



## Short-communication

## Investigation of Pt/WC/C catalyst for methanol electro-oxidation and oxygen electro-reduction

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## ABSTRACT

A Pt/WC/C catalyst is developed to increase the methanol electro-oxidation (MOR) and oxygen electro-reduction (ORR) activities of the Pt/C catalyst. Cyclic voltammetry and CO stripping results show that spill-over of H<sup>+</sup> occurs in Pt/WC/C, and this is confirmed by comparing the desorption area values for H<sup>+</sup> and CO. A significant reduction in the potential of the CO electro-oxidation peak from 0.81 V for Pt/C to 0.68 V for Pt/WC/C is observed in CO stripping test results. This indicates that an increase in the activity for CO electro-oxidation is achieved by replacing the carbon support with WC. Preferential deposition of Pt on WC rather than on the carbon support is investigated by complementary analysis of CO stripping, transmission electron microscopy and concentration mapping by energy dispersive spectroscopy. The Pt/WC/C catalyst exhibits a specific activity of 170 mA m<sup>-2</sup> for MOR. This is 42% higher than that for the Pt/C catalyst, viz., 120 mA m<sup>-2</sup>. The Pt/WC/C catalyst also exhibits a much higher current density for ORR, i.e., 0.87 mA cm<sup>-2</sup> compared with 0.36 mA cm<sup>-2</sup> for Pt/C at 0.7 V. In the presence of methanol, the Pt/WC/C catalyst still maintains a higher current density than the Pt/C catalyst.

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## 1. Introduction

A direct methanol fuel cell (DMFC) is an electrochemical device that converts a chemical potential difference into electricity using methanol and oxygen as the anode and the cathode reactants, respectively. The usage of a liquid fuel, methanol, is a special characteristic of DMFC in that it enables easy handling of fuel. Due to this characteristic, DMFC is considered to be the best alternative to lithium-ion batteries for portable applications such as notebook computers and cellular phones. Nevertheless, the usage of methanol also brings problems such as low catalytic activity at the anode catalyst and methanol cross-over to the cathode electrode. The methanol cross-over causes reduction in the oxygen electro-reduction reaction (ORR) activity of cathode catalysts [1].

Platinum was first introduced as a methanol electro-oxidation reaction (MOR) catalyst, but easy poisoning by CO rapidly reduced the MOR activity of Pt. Incorporation of Ru into Pt can largely improve CO electro-oxidation activity, and now the PtRu catalyst is the state-of-the-art [2]. Ruthenium is an expensive noble metal, however, and therefore a higher activity for MOR is required for its commercial application of DMFC. The most popular and success-

ful approach to achieve both increased activity and lower cost is to incorporate third or fourth metals into the PtRu catalyst. To this end, PtRuFe [3,4], PtRuNi [5–7], PtRuW [8–11], and PtRuMoW [12] have been reported as new promising catalysts.

In the case of the cathode catalyst, Pt is most widely used for the ORR. Nevertheless, it suffers from low catalytic activity for ORR, high cost, and CO poisoning caused by methanol that has crossed-over from the anode. Incorporation of a transition metal into Pt could improve ORR activity, and PtFe [13], PtNi [14], and PtCo [15] were intensively studied as new DMFC cathode catalysts. Unfortunately, dissolution of the transition metals was observed, which was caused by the high potential (0.7–1.2 V) and a low pH of near unity [16,17] of the cathode. Therefore, in addition to the increase of ORR activity, stability is also an important factor to be considered for the cathode catalyst.

