gasteiger, H.; Makovic, N.; Ross, P.; Cairns, E. *J. Electrochem. Soc.* **1994**, *141*, 1795.

(66) Gasteiger, H.; Markovic, N.; Ross, P.; Cairns, E. *J. Phys. Chem.* **1993**, *97*, 12020.

(67) Goodenough, J.; Manoharan, R.; Shukla, A.; Ramesh, K. *Chem. Mater.* **1989**, *1*, 391.

(68) Trasatti, S. *Electrachim. Acta* **1991**, *36*, 225.

(69) Lee, S.; Liu, P.; Seong, M.; Cheong, H.; Tracy, C.; Deb, S. *Electrochem. Solid State Lett.* **2003**, *6*, A40.

(70) Zhang, J.; Jiang, D.; Chen, B.; Zhu, J.; Jiang, L.; Fang, H. *J. Electrochem. Soc.* **2001**, *148*, A1362.

(71) Zheng, J.; Cygan, P.; Jow, T. *J. Electrochem. Soc.* **1995**, *142*, 2699.

(72) Dmowski, W.; Egami, T.; Swider-Lyons, K.; Love, C.; Rolison, D. *J. Phys. Chem. B* **2002**, *106*, 12677.

(73) Iwasita, T. *Electrochim. Acta* **2002**, *47*, 3663.

(74) Hamnett, A. In *Interfacial Electrochemistry*; Wieckowski, A., Ed.; Marcel Dekker: New York, 1999; Chapter 47, p 843.

(75) Watanabe, M.; Motoo, S. *J. Electroanal. Chem.* **1975**, *60*, 267.

(76) Thomas, S.; Ren, X.; Gettesfeld, S. *J. Electrochem. Soc.* **1999**, *146*, 4354.

(77) Ren, X.; Wilson, M.; Gottesfeld, S. *J. Electrochem. Soc.* **1996**, *143*, L12.

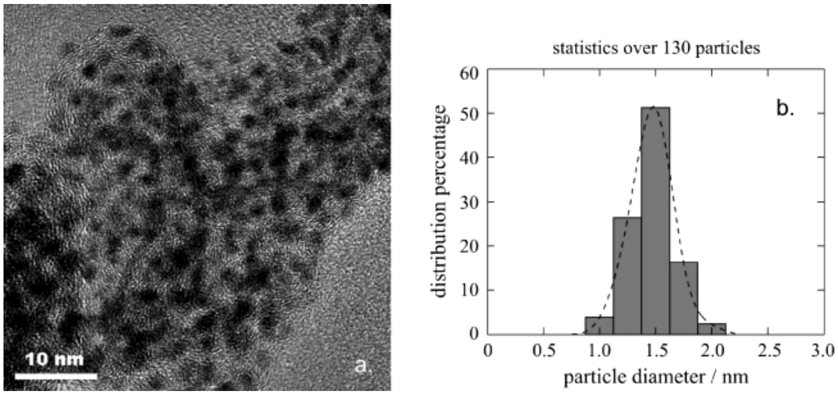

Figure 1. HRTEM image (a) and statistics histogram of the particle size distribution (b) for PtRu/C (40 wt % Pt + 20 wt % Ru).

Table 1. Summary for the Dispersion of Reported PtRu/C Catalysts with Correlative Conditions

