



## Short communication

Electrodeposition preparation of Pt–H<sub>x</sub>WO<sub>3</sub> composite and its catalytic activity toward oxygen reduction reactionY.J. Huang<sup>a</sup>, H.H. Dai<sup>a</sup>, W.S. Li<sup>a,b,\*</sup>, G.L. Li<sup>a,b</sup>, D. Shu<sup>a,b</sup>, H.Y. Chen<sup>a,b</sup><sup>a</sup> School of Chemistry and Environment, South China Normal University, Guangzhou 510006, China<sup>b</sup> Key Lab of Technology on Electrochemical Energy Storage and Power Generation in Guangdong Universities, Guangzhou 510006, China

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## ABSTRACT

Platinum–hydrogen tungsten bronze (Pt–H<sub>x</sub>WO<sub>3</sub>) was prepared on glass carbon electrode by potentiostat in 0.1 mM H<sub>2</sub>PtCl<sub>6</sub> + 4 mM Na<sub>2</sub>WO<sub>4</sub> + 2 M H<sub>2</sub>SO<sub>4</sub>. Its surface morphology, structure and activity toward oxygen reduction reaction were studied with scan electron microscope, X-ray diffraction, Fourier transform infrared spectroscopy, and linear sweeping voltammetry. It is found that platinum and hydrogen tungsten bronze can be co-deposited together on glassy carbon and the activity of platinum toward oxygen reduction can be improved significantly by H<sub>x</sub>WO<sub>3</sub>. Furthermore, the activity of Pt–H<sub>x</sub>WO<sub>3</sub> toward oxygen reduction is hardly influenced by methanol.

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## 1. Introduction

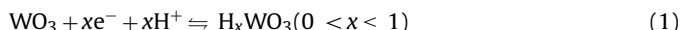
Direct methanol fuel cell (DMFC) can be used as the powers not only for vehicles in large scale but also for portable electronic devices in small scale [1,2]. However, DMFC faces a serious problem that methanol crosses over the proton exchange membrane. Methanol permeates from the anode to the cathode compartment, resulting in the decrease in catalytic activity of platinum from poisonous intermediates of methanol oxidation. This problem has been attracting intensive research [3–9].

Many researchers are focusing their work on developing new membranes to resist the methanol crossover and methanol-tolerant catalysts for oxygen reduction [10–14]. In the development of new membranes, the resistance improvement of methanol crossover used to be at the cost of lowering the proton conductivity of the membrane and the methanol crossover cannot be reduced completely. In the development of methanol tolerant catalysts, the catalysts that were tolerant of methanol used to be lack of their activity toward oxygen reduction. Therefore, it is necessary to develop new catalysts that can be not only tolerant of methanol but also active for oxygen reduction.

In our previous work, it has been found that the modification of platinum with hydrogen molybdenum bronze (H<sub>x</sub>MoO<sub>3</sub>, 0 < x ≤ 2) can improve the activity of platinum, not only for the methanol

oxidation [15–17], but also for the oxygen reduction [18]. This improvement is related to proton intercalation/de-intercalation process taking place in H<sub>x</sub>MoO<sub>3</sub>.

The compounds of tungsten are similar to those of molybdenum. Proton insertion/deinsertion process can also take place during the transformation between tungsten oxide and hydrogen tungsten bronze (H<sub>x</sub>WO<sub>3</sub>) [19–28]:



H<sub>x</sub>WO<sub>3</sub> has been considered as the catalyst for oxygen reduction [29–31], but the conclusions are controversial. H<sub>x</sub>WO<sub>3</sub> was thought to be active to oxygen reduction by some authors [31] but inactive by others [32–34]. Based on the similarity between H<sub>x</sub>WO<sub>3</sub> and H<sub>x</sub>MoO<sub>3</sub>, it can be inferred that the activity of platinum toward oxygen reduction can be improved by its composite with H<sub>x</sub>WO<sub>3</sub>. The purpose of this paper is to develop a new method to prepare co-deposited platinum and hydrogen tungsten bronze as the catalyst for oxygen reduction reaction.