We have focused research on the support of the catalysts as recent studies of WC have shown that the material can be an excellent replacement for present supports. From the beginning, porous carbon blacks (Vulcan XC72R and Ketjen black) were used as the supports of DMFC catalysts as they have high electrical conductivity and are relatively more stable than other electrically conductive metals. WC has attracted much interest due to its special properties of Pt-like behaviour in some reactions [18] and insolubility in acid solutions [19]. Hwu et al. [20–22] have reported that WC can be a potential alternative to the Pt catalyst due to its ability to dissociate

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methanol and desorb CO at relatively low temperatures. In electrochemical analysis, however, WC did not exhibit MOR activity [23]. Ganesan et al. [23,24] found that Pt supported on WC micro-spheres exhibits high MOR activity. In our previous study [25], we used commercial WC as a support for the Pt catalyst and it was observed that CO electro-oxidation by the Pt catalyst was significantly improved. Nevertheless, the large particle size of the commercial WC used in that work induced a large particle size of Pt (7.5 nm), which resulted in low mass MOR activity. Recently, Mellinger et al. [26] reported improved CO oxidation activity for Pt/WC catalysts, and the catalysts were stable until 1.2 V in an acidic medium. Nie et al. [27] used WC as a promoter of Pt/C for the ORR; a 150 mV more positive onset potential was observed with the Pt–WC/C catalyst than with Pt/C.

In the present study, WC is synthesized on a carbon support and then Pt is deposited to produce a Pt/WC/C catalyst with a small Pt particle size. Physical and electrochemical properties are analyzed by X-ray diffraction (XRD), transmission electron microscopy (TEM) equipped with energy dispersive spectroscopy (EDS), cyclic voltammetry (CV), CO stripping, and measurements of MOR and ORR activity.

## 2. Experimental

### 2.1. Synthesis of catalyst

Synthesis of WC on the carbon support (Vulcan XC72R) was performed following the synthesis method disclosed in a previous report [28]. The carbon support was dispersed in de-ionized (DI) water, and then a tungsten precursor (ammonium metatungstate) was dissolved in the dispersion. The W precursor was deposited on the carbon support by evaporating the DI water under vacuum. The amount of W was adjusted to 50 wt.% of the carbon support. WC was synthesized by reacting the resulting powder with a  $\text{CH}_4 + \text{H}_2$  (10:1, volume ratio) gas stream at 900 °C.

Platinum was deposited on the WC/C and C supports by a conventional- $\text{NaBH}_4$  reduction method. The supports were dispersed in a mixture of DI water and isopropylalcohol, and then  $\text{H}_2\text{PtCl}_6$  was dissolved as a Pt precursor. The Pt was reduced by adding  $\text{NaBH}_4$  solution to the mixture at 80 °C. The resulting mixture was filtered and washed with DI water, followed by drying overnight in an oven. The mass ratio of Pt was adjusted to 20 wt.% of total amount of supports (WC + C) and C for the Pt/WC/C and Pt/C catalysts, respectively.

### 2.2. Electrochemical analysis of catalysts

Electrochemical analysis was carried out in a three-electrode beaker cell equipped with a platinum wire as a counter electrode, an Ag|AgCl reference electrode (BAS Co. Ltd., MF-2052 RE-5B) and a glassy carbon working electrode (3 mm dia., BAS Co. Ltd., MF-2012 for MOR and MF-2066 for ORR). The working electrodes were prepared by the thin-film method proposed by Schmidt et al. [29]. The catalysts were dispersed in DI water and then sonicated for homogeneous mixing. The catalyst dispersion was dripped on the glassy carbon electrode and then dried at room temperature. To stabilize the catalyst layer, 5 wt.% Nafion ionomer solution was dripped on the catalyst layer. All potentials in this paper are reported with respect to a reversible hydrogen electrode (RHE). The CV and CO stripping techniques were performed in an electrolyte of 1 M  $\text{HClO}_4$  solution at a scan rate of 15  $\text{mV s}^{-1}$ . For CO stripping, CO was adsorbed by bubbling through the cell for 1 h while keeping the working electrode at 0.1 V. Dissolved CO in the electrolyte was removed by purging the electrolyte with  $\text{N}_2$  for 50 min. Measurements of MOR activity were performed in a 1 M  $\text{H}_2\text{SO}_4 + 1$  M methanol solution as the electrolyte, at a scan rate of 15  $\text{mV s}^{-1}$ . The