nominal metal loading	preparation method	precursors	average diameter (nm)	determination method	ref.
60 wt % PtRu	impregnation	H_2PtCl_6+$RuCl_3$	1.5 ± 0.5	HRTEM	this work
10 wt % PtRu	impregnation	H_2PtCl_6+$H_2RuCl_5\cdot H_2O$	15−20	XRD	36
30 wt % PtRu	impregnation	$Pt(NH_3)_2(NO_2)_2$+$RuCl_3$	3.9 ± 4.3	HRSEM	37
30 wt % PtRu	impregnation	$Pt(NH_3)_2(NO_2)_2$+$RuNO(NO_3)_x$	2.7 ± 0.6	HRSEM	37
1−2 wt % PtRu	impregnation	$PtRu_5C(CO)_{16}$	1.5	STEM	40
20 wt % PtRu	organometallic colloid	$PtRu(AlR_3)$	1.5 ± 0.4	HRTEM	20
20 wt % PtRu	organometallic colloid	$Pt_{0.5}Ru_{0.5}N(oct)_4Cl$	2.3 ± 0.5	HRTEM	22
20 wt % PtRu	metal oxide colloid	$Pt(NH_3)_4Cl_2$+$RuNO(NO_3)_x(OH)_y$	2.6 ± 0.2	XRD	24
20 wt % PtRu	metal oxide colloid	H_2PtCl_6+$RuCl_3$	2−3	TEM	29
20 wt % PtRu	metal oxide colloid	H_2PtCl_6+$RuCl_3$	2	HRTEM	27
30 wt % PtRu	metal oxide colloid	H_2PtCl_6+$RuCl_3$	1.85	XRD	25
60 wt % PtRu	metal oxide colloid	H_2PtCl_6+$RuCl_3$	2.1	XRD	25
40 wt % PtRu	microemulsion	H_2PtCl_6+$RuCl_3$	2−5	TEM	17
50 wt % PtRu	carbonyl complexes	$[Pt(CO)_2]_x$+$Ru_3(CO)_{12}$	2.5 ± 0.45	HRTEM	18
16 wt % PtRu	microwave heating	$(\eta\text{-}C_2H_4)(Cl)Pt(\mu\text{-}Cl)_2Ru(Cl)$	3.4 ± 0.9	HRTEM	19
50 wt % PtRu	microwave heating	$(\eta\text{-}C_2H_4)(Cl)Pt(\mu\text{-}Cl)_2Ru(Cl)$	5.4 ± 3.2	HRTEM	19
10 wt % PtRu	co-deposition	H_2PtCl_6+$RuCl_3$	3	XRD	44

(fcc) structure was fitted to a Gaussian line shape on a linear background using the Levenberg−Marquardt algorithm, so that the position of the peak maximum (θ_{max}) and the full width at half-maximum (fwhm) could be obtained precisely.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Kratos XSAM-800 spectrometer with an Mg Kα radiator. The Pt(4f) and Ru(3p) signals were collected and analyzed by deconvolution of the spectra using the software XPSPeak.

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were simultaneously performed on a WCT-1A differential thermal balance (Beijing Optical Instruments). A sample weighing 10 mg was tested over temperatures ranging from room temperature to 1000 °C at 10°C/min under flowing argon (99.999%).

Electrochemical Measurement. To prepare the working electrode, 10 mg of PtRu/C was dispersed ultrasonically in 1 mL of diluted Nafion alcohol solution (0.05 wt %), and 5 μL of the suspension was pipetted onto a glassy carbon (GC) substrate (ϕ 5 mm), which was buff-polished with an alumina suspension (ϕ 0.05 μm) prior to use. The coated electrode was dried under an infrared lamp.

A thermostatic electrochemical cell equipped with the working electrode, a platinum coil counter electrode, and a salt bridge connected to the reference electrode compartment was used for all electrochemical measurements. The reference electrode was a reversible hydrogen electrode (RHE)[78] in the same electrolyte as the electrochemical cell. All potentials throughout this paper are referred to RHE.

To evaluate the catalytic activity for methanol oxidation, the working electrode was polarized, via a CHI-600A potentiostat, to selected potentials (0.4 V, 0.45 V, and 0.5 V) in deaerated 2 mol/L CH_3OH + 0.5 mol/L H_2SO_4 solution. After 30 min polarization, the pseudo steady-state current was recorded and normalized to mass-specific current density (mA per mg noble metal).