## 2. Experimental

Solutions containing 0.1 mM H<sub>2</sub>PtCl<sub>6</sub> + 2 M H<sub>2</sub>SO<sub>4</sub>, 4 mM Na<sub>2</sub>WO<sub>4</sub> + 2 M H<sub>2</sub>SO<sub>4</sub> and 0.1 mM H<sub>2</sub>PtCl<sub>6</sub> + 4 mM Na<sub>2</sub>WO<sub>4</sub> + 2 M H<sub>2</sub>SO<sub>4</sub> were used to prepare catalysts platinum (Pt), hydrogen tungsten bronze (H<sub>x</sub>WO<sub>3</sub>) and their composite (Pt–H<sub>x</sub>WO<sub>3</sub>), respectively. Solution was prepared freshly with distilled water for each experiment. H<sub>2</sub>PtCl<sub>6</sub> is spectrum grade and other chemicals are analytical grade.

\* Corresponding author. Tel.: +86 20 39310256; fax: +86 20 39310256.  
E-mail address: [liwsh@sncu.edu.cn](mailto:liwsh@sncu.edu.cn) (W.S. Li).

The electrochemical experiments were carried out in a three-electrode configuration with a potentiostat (Eco Echemine BV). A rotating glassy carbon disk electrode with a diameter of 3 mm on an instrument (RDE, model ATA-1B) was used as working electrode, a platinum sheet electrode was used as the counter electrode and an Ag/AgCl/saturated KCl electrode was used as the reference electrode. The potentials in this paper are with respect to this reference electrode. Before the preparation of the catalysts, the working electrode was polished with 0.05  $\mu\text{m}$  alumina, cleaned by ultrasonication in acetone and distilled water and then cycling in 0.5 M  $\text{H}_2\text{SO}_4$  between 0.2 and 0.9 V at 50  $\text{mV s}^{-1}$ .

The catalysts were deposited on glassy carbon electrode by potentiostat at  $-0.1$  V for 2000 s in the quiescent solutions. In the electrochemical measurement involved in oxygen reduction, the solution was saturated with oxygen, otherwise, the solution was deaerated with nitrogen.

X-ray diffraction was carried out on X-ray diffractometer (Rigaku D/max 2200 vpc). FTIR was recorded on PerkinElmer instruments (Spectrum One FTIR Spectrometer). Surface morphology of the catalysts was observed on SEM-EDS-EBSD (model Quanta 400F, FEI/OXFORD/HKL).

### 3. Results and discussions

#### 3.1. Formation and voltammetric characterization of catalysts

Fig. 1 presents the chronoamperograms for the preparation of Pt(a), Pt- $\text{H}_x\text{WO}_3$  (b) and  $\text{H}_x\text{WO}_3$  (c) on glassy carbon electrode at  $-0.1$  V for 2000 s. The current for the formation of Pt- $\text{H}_x\text{WO}_3$  is almost equal to the sum of those for the individual formation of Pt and  $\text{H}_x\text{WO}_3$ . For example, the current for the formation of Pt,  $\text{H}_x\text{WO}_3$  and Pt- $\text{H}_x\text{WO}_3$  at 1400 s is  $-0.0013$ ,  $-0.0020$  and  $-0.0032$  mA, respectively. This suggests that the co-deposition of Pt and  $\text{H}_x\text{WO}_3$  takes place and the quantity of the Pt or the  $\text{H}_x\text{WO}_3$  in the co-deposited Pt- $\text{H}_x\text{WO}_3$  is almost equal to that in its individual form. The charge for the preparation of Pt is 0.004 C, thus the quantity of the Pt in its individual deposition or in the co-deposition is  $0.028 \text{ mg cm}^{-2}$  on the glassy carbon electrode. The charge for the formation of  $\text{H}_x\text{WO}_3$  is 0.005 C. Assuming the  $x$  in  $\text{H}_x\text{WO}_3$  is 0.5, the quantity of  $\text{H}_x\text{WO}_3$  in its individual deposition or in the co-deposition is  $0.340 \text{ mg cm}^{-2}$  on the glassy carbon electrode.