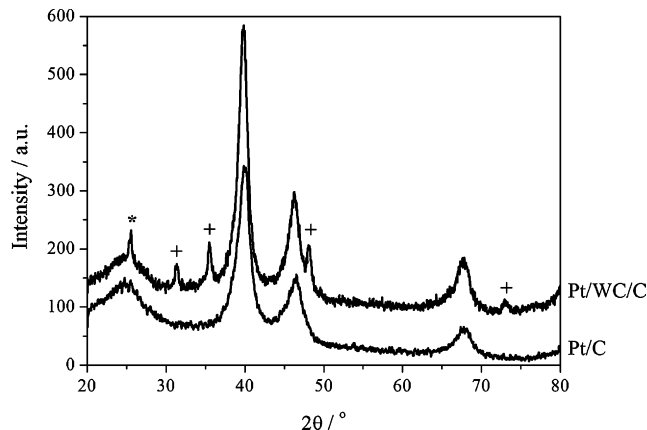


Fig. 1. XRD patterns for Pt/WC/C and Pt/C catalysts. WC (+) and  $\text{WO}_3$  (\*) peaks are designated.

ORR activity was determined by using a rotating disc electrode in oxygen saturated 1 M  $\text{HClO}_4$  solution as the electrolyte at a scan rate of 5  $\text{mV s}^{-1}$  and a rotating speed of 2000 rpm. The same experiment was performed in an oxygen saturated 1 M  $\text{HClO}_4 + 0.1$  M methanol solution as the electrolyte for the measurement of ORR activity in the presence of methanol.

## 3. Results and discussion

The XRD patterns of the Pt/WC/C and Pt/C catalysts, are given in Fig. 1. Formation of WC is clearly discernible with a small amount of  $\text{WO}_3$ . This is not observed for WC/C (not shown in figure) and therefore indicates that  $\text{WO}_3$  is formed during the  $\text{NaBH}_4$  reduction process [8]. The particle size of WC is 17.5 nm, which is determined by the Scherrer equation. The Pt particle sizes are 4.5 and 4.1 nm for the Pt/WC/C and Pt/C catalysts, respectively.

The CV results are shown in Fig. 2. The patterns are similar to our previously published results [25]. Formation of PtO is largely reduced and a new peak near 0.25 V, which suggests spill-over of  $\text{H}^+$ , is also shown in the Pt/WC/C catalyst. The electrochemically active surface-area (EAS) from  $\text{H}^+$  desorption (EAS- $\text{H}^+$ ) is 7.5 and 5.6  $\text{m}^2 \text{g}_{\text{cat}}^{-1}$  for the Pt/WC/C and Pt/C catalysts, respectively. This 33% larger EAS- $\text{H}^+$  value of the Pt/WC/C catalyst is not a reason for this result due to the similar Pt particle size in Pt/C and Pt/WC/C. Especially large EAS- $\text{H}^+$  of Pt/WC/C has been observed previously [25] and the spill-over of  $\text{H}^+$  from Pt to WC may be the reason for

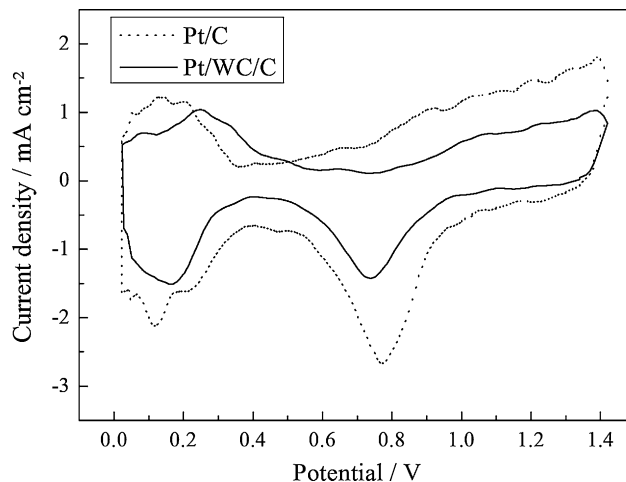
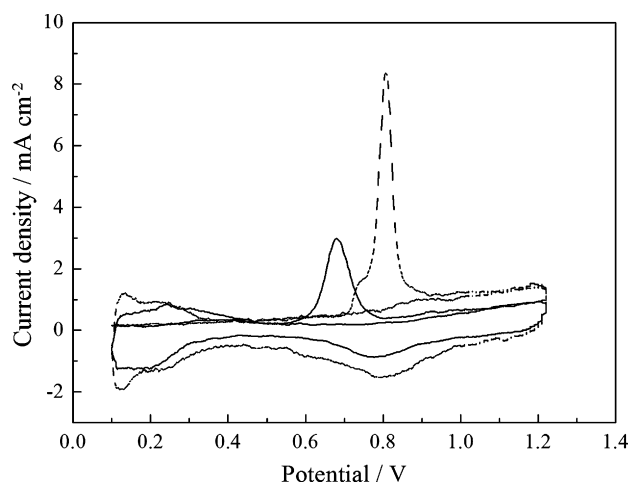


