

Short communication

A study of oxygen reduction on improved Pt-WC/C electrocatalysts

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Abstract

Pt on a tungsten carbide nanocrystalline support (Pt-WC/C) has been prepared by the direct reduction of a platinum salt precursor combined with intermittent microwave heating (IMH). The Pt-WC/C electrocatalyst shows better performance for oxygen reduction in acidic media than that of pure Pt/C or Pt-WC/C prepared by a mechanical mixing method. The results reveal that the Pt-WC/C electrocatalyst prepared by present method is very active for oxygen reduction reaction (ORR) with an onset potential of 1.05 V versus standard hydrogen electrode (SHE) at ambient temperature, which is over 150 mV more positive compared to that of commercial Pt/C electrocatalysts.

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1. Introduction

Tungsten carbides have been intensively studied in catalysis since they show exceptionally high activities for a number of reactions [1]. Recently, enhanced activity was found by the addition of tungsten carbides to Pt for the oxygen reduction reaction (ORR) both in acidic and alkaline solutions [2,3]. The ORR is an important electrochemical reaction involved in low-temperature fuel cells [4–7]. The use of efficient electrocatalysts for the ORR is important. Traditionally, Pt-based electrocatalysts are used and show best performance [8–12]. It is recognized that apart from the discovery of new electrocatalysts, the improvement in the preparation technique of the electrocatalyst is important since this directly relates to the properties and cost of the electrocatalyst [13]. It is obvious that the particle size and the dispersion of the electrocatalyst on the support are crucial to the catalytic reaction. Previously reported tungsten carbide supported Pt electrocatalysts were prepared by simply mixing the WC/C nanomaterial and commercially purchased Pt/C [14]. We believe that the Pt particle size and dispersion will be significantly improved if Pt is directly reduced on the surface of

WC/C and subsequently the catalytic activity for ORR will be increased. We have demonstrated that the nanomaterials can be readily prepared by using an intermittent microwave heating (IMH) method [14,15]. In contrast to other methods [16–19], the method described here provides the possibility of a rapid and one-step preparation for the high loading of metal nanomaterials supported on a matrix.

Here, we report oxygen reduction on improved Pt electrocatalysts supported on tungsten carbide nanocrystals (denoted as Pt-WC/C). The details of the preparation of the Pt-WC/C electrocatalysts by IMH method and the characterization are described.

2. Experimental

2.1. Preparation

2.1.1. Tungsten carbide nanocrystals

Tungsten powder (1 g) was added to a mixture of 10 mL 30% (v/v) H₂O₂, 5 mL 2-propanol and 10 mL water. The solution was left for 24 h or more before 1 g of Vulcan XC-72 carbon powder (Cabot Corp., USA) was added. The mixture was treated in an ultrasonic bath to form a uniformly dispersed ink. The ink was dried in an oven and was then heated in a microwave oven (Galanz, WD900ASL23-2, China, 900 W, 2.45 GHz) with

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a heating procedure of 5 s on and 5 s pause for six times. The dried powder was used as the precursor of the tungsten carbides. The precursor powder in a crucible was bubbled for 10 min with argon and further treated for 10 min continuously by the intermittent microwave heating procedure.

2.1.2. Tungsten carbide nanocrystal supported Pt electrocatalysts

Two milligrams of as-prepared WC/C powder, 0.27 mL H_2PtCl_6 solution (3.7 mg mL^{-1} Pt) and excess 1 mol dm^{-3} NaBH_4 solution were mixed together for half an hour. The deposit was rinsed three times with distilled-deionized water to remove sodium ions and neutralized. One millilitre of 2-propanol was then added and treated by ultrasonics for 20 min, resulting in a uniformly dispersed Pt-WC/C electrocatalyst with a Pt to WC ratio of 2:1.

2.1.3. Electrodes

A graphite rod with a diameter of 6 mm was used as the electrode substrate and the top surface of the rod was pre-cleaned with sandpaper. Typically, 1 mg electrocatalyst was mixed with 1.5 mL 2-propanol. The mixture was treated ultrasonically for 20 min for uniform dispersion. A certain amount of mixture was then dropped onto the top surface of the graphite rod to prepare electrodes with different electrocatalyst loadings. Finally, a drop of 0.5 wt.% Nafion suspension was covered on the electrode top to prevent damage to the electrocatalyst layer.

2.2. Characterization

The morphology, particle size and distribution of the samples were studied by high-resolution transmission electron microscopy (HRTEM, JOEP JEM-2010, JEOL Ltd.) operating at 200 kV and scanning electron microscopy (SEM, LEO 1530VP, Germany) in conjunction with energy dispersive X-ray spectroscopy (EDX). XRD measurements were carried out on a D/Max-III A Diffractometer (Rigaku Co., Japan) using $\text{Cu K}\alpha_1$, $\lambda = 1.54056 \text{ \AA}$ as the radiation source. Electrochemical measurements were performed on an IM6e electrochemical workstation (Zahner-Electrik, Germany). A standard three-electrode cell with separate anode and cathode compartments was used. A platinum foil and SCE electrodes were used as counter electrode and reference electrode, respectively. All potentials shown in the figures are against the standard hydrogen electrode (SHE).