Fig. 2 shows the cyclic voltammograms of catalysts Pt,  $\text{H}_x\text{WO}_3$  and Pt- $\text{H}_x\text{WO}_3$  in 0.5 mol  $\text{L}^{-1}$   $\text{H}_2\text{SO}_4$ . As seen from curve a of Fig. 2, the hydrogen adsorption and desorption currents on platinum

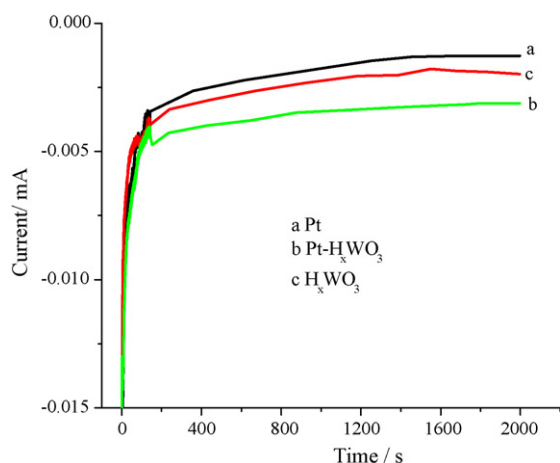


Fig. 1. Chronoamperograms for the preparation of Pt (a), Pt- $\text{H}_x\text{WO}_3$  (b) and  $\text{H}_x\text{WO}_3$  (c) on glassy carbon electrode at  $-0.1$  V for 2000 s.

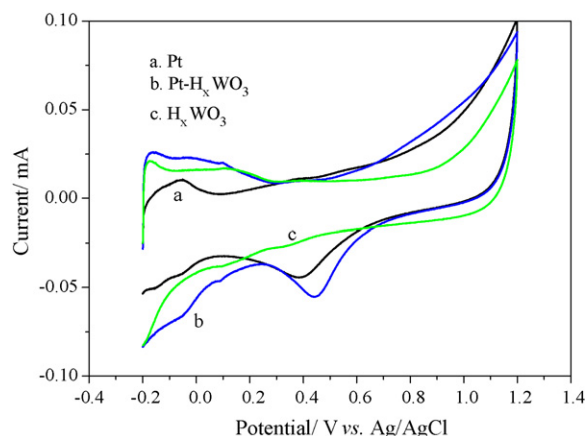
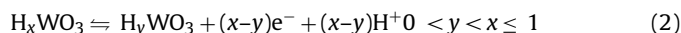


Fig. 2. Cyclic voltammograms of Pt (a), Pt- $\text{H}_x\text{WO}_3$  (b) and  $\text{H}_x\text{WO}_3$  (c) in 0.5 M  $\text{H}_2\text{SO}_4$  solution, scan rate: 50  $\text{mV s}^{-1}$ .

appear at the potentials between  $-0.2$  and 0 V, the formation current of platinum oxide appears at the potentials higher than 0.4 V and the reduction current peak appears at about 0.4 V. Comparing the curve b with a of Fig. 2, it can be found that the oxidation and reduction currents for Pt- $\text{H}_x\text{WO}_3$  at the potentials between  $-0.2$  and 0.3 V are larger than those for Pt. This suggests that  $\text{H}_x\text{WO}_3$  in Pt- $\text{H}_x\text{WO}_3$  is involved in the oxidation and reduction at the potentials for the hydrogen adsorption and desorption on Pt. The oxidation and reduction of  $\text{H}_x\text{WO}_3$  can be confirmed by the voltammogram of  $\text{H}_x\text{WO}_3$ , as seen from curve c of Fig. 2. The involved reactions can be ascribed to the hydrogen ion insertion into or desorption from the  $\text{H}_x\text{WO}_3$ :