Fig. 2. Cyclic voltammograms for Pt/WC/C (solid line) and Pt/C (dotted line) catalysts. Experiment carried out in 1 M  $\text{HClO}_4$  as electrolyte and at a scan rate = 15  $\text{mV s}^{-1}$ .



**Fig. 3.** CO stripping results for Pt/WC/C (solid line) and Pt/C (dotted line) catalysts. 1 M HClO<sub>4</sub> solution used as electrolyte; scan rate = 15 mV s<sup>-1</sup>.

this behaviour. Further investigation of the EAS was performed by CO stripping to compare the desorption area values between H<sup>+</sup> and CO.

The CO stripping results are presented in Fig. 3. The EAS values calculated from the CO electro-oxidation area (EAS-CO) are 3.8 and 5.9 m<sup>2</sup> g<sub>cat.</sub><sup>-1</sup> for Pt/WC/C and Pt/C, respectively. In the case of Pt/C, the two EAS values are closer, namely: 5.6 m<sup>2</sup> g<sub>cat.</sub><sup>-1</sup> for H<sup>+</sup> and 5.9 m<sup>2</sup> g<sub>cat.</sub><sup>-1</sup> for CO. For Pt/WC/C, however, EAS-H<sup>+</sup> (7.5 m<sup>2</sup> g<sub>cat.</sub><sup>-1</sup>) is much larger than EAS-CO (3.8 m<sup>2</sup> g<sub>cat.</sub><sup>-1</sup>). As noted earlier, this difference can be attributed to a spill-over of H<sup>+</sup> from Pt to WC. One more interesting finding from the CO-stripping study is that the CO electro-oxidation potential is markedly reduced in Pt/WC/C. The peak potentials for CO electro-oxidation are 0.68 and 0.81 V for Pt/WC/C and Pt/C, respectively, and this demonstrates the improved CO electro-oxidation activity of the Pt/WC/C catalyst. The peak

