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Catalysis Today 132 (2008) 117–122

CATALYSIS TODAY

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Pt/WC as an anode catalyst for PEMFC: Activity and CO tolerance

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Abstract

A mesoporous tungsten carbide of WC-phase was synthesized by using ammonium meta tungstate as tungsten precursor and resorcinol–formaldehyde polymer as carbon source in the presence of a surfactant. The platinum supported on this material with a low loading (7.5 wt%) served as an effective CO tolerant electro anode catalyst. The Pt/WC catalyst showed two times higher activity per mass of Pt for hydrogen electro-oxidation compared to a commercial Pt/C catalyst (E-Teck). In addition, it exhibited much improved resistance to CO poisoning relative to the Pt/C catalyst. Since the catalyst is also stable in electrochemical environment, it could become an alternative anode catalyst for PEMFC.

Keywords: Pt/WC; Mesoporous; CO tolerance; Hydrogen oxidation; Fuel cells

1. Introduction

Among various fuel cells, polymer electrolyte membrane fuel cell (PEMFC) is suitable for applications including automobiles and residential heat and power supply [1]. The key components that determine the performance and cost of PEMFC are electrocatalysts and the proton exchange membrane. Platinum is the dominant electrocatalytic material both in anode and cathode sides of PEMFC because Pt-based catalysts show high and stable activity for electro-oxidation of hydrogen and reduction of oxygen [2,3]. But Pt is expensive and its supply is limited. It is also susceptible to CO poisoning, and lose their catalytic activity with respect to time [4]. Carbon monoxide is a by-product obtained during processing of fossil fuels such as methane and gasoline and poisons Pt surface by blocking active sites for the hydrogen oxidation reaction [5]. Thus, for a widespread application of PEMFC, a low cost electrocatalyst that shows high CO resistance as well as high catalytic activity towards hydrogen oxidation is in a great demand [6].

Tungsten carbide-based materials have received considerable attention in recent years because of the resemblance of their reactivity to Pt in various catalytic reactions [7–9]. As electrocatalysts, they are known to be highly resistant to CO poisoning and stable in acidic and basic solutions, yet their electrocatalytic activity for methanol oxidation and hydrogen oxidation is very low [10,11]. However, this low activity of tungsten carbide could be improved dramatically by adding a small amount of platinum to tungsten carbide [12,13].

We recently prepared a mesoporous tungsten carbide of hexagonal WC-phase with a high surface area (76 m^2/g) by a polymer method [14,15]. The mesoporous WC alone did not show any activity of methanol electro-oxidation. Loading a small amount of Pt onto this mesoporous WC, however, produced a noble-metal economic electrocatalyst that showed higher activity for methanol oxidation than a commercial Pt–Ru/C catalyst. In the present study, we examine this material as a potential anode electrocatalyst for PEMFC. Thus, a slightly platinized mesoporous WC was studied in the electro-oxidation of hydrogen in acid solution with a particular attention to its resistance to CO poisoning. Its performance is compared with a commercial 20% Pt/C catalyst (E-Teck).

2. Experimental

2.1. Electrocatalyst preparation

Mesoporous WC was prepared by polycondensation of resorcinol and formaldehyde in the presence of ammonium metatungstate salt (AMT) as a tungsten source and cetyltrimethylammonium bromide (CTABr) as a surfactant. In a

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doi:10.1016/j.cattod.2007.12.076

typical synthesis, 6.5 g of CTABr is dissolved in 20 ml of water and stirred for 30 min. The solution containing 5 g of AMT and 1.2 g of resorcinol and 1.8 ml of formaldehyde was added to the CTABr solution and heated at 358 K for 1 h. The resulting gel was autoclaved at 423 K for 48 h. The red colored solid was dried at 383 K for 12 h, placed in an alumina boat and calcined at 1173 K for 1 h in argon flow and 2 h in hydrogen flow (44.6 μmol/s) in a tubular furnace with the thermocouple. The platinum particles were loaded on tungsten carbide by the conventional borohydride reduction method in alkaline media [16]. A commercial 20 wt% Pt/C was purchased from E-Teck and used as received.