Results and Discussion

HRTEM Examination. The dispersion of metal particles in PtRu/C was examined using high-resolution transmission electron microscopy. Figure 1a shows the bright field HRTEM image. It can be clearly seen that metal particles distribute rather densely, owing to the relatively high metal loadings (40 wt % Pt + 20 wt % Ru), and the particle size appears quite uniform. Figure 1b is a statistics histogram of the particle size distribution based on 130 particles in Figure 1a. The particle diameter average is 1.5 nm and distributes in a very narrow range, ±0.5 nm.

Table 1 summarizes the dispersion data of PtRu/C catalysts found in the literature. PtRu catalysts dispersed on carbon nanotubes or graphite nanofibers (CNTs/GNFs)[31−34] are not included in this table in view of the specificity of CNTs/GNFs. As mentioned in the Introduction, the dispersion of PtRu/C prepared by impregnation with chlorine-containing precursors was poor in previous reports;[36,37] whereas in this work, the dispersion is excellent even with a metal loading as high as 60 wt %. Therefore, Table 1 clearly illustrates the merits of our method in that it is the simplest and lowest cost among the known methods and is yet able to produce PtRu/C catalysts with the highest dispersion at high metal loadings.

EDAX Analysis. Figure 2 shows the EDAX results for the PtRu/C sample. The atomic composition of PtRu

---

(78) Gong, S.; Lu, J.; Yan, H. *J. Electroanal. Chem.* **1997**, *436*, 291.

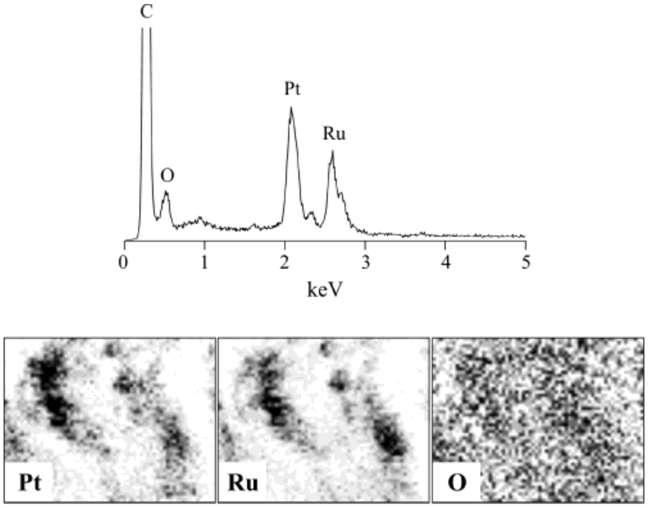

Figure 2. EDAX spectrum (top) and elements distribution in a micro-region (bottom) for PtRu/C (40 wt % Pt + 20 wt % Ru).

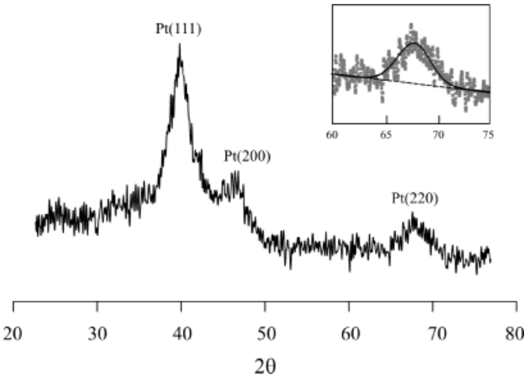

Figure 3. XRD pattern of PtRu/C (40 wt % Pt + 20 wt % Ru). Inset: peak profile fitting for the Pt(220) reflection.

turns out to be $Pt_{0.54}Ru_{0.46}$, close to that in the precursor solution. Oxygen was also detected with an atomic content as high as Pt. The micro-region distribution of Pt−Ru−O indicates that Pt and Ru distribute concomitantly while O exists both on the sites of the metal and on the background, which is thought to be caused by the celloidin support in the specimen.