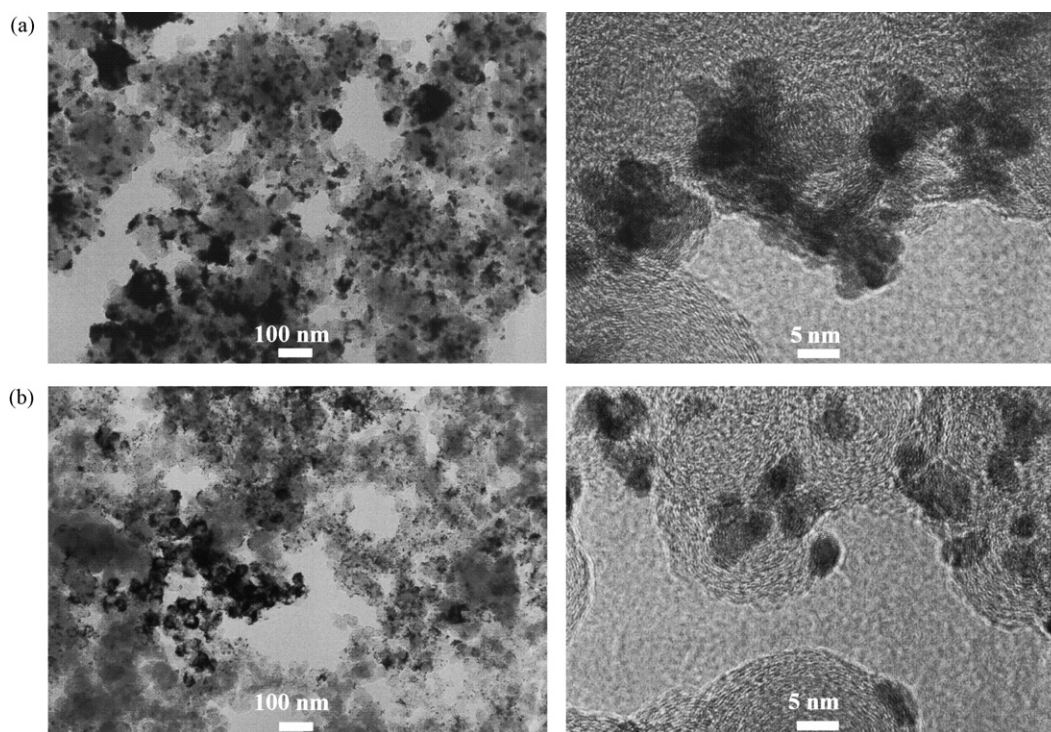
**Table 1**

TEM-EDS analysis results for 10 different points on Pt/WC/C catalyst

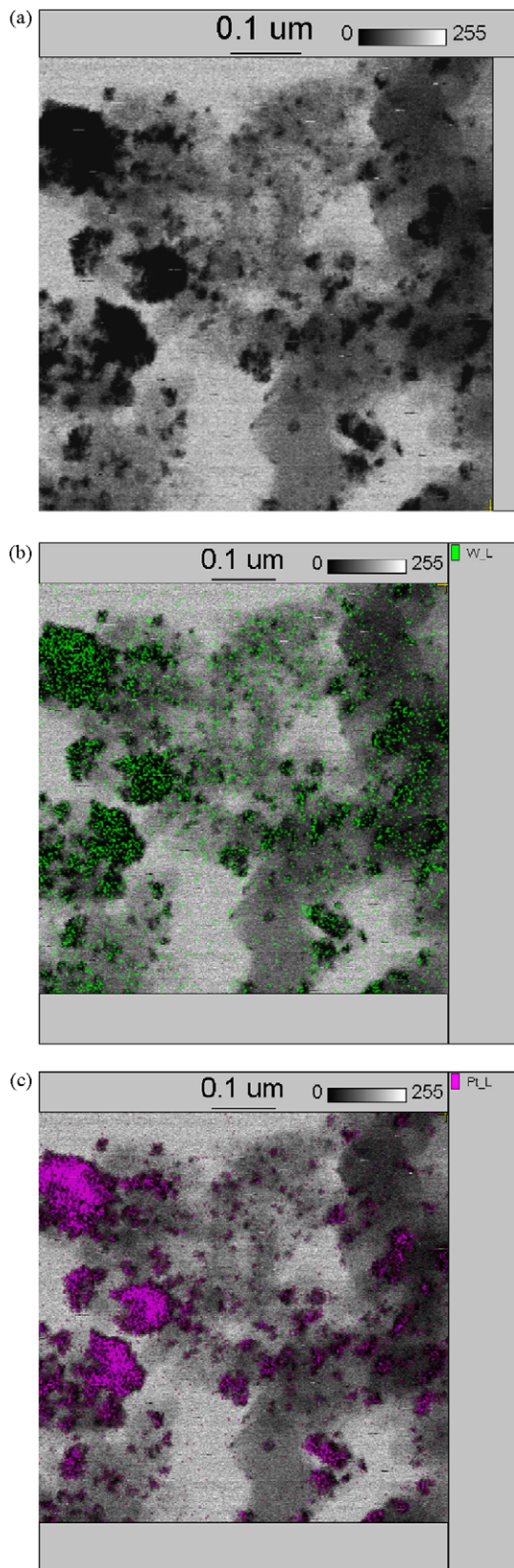
Analysis point	Concentration (at.%)			
	C	O	Pt	W
1	96.35	0.16	3.10	0.39
2	95.80	0.28	3.23	0.69
3	94.55	1.35	3.68	0.42
4	94.11	0.06	4.83	1.00
5	84.89	0.00	13.47	1.64
6	94.38	3.37	1.90	0.35
7	94.09	1.97	3.50	0.44
8	97.93	1.85	0.06	0.16
9	98.54	1.42	0.02	0.02
10	98.41	1.59	0.00	0.00