3. Results and discussion

Fig. 1 shows the scanning electron micrographs of the Pt-WC/C electrocatalyst. The powder is uniform with a narrow size distribution. The enlarged micrograph (the inset of Fig. 1) shows that the particles consisted of nanosized units. This is extremely important in terms of utilization of Pt in the catalyst. The aggregation of the particles observed in the figure is due to the active nature of the nano-scaled particles. However, it was demonstrated that the aggregated particles could be re-separated in an appropriate media. Transmission electron microscopic images (see Fig. 2) show that the particle size of both WC and Pt-WC

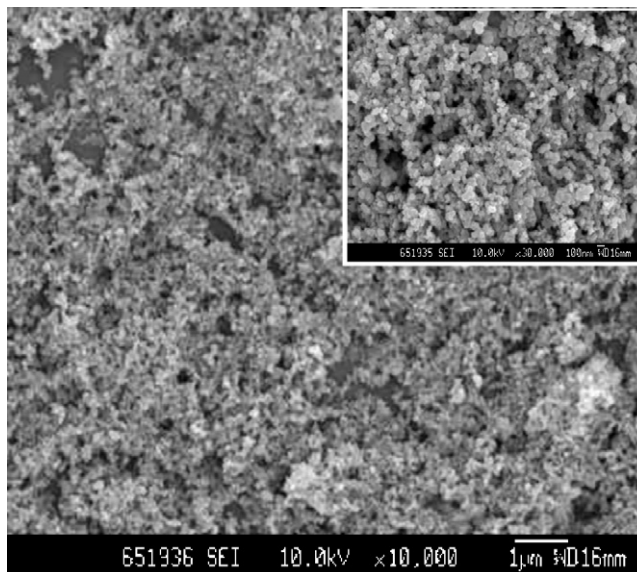


Fig. 1. SEM micrographs of the Pt-WC/C powder. The inset is an enlarged micrograph with the magnification bar of 100 nm.

were less than 10 nm. The identification of the Pt particle size is difficult due to the same contrast between the Pt and WC particles in the TEM image. The elemental analysis by EDX is shown in the inset of the corresponding figure. Pt exists in the electrocatalyst (inset in Fig. 2b).

The tungsten carbides and the Pt supported on the tungsten carbide powders were analyzed by X-ray diffraction (XRD). Fig. 3a shows the existence of nanocrystalline WC and W_2C . For W_2C , the 2θ of 38.04, 39.52, 40.28, 52.26, 73.16 and 74.90 with the d values of 2.3635, 2.2783, 2.2371, 1.7490, 1.2925 and 1.2667 correspond to the (2 0 0), (1 2 1), (1 0 2), (2 2 1), (3 2 1) and (2 4 0) peaks. For WC, the 2θ of 31.52, 35.66 and 48.32 with the d values of 2.8359, 2.5156 and 1.8819 correspond to the (0 0 1), (1 0 0) and (1 0 1) peaks [20,21]. The results in Fig. 3b indicate the co-existence of crystalline WC, W_2C and Pt. For Pt, the 2θ of 40.22, 48.20 and 69.78 with the d values of 2.2403, 1.8864 and 1.3466 correspond to the (1 1 1), (2 0 0) and (2 2 0) peaks. However, the peaks around the 40° of 2θ are overlapped due to the similar d values of Pt and W_2C . For example, for W_2C , the 2θ of 39.52 and 40.28 with the d values of 2.2783 and 2.2371 correspond to the (1 2 1) and (1 0 2) peaks. For Pt, the 2θ of 40.22 with the d value of 2.2403 correspond to the (1 1 1).

The performance of WC/C, Pt/C and Pt-WC/C electrocatalysts for oxygen reduction in sulfuric acid solution are compared in Fig. 4. In contrast to alkaline solutions, WC/C is inert towards the oxygen reduction in acidic solution [2]. Both, Pt/C and Pt-WC/C are active, however, there is a significant difference in onset potentials. The Pt-WC/C electrocatalyst is more favorable for the reduction of oxygen with a more positive onset potential compared to the Pt/C electrocatalyst. The cathode electrocatalyst with a lower overpotential is significant for applications in proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). Curves 3 and 4 in Fig. 4a are the CVs of oxygen reduction on Pt-WC/C prepared by mixing of WC and Pt/C [14], and prepared by direct reduction of Pt on WC,