XRD Analysis. The XRD pattern of PtRu/C is shown in Figure 3. Characteristic reflections of Pt fcc structure can be observed, but no distinct presence of peaks related to tetragonal RuO_2 or hexagonal close-packed (hcp) Ru phases can be found. The cell parameter of Pt fcc crystalline, a_{fcc}, was calculated to be 3.893 Å according to the Vegard's law, which is smaller than the value of 3.923Å for pure unsupported Pt or 3.916Å for pure Pt/C.[55] This variation was often attributed to the incorporation of Ru atoms into the Pt lattice to form a PtRu alloy,[25,27,36,50,55,63] although this interpretation was argued by some investigators.[47,48,79] Using the formula proposed by Antolini et al.,[36,55] the Ru atomic fraction in the alloy, x_{Ru}, is calculated to be ca. 0.2, implying that only a small part of Ru was alloyed while most Ru existed in amorphous states. Similar phenomena were also reported for commercial PtRu/C catalysts.[25,55,63] In our study, x_{Ru} was found to be tunable by additional heat treatment. Fully alloyed PtRu can be obtained when the as-prepared catalyst was further calcinated at 500 °C in argon atmosphere.

Table 2. Data from Curve-Fitted XPS Spectra and NIST Database

				NIST XPS database ref 80	
species	atomic ratio %	binding energy/ev		binding energy/ev	formula
Pt 4f		$4f_{7/2}$	$4f_{5/2}$	$4f_{7/2}$	
	10.0	70.6	74.1	70.8	Pt
	10.5	71.6	75.1	72.4	PtO
	7.5	73.0	76.8	72.8	$Pt(OH)_2$
Ru 3p		$3p_{3/2}$		$3p_{3/2}$	
	10.9	460.6		461.1	Ru
	24.9	462.2		462.4	RuO_2
	36.2	464.3			

Although the crystalline size of PtRu alloy can be calculated by the fwhm of the Pt(220) peak according to the Scherrer formula, the result thus-obtained is influenced by many factors and may be misleading for ultrafine particles.[55] Hence no attempt was made to calculate the crystalline size from the XRD data in this work.

XPS Analysis. The nature of surface species of PtRu/C was investigated by XPS analysis. Figure 4 shows the Pt(4f) and Ru(3p) spectra. Ru(3p) spectrum was taken instead of the Ru(3d) one in order to avoid the interference of C(1s) signal. Both Pt(4f) and Ru(3p) signals are broad and each can be deconvolved into three components. The atomic ratio and the binding energy (BE) of each component are listed in Table 2, related BE values taken from the U. S. National Institute of Standards and Technology (NIST) XPS database[80] are also listed for reference. All three components of the Pt(4f) signal can be well recognized and assigned to Pt^0, PtO, and $Pt(OH)_2$, respectively. No PtO_2 (BE = 74.6 eV) species was found in this work, although it was often reported in the literature.[29,50,63,67,81,82] This may imply that PtRu/C catalysts prepared in this work possess relatively lower surface oxidation states. Ru^0 and RuO_2 have been resolved in the Ru(3p) signal whereas the component with highest BE (464.3 eV) cannot find a match in the NIST database. This component cannot be assigned to Ru^V (BE = 465 eV)[67,83] or Ru^{VI} (BE = 466.9 eV),[63] but matches the character of hydrous RuO_2 (also written as RuO_xH_y), which was reported to take on a very broad peak[48] and to have a higher BE, e.g., 463.8 eV,[79] than that of its anhydrous form.

The atomic ratio of all six components (Table 2) reveals that Ru was enriched on the surface of PtRu/C and the predominant form of surface ruthenium was most probably RuO_xH_y.

TGA/DTA Analyses. To ascertain the presence of RuO_xH_y, PtRu/C was subjected to TGA/DTA analyses. As shown in Figure 5, an initial endothermic loss between ambient and ca. 100 °C can be reasonably attributed to the removal of physisorbed water from the catalyst; the exothermic loss occurring between 300 and

---

(79) Roth, C.; Goetz, M.; Fuess, H. *J. Appl. Electrochem.* **2001**, *31*, 793.