2.2. Physicochemical characterization

Before TPD experiments, the catalysts were activated at 473 K in hydrogen for 1 h. After cooling to room temperature CO chemisorption was done at room temperature for 1 h. Finally CO was desorbed by heating from room temperature to 573 K in He flow. The amount of CO was measured by a mass spectrometer. The powder X-ray diffraction (XRD) measurements were conducted using 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 studied by scanning electron microscopy (FE-SEM, FEI XL30S) and high-resolution transmission electron microscope (HRTEM, JEOL 2001) operating at 100 kV. The specimens for TEM analysis were prepared by ultrasonically suspending the electrocatalyst powder in ethanol.

2.3. Electrochemical characterization

The working electrodes for the electrochemical measurements were fabricated by dispersing the catalyst in 1 ml of distilled water and 10 μl of 5 wt% Nafion. The dispersion was ultrasonicated for 20 min. A known amount of suspension was added on to the glassy carbon and solvent was slowly evaporated. 10 μl of 5 wt% Nafion was again added on the coatings and solvent was slowly evaporated. Pt foil and Ag/AgCl/3 M NaCl were used as counter and reference electrodes, respectively. A solution of 1 M H_2SO_4 was used for all electrochemical experiments. For CO tolerance experiment, a solution of 1 M H_2SO_4 was purged with 1% CO and 99% H_2 gas for an hour. Electrochemical studies were performed on a Princeton Applied Research (PAR) voltammetry. The cyclovoltammogram (CV) was taken after 15 repeating cycles when the spectrum was stabilized with a scan rate of 50 mV/s.

3. Results and discussion

3.1. Preparation and characterization of electrocatalyst

A mesoporous tungsten carbide of hexagonal WC-phase was synthesized following the method reported previously [14,15]. The procedure involves polycondensation of resorcinol–formaldehyde (RF) in the presence of ammonium metatungstate and cetyltrimethylammonium bromide at 423 K giving a composite of AMT and RF polymer. The composite is treated under Ar flow at 1173 K for 1 h and then under H_2 flow for 2 h. The H_2 treatment was done to remove the free carbon deposited on WC surface. The presence of CTABr surfactant was essential to obtain a large amount of mesopores, which was beneficial for high electrochemical activity compared with the samples with micropores or a small amount of pores [15].

The XRD pattern of WC in Fig. 1a corresponds to WC of a simple hexagonal phase with lattice parameters of $a = 2.906$ Å and $c = 2.83$ Å (JCPDS card no. 12,070-12-1). There were no impurity peaks corresponding not only to carbon, tungsten trioxide or metallic tungsten, but also W2C (hcp-phase) and WC1-x (fcc-phase). The last two tungsten carbides make three major phases of tungsten carbide together with WC (hex-phase) and are common impurities observed when the preparation conditions are not controlled.

The SEM image of the mesoporous WC in Fig. 2a shows a lot of pores on the external surface and the sample appeared to be collection of WC nanoparticles. The particle size calculated from the XRD peaks in Fig. 1a using Debye–Scherrer equation was 5–7 nm. The HRTEM image of WC in Fig. 2b shows high crystallinity as evidenced by clean lattice fringes. The spacing of the lattice fringes was about 0.25 nm corresponding to the interplanar spacing of (1 0 0) planes of simple hexagonal WC. The selected area electron diffraction in the inset also showed a single crystal-like spot pattern. The elemental analysis of WC showed that the material had the composition of $WC_{1.756}$. Thus, there is an excess carbon on the surface that partly blocks the tungsten carbide surface.