The charge for the formation of adsorbed hydrogen on platinum and hydrogen-abundant  $\text{H}_x\text{WO}_3$  on the catalysts can be estimated by integrating the voltammograms of Fig. 2 at the potentials from  $-0.2$  to 0.3 V. It is 0.001, 0.003 and 0.004 mC for Pt,  $\text{H}_x\text{WO}_3$  and Pt- $\text{H}_x\text{WO}_3$ , respectively. By deduction of the charge for the hydrogen insertion into  $\text{H}_x\text{WO}_3$ , it can be found that there is the same charge for the adsorbed hydrogen on platinum in Pt and Pt- $\text{H}_x\text{WO}_3$ . This suggests that there is the same platinum surface area in Pt and in Pt- $\text{H}_x\text{WO}_3$ .

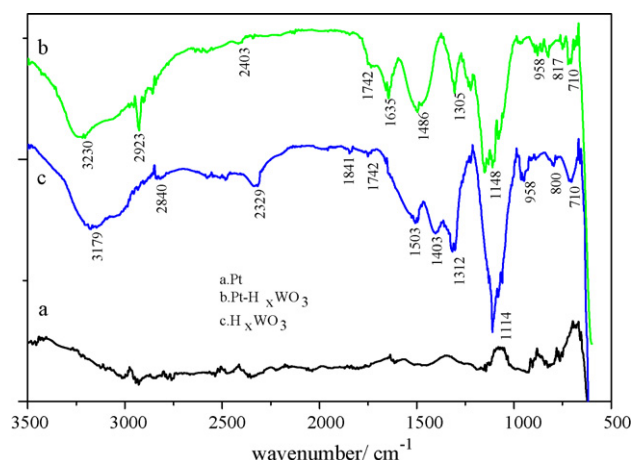


Fig. 3. FTIR spectra of Pt (a), Pt- $\text{H}_x\text{WO}_3$  (b) and  $\text{H}_x\text{WO}_3$  (c).

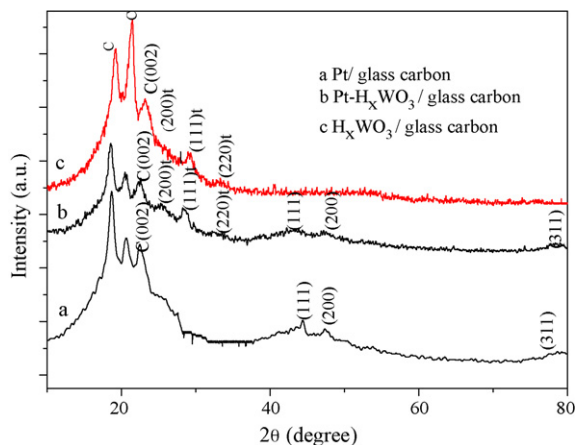


Fig. 4. X-ray diffraction patterns of Pt (a), Pt- $H_xWO_3$  (b) and  $H_xWO_3$  (c).

### 3.2. FTIR of the catalysts

The FTIR spectra for Pt,  $H_xWO_3$  and Pt- $H_xWO_3$  are shown in Fig. 3. There are weak IR adsorptions for Pt, as shown in curve a of Fig. 3. The IR adsorptions of Pt- $H_xWO_3$  (curve b of Fig. 3) are similar to those of  $H_xWO_3$  (curve c of Fig. 3), indicating that the structure and composition of the hydrogen tungsten bronze is similar for Pt- $H_xWO_3$  and  $H_xWO_3$ . Proton in the catalysts exists in the form of O-H, corresponding to the adsorptions at 3150–3450  $cm^{-1}$ . There is no IR adsorptions corresponding to H-O-H, this is in accordance with the result obtained by Deepa [26]. The bending vibration of OH appears at 1503, 1635  $cm^{-1}$  for  $H_xWO_3$  and Pt- $H_xWO_3$ , respectively. This is identical with the results of reference [35]. This suggests that no water exists in Pt- $H_xWO_3$  or  $H_xWO_3$ , i.e., the tungsten in the catalysts exists in the form of  $H_xWO_3$  but not  $WO_3 \cdot xH_2O$ . The existence of hydroxyl groups bonded to tungsten ion (W-OH or  $OH_2$ ) in  $H_xWO_3$  or Pt- $H_xWO_3$  is confirmed by the adsorption at 1403 ( $H_xWO_3$ ) and 1486 (Pt- $H_xWO_3$ )  $cm^{-1}$ . The adsorptions at 958  $cm^{-1}$  and 1114 (1148)  $cm^{-1}$  correspond to W=O [36,37], and the adsorption at 710  $cm^{-1}$  corresponds to O-W-O [38,39].