(80) U. S. National Institute of Standards and Technology (NIST) XPS database. http://srdata.nist.gov/xps/ and references therein.

(81) Allen, G.; Tucker, P.; Capon, A.; Parsons, R. *J. Electroanal. Chem.* **1974**, *50*, 335.

(82) Kim, K.; Winograd, N.; Davis, R. *J. Am. Chem. Soc.* **1971**, *93*, 6296.

(83) Kotz, R.; Lewerentz, H.; Stucki, S. *J. Electrochem. Soc.* **1983**, *130*, 825.

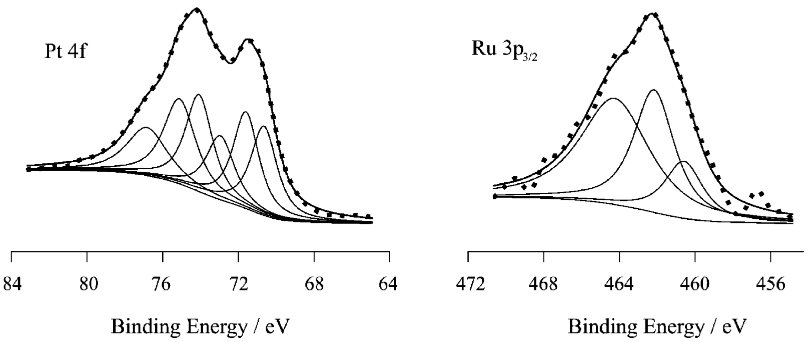

Figure 4. XPS spectra of Pt(4f) and Ru(3p) signals for PtRu/C (40 wt % Pt + 20 wt % Ru). Dots: experimental data; lines: fitting curves.

Table 3. Experimental Conditions in Figure 6

no.	nominal metal loadings	carbon support	concentration	temperature	test protocol	producer
1	30 wt % PtRu	Vulcan XC-72	0.5M H_2SO_4 + 2M MeOH	60°C	30min/potential	this work
2	30 wt % PtRu	Vulcan XC-72	0.5M H_2SO_4 + 2M MeOH	60°C	30min/potential	Schmidt ref 85
3	30 wt % PtRu	unknown	0.5M H_2SO_4 + 1M MeOH	60°C	30min/potential	Takasu ref 37
4	30 wt % PtRu	Vulcan XC-72	0.5M H_2SO_4 + 0.5M MeOH	60°C	30min/potential	E-Tek ref 85
5	20 wt %PtRu	Vulcan XC-72R	1.5M H_2SO_4 + MeOH vapor	60°C	30min/potential	Watanabe ref 29

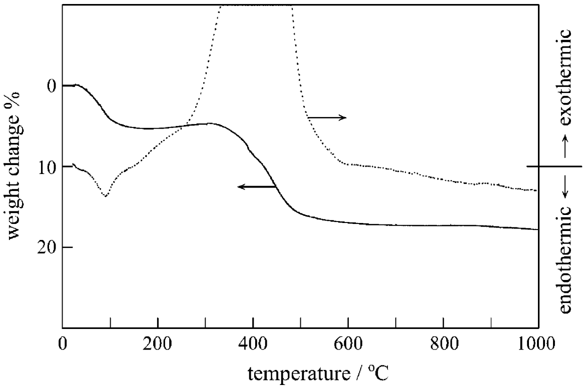

Figure 5. TGA/DTA results for PtRu/C (40 wt % Pt + 20 wt % Ru).

ca. 600 °C is important evidence for the structural reconstruction accompanied by loss of structural water.[47,48] This behavior has been considered as the unambiguous character of hydrous oxides.[48] The decomposition of RuO_2 cannot be seen in Figure 5 because it only happens above 1000 °C.[84]

Electrochemical Evaluation. The catalytic activity of PtRu/C toward methanol oxidation was evaluated and compared with those in the literature reports. In most studies, metal loadings in PtRu/C were 20 wt % Pt + 10 wt % Ru. For strict comparison, homemade PtRu/C with the same metal loading was used in this section. Difficulties were encountered in the choice of reported data for comparison, because the experimental conditions reported in the literature for electrochemical evaluation of the catalytic activity of PtRu/C were rather scattered. The working temperature and the current acquisition protocol were considered here as the most important conditions for comparison. Data shown in Figure 6 were all acquired at 60 °C and after 30 min polarization at selected potentials. Related experimental conditions are listed in Table 3.