The shape and hysteresis of nitrogen adsorption/desorption isotherms in Fig. 3a indicate that the sample contains an ample amount of mesopores. The pore size distribution was calculated from the desorption isotherm as shown in the inset. The average pore size was 4.3 nm and the BET surface area and pore volume

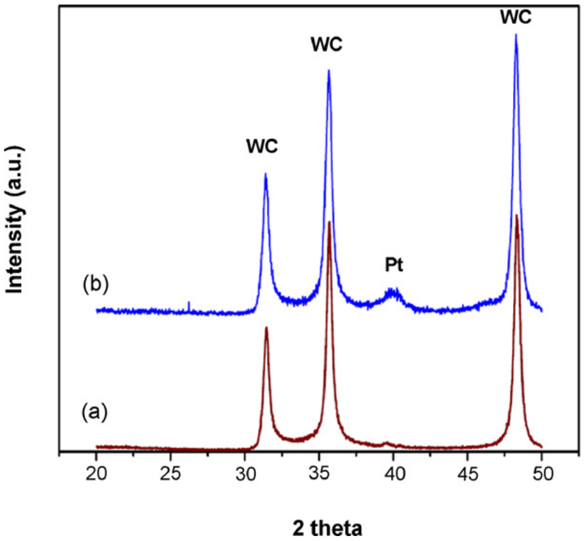

Fig. 1. XRD patterns of (a) mesoporous WC and (b) 7.5 wt% Pt/mesoporous WC.

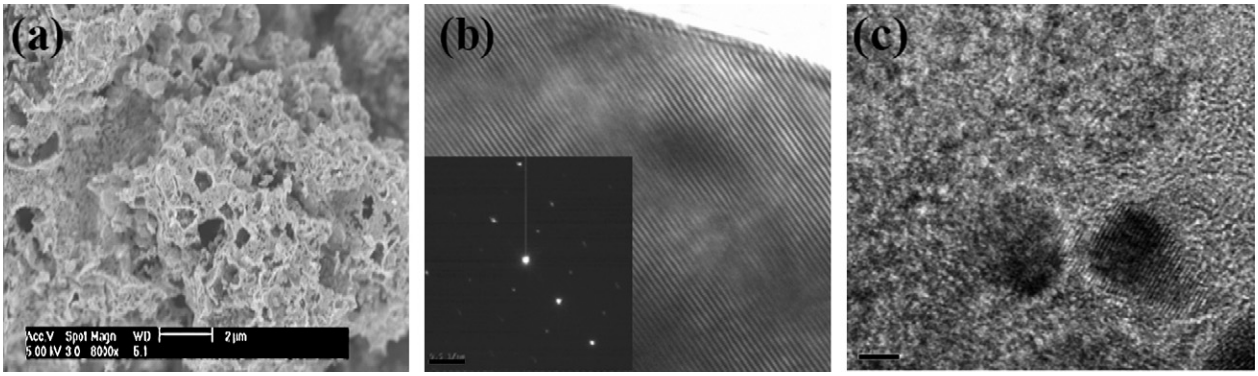

Fig. 2. (a) SEM image of mesoporous WC and (b) HRTEM image of mesoporous WC. The inset shows the electron diffraction pattern. (c) HRTEM image of 7.5 wt% Pt/mesoporous WC.

were 76 m^2/g and 0.24 cm^3/g, respectively. The BET surface area corresponds to a spherical WC particle size of ca. 5 nm in agreement with the value calculated from XRD peaks. The sample prepared without the surfactant showed a very small volume of 0.086 cm^3/g, indicating that the surfactant CTABr introduced during the polycondensation reaction has increased the pore volume of the sample. The CO uptake was calculated from temperature programmed desorption (TPD) shown in Fig. 3b by referring the area under the CO mass signal (28) to the known quantity of CO. The CO uptake value (106 μmol/g) corresponded to 10% of total tungsten atoms on the surface of the sample. Thus, in spite of the presence of excess carbon on WC surface, a substantial fraction of the surface is still active and clean enough to chemisorb 106 μmol/g of CO.