potential of 0.68 V in Pt/WC/C is the same value as that reported for in Pt/WC [23]. This is an important point as it suggests that CO electro-oxidation activity can be improved by replacing the carbon support with WC, which is much cheaper than Ru. Two questions arose from the CO stripping results: (i) why is EAS-CO of Pt/WC/C only 64% of Pt/C even though they have similar Pt particle sizes, and (ii) how can all the CO be removed at a lower potential in Pt/WC/C than that in Pt/C even though C was not fully covered by WC? To answer these questions, TEM images were taken and the examples are presented in Fig. 4.

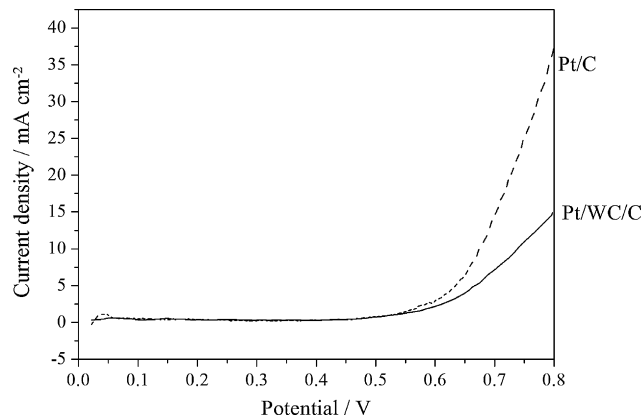
It is observed that the particle sizes of Pt are similar in Pt/WC/C and Pt/C, as in the XRD results; but the dispersion of the two catalysts appears significantly different. The Pt particles are not dispersed well in Pt/WC/C, while in Pt/C almost all Pt particles are deposited solely on the C. This difference explains why a smaller EAS-CO is obtained for Pt/WC/C and how all the CO could be removed at a lower potential than that for Pt/C. This result also confirms that Pt is selectively deposited on WC during the NaBH<sub>4</sub> reduction. Composition mapping results by TEM-EDS are given in Fig. 5. The Pt concentration is proportional to that of W. Composition analysis results of 10 points are listed in Table 1 and a



**Fig. 4.** TEM images of (a) Pt/WC/C and (b) Pt/C.



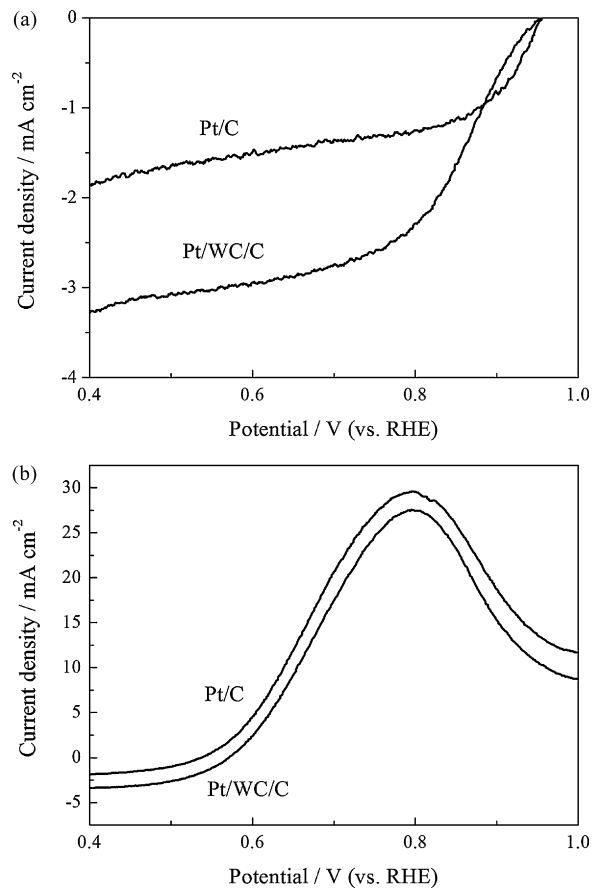
**Fig. 5.** TEM-EDS composition mapping of Pt/WC/C catalyst: (a) TEM image; (b) W concentration; (c) Pt concentration.