As shown in Figure 6, the PtRu/C prepared in this work (curve 1) exhibited excellent performance for methanol oxidation in comparison with those of the state-of-the-art PtRu/C catalysts found in the literature. Although data reported by Watanabe et al.[29] (curve 5) appeared to have the best performance, it should have benefited from the vapor-fed mode of methanol. It has been pointed out that in the gas-fed mode methanol molecules interact with the catalyst surface through their hydroxyl end, different from the carbon end interaction in the electrolyte-fed mode, resulting in an enhanced activity.[86] The outstanding performance of the PtRu/C prepared in this work is most probably due to the very high dispersion of PtRu particles and the extensive presence of RuO_xH_y. Both these merits ought to benefit from the proper preparation technology, especially the heat treatment at a relatively low temperature. Although residual chloride in the catalyst was thought difficult to completely remove in such low temperature heat treatment and harmful to the cataly-

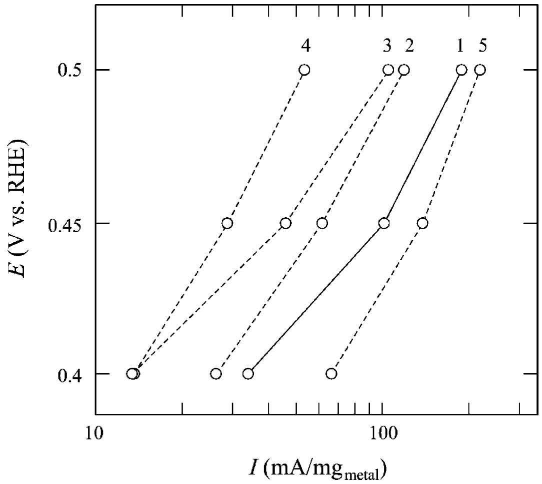

Figure 6. Comparison of the catalytic activity of different PtRu/C catalysts toward methanol oxidation. Detailed experimental conditions are listed in Table 3.

---

(84) Campbell, P.; Ortner, M.; Anderson, C. *Anal. Chem.* **1961**, *33*, 58.

(85) Schmidt, T.; Gasteiger, H.; Behm, R. *Electrochem. Commun.* **1999**, *1*, 1.

(86) Lin, A.; Kowalak, A.; O'Grady, W. *J. Power Sources* **1996**, *58*, 67.

sis,[87,88] this negative effect seemed negligible in this study.

An interesting phenomenon appears in Figure 6. The Tafel slopes (d*E*/dlog*I*) of curve 1 and 3 are very similar but obviously smaller than those of the other curves. It happened that the PtRu/C catalysts corresponding to curve 1 and 3 were prepared by impregnation methods, whereas the others were prepared by colloidal chemistry methods. The Tafel slope in methanol oxidation reactions was thought to be related to the oxidation state of the catalyst surface,[85] with larger Tafel slopes being indicative of higher surface oxidation states. According to this point of view, the PtRu/C catalysts prepared by impregnation methods seemed to possess relatively lower surface oxidation states, in agreement with the XPS findings described above.

Acknowledgment. We are all grateful to the following projects for financial support: the State Key Fundamental Research Program (TG2000026408), the National Hi-Tech R&D Program (2002AA517030), and the FORD-NSFC China Research and Development Fund (20122101).

CM034306R

---

(87) Schmidt, T.; Paulus, U.; Gasteiger, H.; Behm, R. *J. Electroanal. Chem.* **2001**, *508*, 41.

(88) Breiter, M. *Electrochim. Acta* **1964**, *9*, 827.