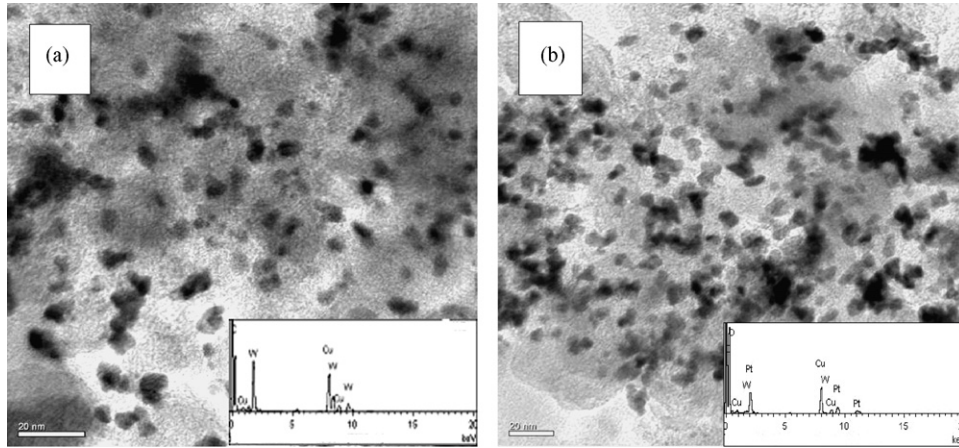


Fig. 2. TEM images of (a) the tungsten carbide and (b) Pt-WC/C. The EDX patterns are shown in the insets of the figures.

respectively. The oxygen reduction on the former electrocatalyst is over 100 mV more positive compared to that of a traditional Pt/C electrocatalyst as reported previously [3]. However, the latter electrocatalyst shows better performance than the former. It is apparent that the preparation method of an electrocatalyst relates to its reactivity. The tremendous enhancement in the activity for oxygen reduction on latter electrocatalyst is attributed to the uniform distribution of Pt prepared by the present on-site reduction method.

The electrochemical active areas of both Pt-WC/C electrodes were determined by cyclic voltammetry. The inset in Fig. 4a compares the results. By integrating the charge in the hydrogen adsorption/desorption region, we found that the active surface

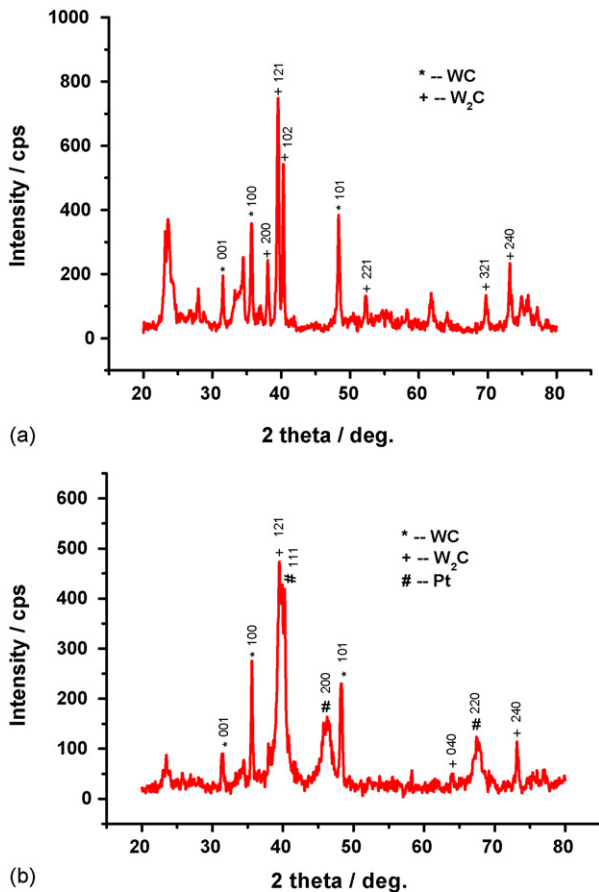


Fig. 3. XRD patterns of (a) the tungsten carbide and (b) Pt-WC/C.