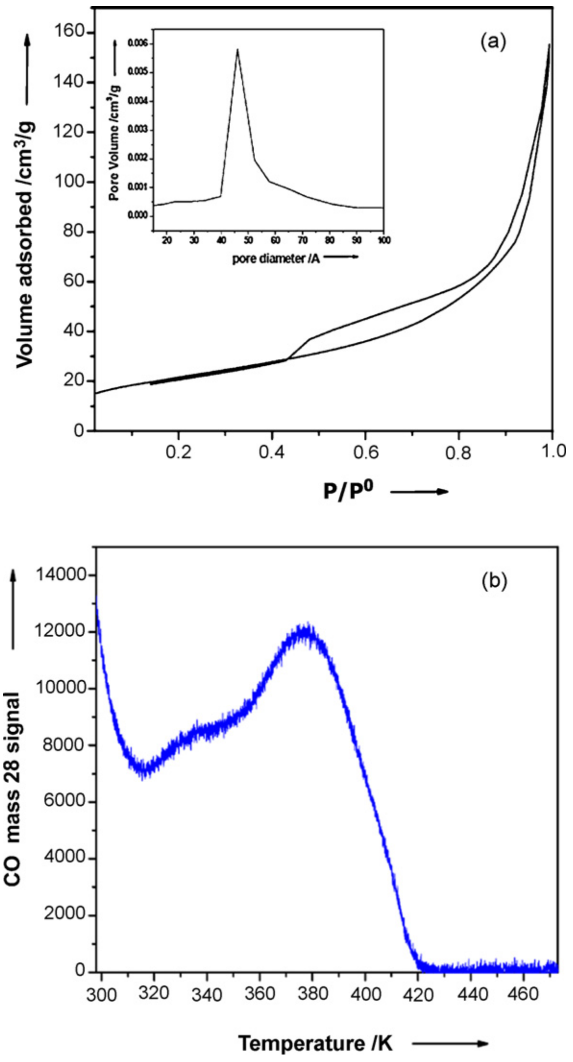

Fig. 3. (a) The nitrogen adsorption/desorption isotherms of mesoporous WC. The inset shows the pore size distribution from BJH desorption branch. (b) Temperature-programmed desorption graph of CO (mass 28).

Now 7.5 wt% Pt was loaded on WC (Pt/WC) by the conventional borohydride reduction method in alkaline media [16]. The XRD peak at the 2θ value of 39.8 in Fig. 1b represents Pt (1 1 1) lattice plane. The HRTEM image of 7.5 wt% Pt supported on mesoporous WC is shown in Fig. 2c. Pt particles on mesoporous WC appear highly crystalline as evidenced by clean lattice fringes. The average Pt particle size on WC is around 5.7 nm calculated from the characteristic Pt XRD peak using Debye–Scherrer equation, which is in good agreement with the value from HRTEM (ca. 5.1 nm) in Fig. 2c.

3.2. Electrocatalytic activity of hydrogen oxidation and CO tolerance

The electrocatalytic activity of 7.5 wt% Pt/WC and the commercial 20 wt%/C (E-Teck) electrocatalysts for hydrogen oxidation was probed by cyclic voltammogram (CV) analysis in 1 M H_2SO_4 solution as shown in Fig. 4. The main Pt–H adsorption/desorption peaks appear around 0.0 V. This represents the half-cell anode reaction of PEMFC. Two types of information could be extracted form the CV. First, the electrochemical surface areas (ESA) are estimated from the integration of the Pt–H adsorption/desorption peak between −0.2 V and +0.2 V. This represents the hydrogen adsorption area per unit mass of Pt (m^2/g-Pt) under electrocatalytic reaction condition. The second parameter relevant to the activity of hydrogen oxidation is the specific current (mA/cm^2 electrode) at 0.0 V. This specific current can be divided by the Pt loading on the electrode to obtain mass activity at 0.0 V (mA/mg-Pt). The numerical values of these parameters are listed in Table 1.