**Fig. 6.** MOR activity measurements for Pt/WC/C (solid line) and Pt/C (dotted line). Experiments performed in 1 M  $\text{H}_2\text{SO}_4$  + 1 M methanol as electrolyte; scan rate =  $15 \text{ mV s}^{-1}$ .

correlation between the quantities of Pt and W is found. At points where W is rarely observed, the Pt concentration is also very low, which indicates that the Pt particles deposit preferentially on the WC surface instead of on the carbon support.

Results for MOR activity are shown in Fig. 6. The mass activities are  $630$  and  $690 \text{ mA g}_{\text{cat}}^{-1}$  for Pt/WC/C and Pt/C, respectively. In this work, we have tried to obtain a high mass activity by synthesizing a high surface area WC/C support, but this has not been successful because of the selective deposition of Pt on WC. Nevertheless,



**Fig. 7.** ORR activity measurements for Pt/WC/C and Pt/C. Oxygen-saturated solutions of (a) 1 M  $\text{HClO}_4$  and (b) 1 M  $\text{HClO}_4$  + 0.1 M methanol used as electrolytes. Rotating speed of RDE = 2000 rpm; scan rate =  $5 \text{ mV s}^{-1}$ .

the specific activity of  $170 \text{ mA m}^{-2}$  with Pt/WC/C is still 42% higher than that with Pt/C, viz.,  $120 \text{ mA m}^{-2}$ . This improvement by WC can be explained by a bi-functional mechanism [30] as it has been reported that WC can discharge water to produce WC–OH on its surface [21].

The ORR activity results are presented in Fig. 7(a). A much higher activity is given by the Pt/WC/C catalyst; current densities at 0.8 V are 0.68 and  $0.25 \text{ mA cm}^{-2}$  for Pt/WC/C and Pt/C, respectively, i.e., the current density of Pt/WC/C is 170% higher than that of Pt/C. At 0.7 V, the current density of Pt/WC/C,  $0.87 \text{ mA cm}^{-2}$ , is still 140% higher than the  $0.36 \text{ mA cm}^{-2}$  of Pt/C. In the presence of methanol, shown in Fig. 7(b), the Pt/WC/C catalyst maintains its higher activity, which implies that Pt/WC/C is a promising catalyst for DMFC cathode applications.

#### 4. Conclusions

A Pt/WC/C catalyst has been synthesized and its physical and electrochemical properties analyzed, during which the following special characteristics are observed: (i) the Pt/WC/C catalyst exhibits a lower CO electro-oxidation peak potential of 0.68 V compared with that of Pt/C, 0.81 V; (ii) CO stripping and TEM results reveal that Pt particles are selectively deposited on WC, which causes a reduced EAS; (iii) the difference in the EAS values from CV and CO stripping studies shows that  $\text{H}^+$  spill-over occurs in the Pt/WC/C catalyst. The Pt/WC/C catalyst gives a 42% higher specific activity for MOR compared with the Pt/C catalyst. For ORR, the Pt/WC/C catalyst delivers a 170% higher current density than Pt/C at 0.8 V; in addition, a superior current density is maintained in the presence of methanol. These findings suggest that Pt/WC/C is a promising catalyst for both the anode and cathode applications in DMFCs.

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