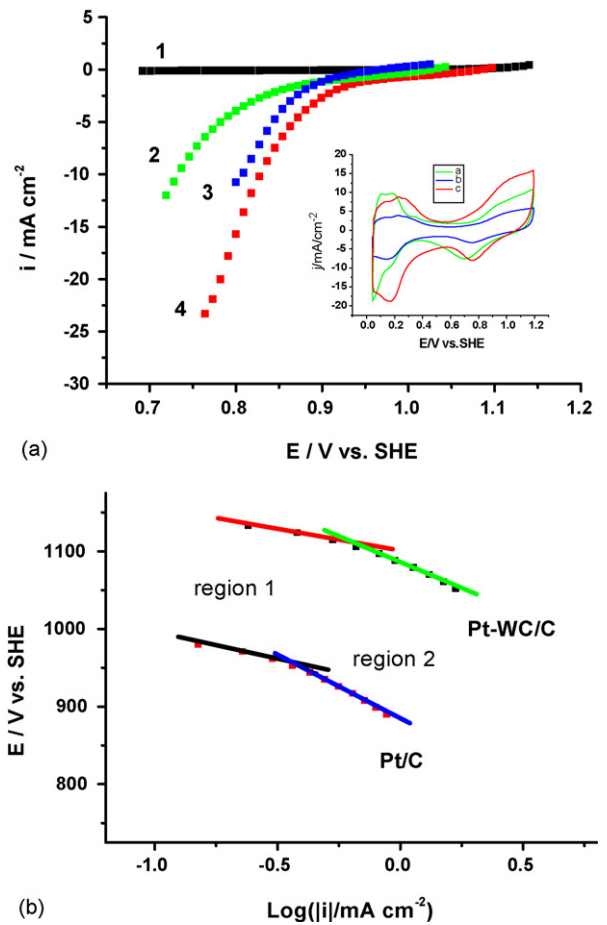


Fig. 4. (a) Linear potential sweep curves of oxygen reduction on different electrocatalysts in O₂ saturated 0.5 mol dm⁻³ H₂SO₄ solution at 25 °C; scan rate: 2 mV s⁻¹. Curve 1, 60 μg WC; curve 2, 60 μg Pt; curve 3, 30 μg Pt + 15 μg WC [2]; curve 4, 30 μg Pt + 15 μg WC. Inset: Cyclic voltammograms of (a) 60 μg Pt, (b) 30 μg Pt + 15 μg WC [2] and (c) 30 μg Pt + 15 μg WC. Scan rate: 50 mV s⁻¹. (b) Tafel plots for ORR on Pt/C and Pt-WC/C electrocatalysts.

Table 1
Comparison of the kinetic parameters for the ORR on Pt/C and Pt-WC/C electrocatalysts

Electrocatalyst	Onset potential (mV) vs. SHE	Tafel slope (mV dec ⁻¹)		<i>i</i> _o (A cm ⁻²)	
		Region 1	Region 2	Region 1	Region 2
Pt/C	900	-59	-137	6.90 × 10 ⁻¹⁰	1.91 × 10 ⁻⁶
Pt-WC/C	1050	-52	-110	3.30 × 10 ⁻⁶	4.80 × 10 ⁻⁵

area is larger for the Pt-WC/C prepared by the present method than that prepared by the mixing method [14] for the same Pt loadings, revealing the better utilization of Pt in the well-dispersed Pt-WC/C. On the other hand, the Pt/C electrode with doubled amount of Pt gives the similar active surface area as that of the Pt-WC/C electrode. But, the activity for ORR is lower than that of the Pt-WC/C electrode with a lower Pt loading, showing a synergistic effect due to the presence of WC.

The mechanism for why tungsten carbide nanocrystals have no activity for oxygen reduction in acidic solution, while are active in alkaline solutions is still unknown. But, the fact that the addition of tungsten carbide nanocrystals into Pt significantly increases the activity of ORR both in acidic and alkaline solutions has been verified [2,3]. This work shows that the direct reduction of Pt on WC further improves the activity due to uniform dispersion. The kinetic parameters of the novel electrocatalysts were determined from the Tafel plot as shown in Fig. 4b and the data are summarized in Table 1. The Tafel plots show two well-defined linear regions for both Pt/C and Pt-WC/C electrocatalysts with similar slopes. The slopes in the low current density region (region 1) for Pt/C and Pt-WC/C are -59 and -52 mV per decade, respectively. The slopes are -137 and -110 mV per decade in the high current density region (region 2). The change in the Tafel slope is attributed to the change in the kinetics for oxygen reduction. The exchange current densities (*i*_o) for O₂ reduction on two electrodes corresponding to each Tafel slope are shown in Table 1. The exchange current densities of oxygen reduction on Pt-WC/C are larger compared to that of Pt/C.

4. Conclusion

The direct reduction of Pt onto tungsten carbide nanocrystals (Pt-WC/C) prepared by the IMH method were tested for the reduction of oxygen in acidic media. The results revealed that the Pt-WC/C electrocatalyst prepared by the direct method is active for ORR with an onset potential of 1.05 V versus SHE, which is over 150 mV more positive compared to that of a commercial Pt/C electrocatalyst. The exchange current densities both at high and low overpotentials are higher than that on pure Pt/C or Pt-WC/C prepared by mechanical mixing. This demonstrates that the catalytic activity of the Pt-WC/C electrocatalyst is improved

by the new preparation technique due to the improvement in the dispersion of the Pt particles on the support with a small particle size distribution. The stability of the Pt-WC/C in acidic media will be next studied since WC is corrosive in sulfuric acid solution [22].

Acknowledgements

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