The commercial 20% Pt/C catalyst showed an ESA value of 106 m^2/g, which is similar to the expected physical surface area

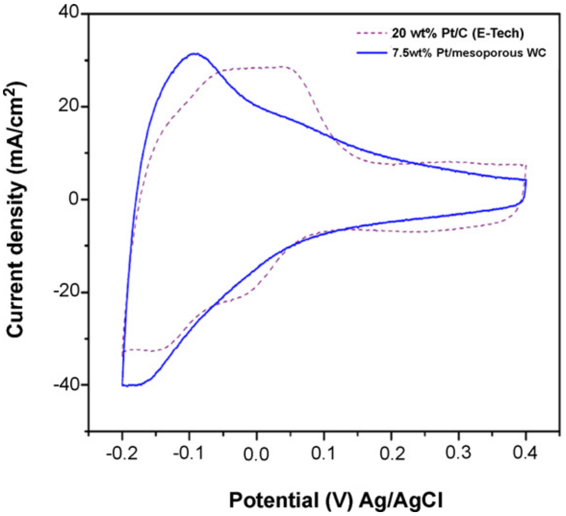

Fig. 4. Cyclic voltammogram of 20 wt% Pt/C (E-Teck) commercial catalyst and 7.5 wt% Pt/mesoporous WC in 1 M H_2SO_4 (without 1% CO) under a scan rate of 50 mV/s at 298 K.

for its Pt particle size (<2 nm). However, the Pt/WC catalyst showed a much higher ESA of 377 m^2/g. This surface area corresponds to spherical Pt particles with a diameter of ca. 0.4 nm. But from TEM and XRD measurements, the diameter of Pt particles in 7.5 wt% Pt/WC was found to be 5–6 nm. Thus, the much higher ESA value for the Pt/WC catalyst could be accounted for by active participation of WC in electrochemical hydrogen oxidation together with Pt. The similar interplay between Pt and WC was also observed for electro-oxidation of methanol on Pt/WC [13–15]. This difference in ESA values is also reflected in the mass activity (mA/mg of Pt taken at 0.0 V). Thus mass activity of 7.5% Pt/WC (136 mA/mg) was around two times higher than that of the commercial 20% Pt/C E-Teck catalyst (71 mA/mg). The activity data clearly show that Pt dispersed on tungsten carbide provides much better utilization of Pt than on conventional carbon support. WC alone without Pt showed little activity under the same reaction condition. Thus, hydrogen may adsorb first on Pt and then migrate to WC surface probably by a hydrogen spillover mechanism [17]. The electro-oxidation then takes place on both Pt and WC, and gives higher mass activity than the activity that could be obtained on Pt alone.

An interesting observation in Fig. 4 is the difference in the voltage range where hydrogen oxidation takes place. The 20% Pt/C E-Teck catalyst showed a much wider and higher range of voltage for hydrogen oxidation peak than that of 7.5% Pt/WC. The different position of this peak represents different reactivity of Pt for hydrogen oxidation due to, for example, different exposed surface [18]. Thus it appears that 20% Pt/C catalyst contains more heterogeneous hydrogen oxidation sites than 7.5% Pt/WC.

Carbon monoxide is a common impurity in hydrogen feed because hydrogen is usually produced from a carbon-containing feedstock. It poisons Pt surface by blocking active sites for the hydrogen oxidation reaction and thus its concentration should be maintained below 10 ppm [5]. In our previous study of methanol electro-oxidation, Pt/WC showed higher mass activity than a commercial Pt–Ru/C catalyst [13–15]. One of the factors contributing to the high activity was suggested to be the facile removal of CO intermediate formed on Pt surface during methanol decomposition by high activity of water activation of WC-like Ru in Pt–Ru/C catalyst. Then it is expected that WC could improve CO tolerance of Pt in hydrogen electro-oxidation as well. This hypothesis was tested for Pt/WC electrocatalyst.

To introduce CO into the 1 M H_2SO_4 electrolyte solution, 1% CO and 99% H_2 gas was purged into the electrolyte for 1 h. Fig. 5 and Table 1 compares the CO tolerance of 20 wt% Pt/C (E-Teck) and 7.5 wt% Pt/WC. It is shown that the current density and ESA value of 20 wt% Pt/C catalyst decreased by ca. 20% when CO was introduced in the electrolyte. But in case of 7.5 wt% Pt/WC electrocatalyst, the difference between with and without CO was only 6–7%. This indicates that Pt/WC catalyst has significantly higher CO tolerance than Pt/C catalyst. The CO tolerance was also tested by chronoamperometry at a fixed voltage of 0.1 V. As shown in Fig. 6, 7.5 wt% Pt/WC electrocatalyst showed much better CO tolerance than 20 wt% Pt/C catalyst. Thus, the drop in current was about 35% for Pt/C, whereas it was about 25% for Pt/WC.

As mentioned, CO binds very strongly on Pt and cannot be desorbed at the operating temperature of PEMFC (<100 °C). But this CO could be removed from the surface by reaction with surface hydroxyls. These surface hydroxyls are not easily formed on the Pt surface due to difficult water activation (0.7 V), but their formation is relatively easy on the Ru surface (0.2 V). This is the reason why Pt–Ru alloys are used for methanol electro-oxidation. Tungsten carbide can activate water and form surface hydroxyls easily as demonstrated by Zellner and Chen [10] on a single crystal WC surface. Thus CO adsorbed on Pt and hydroxyl formed on WC would react as follows:

$$\mathrm{Pt{-}CO} + \mathrm{WC{-}OH} \rightarrow \mathrm{Pt} + \mathrm{WC} + \mathrm{CO_2} + \mathrm{H^+} + \mathrm{e^-} \qquad (1)$$

Table 1
Electrocatalytic activity and CO tolerance of various catalysts for hydrogen electro-oxidation

Catalyst	Condition of electrolyte	Electrochemical surface area (m^2/g-Pt)	Specific activity at 0.0 V (mA/cm^2)	Mass activity at 0.0 V (mA/mg-Pt)
7.5% Pt/WC	Without CO	377	20.5	136
	With CO	351	19.3	128
20% Pt/C (E-Teck)	Without CO	106	28.3	71
	With CO	85	23.5	59

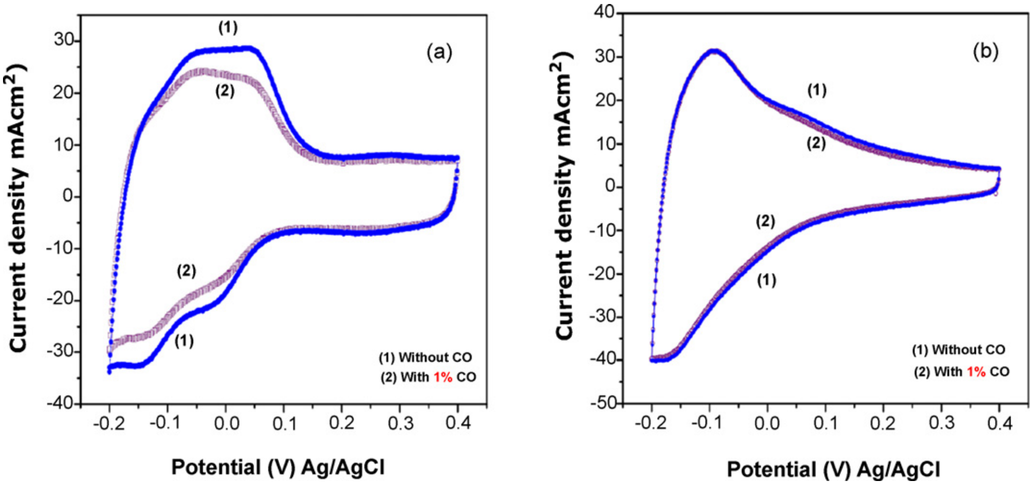

Fig. 5. Cyclic voltammogram of (a) commercial 20 wt% Pt/C (E-Teck) and (b) 7.5 wt% Pt/mesoporous WC in (1) a 1 M H_2SO_4 solution and (2) a 1 M H_2SO_4 solution purging with 1% CO and 99% H_2 gas for an hour under a scan rate of 50 mV/s at 298 K.

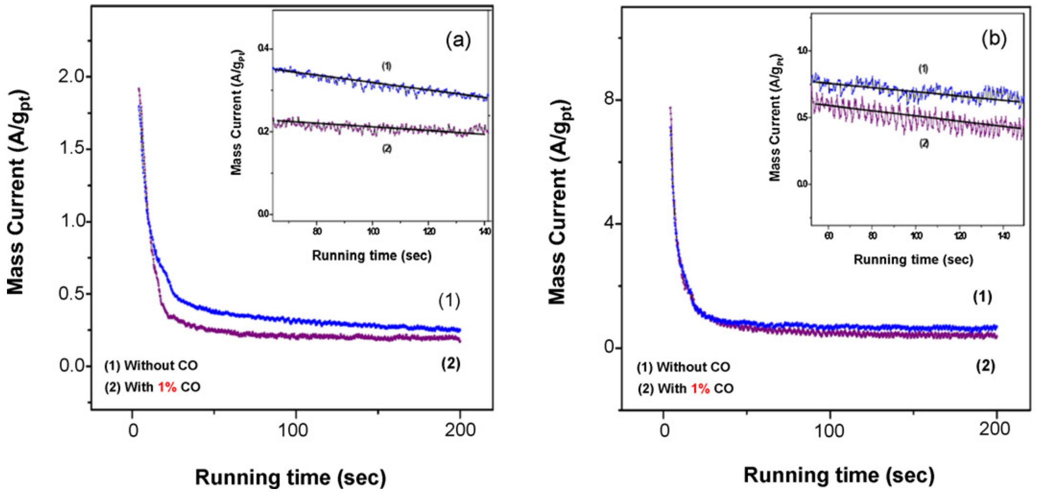

Fig. 6. Chronoamperometry curves of (a) 20 wt% Pt/C (E-Teck) and (b) 7.5 wt% Pt/mesoporous WC in (1) a 1 M H_2SO_4 solution and (2) a 1 M H_2SO_4 solution purging with 1% CO and 99% H_2 gas for an hour under a scan rate of 50 mV/s at 298 K.

It has been reported that WC alone is completely resistant to CO poisoning in electro-oxidation of hydrogen although the activity was very low [19]. For Pt/WC electrocatalyst, the effect is not as dramatic probably because both Pt and WC are actively participating in the reaction and CO poisoning of Pt cannot be completely avoided. Nevertheless, it is clear that the Pt/WC electrocatalyst shows higher CO tolerance in hydrogen oxidation in spite of using smaller amount of Pt comparing with a commercial Pt/C electrocatalyst.

4. Summary and conclusions

In this work, we have demonstrated that Pt supported on mesoporous tungsten carbide (WC-phase) serves as an effective CO tolerant electro-anode catalyst for hydrogen oxidation. A Pt/nanoporous WC catalyst shows not only two times higher mass activity but also much improved resistance to CO poisoning for hydrogen electro-oxidation than a commercial Pt/C catalyst. The high activity could be attributed to the active participation of WC in the electro-oxidation together with Pt and the high CO tolerance to facile formation of surface hydroxyls on WC that could react away CO strongly adsorbed on Pt. Since the catalyst is also stable in electrochemical environment, it could become an alternative electrocatalyst for PEMFC.

Acknowledgements

This work has been supported by Hydrogen R&D Center funded by the Ministry of Science and Technology of Korea and BK-21 program endorsed by the Ministry of Education and Human Resources of Korea.

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