### 3.3. XRD of the catalysts

Fig. 4 presents the XRD patterns of Pt, Pt- $H_xWO_3$  and  $H_xWO_3$ . The diffractions at 44° (42° in curve b of Fig. 4), 47° and 80° are corresponding to Pt (1 1 1), Pt (2 0 0) and Pt (3 1 1), respectively. The diffraction of Pt (1 1 1) that shifts from the literature value 39.6° may be caused by glass carbon substrate. The diffraction at 28° is W (1 1 1) and that at 32° is W (2 2 0). The diffractions at 2θ between

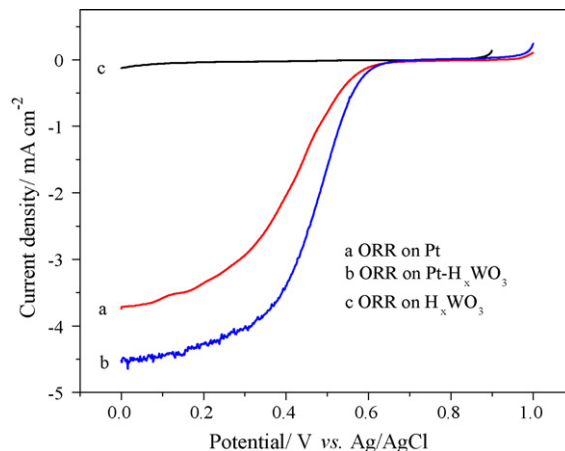


Fig. 6. Linear sweeping voltammograms of Pt (a), Pt- $H_xWO_3$  (b) and  $H_xWO_3$  (c) on rotating glassy carbon disk electrode with a geometric surface of 0.071  $cm^2$  in 0.5 M  $H_2SO_4$  solution saturated with  $O_2$ , rotating rate: 600  $rpm^{-1}$ ; scan rate: 5  $mVs^{-1}$ .

18 and 23° correspond to the crystalline phase for glass carbon. The broad hump centered at 26° (curve b and c of Fig. 4) corresponds to typical amorphous structure of the  $H_xWO_3$  [27]. This confirms that the tungsten in the catalysts exists in the form of  $H_xWO_3$ .

### 3.4. Surface morphology of the catalysts

The surface morphology of the catalysts Pt and Pt- $H_xWO_3$  was observed by scan electron spectroscopy. The results obtained are shown in Fig. 5. Fig. 5a shows that the platinum disperses homogeneously on the base of glassy carbon in grain size with an average diameter of about 100 nm. Fig. 5b shows that the co-deposited platinum also disperses homogeneously in grain size a little larger than that of Fig. 5a and the co-deposited hydrogen tungsten bronze exists in typical amorphous structure which attached to the platinum grain.

### 3.5. Oxygen reduction reaction on the catalysts

The linear sweeping voltammograms of  $H_xWO_3$ , Pt and Pt- $H_xWO_3$  in 0.5 M  $H_2SO_4$  solution saturated with  $O_2$  are shown in Fig. 6. It can be found from the curve c of Fig. 6 that the  $H_xWO_3$  has no activity towards oxygen reduction, this is in accordance with the references [32–34]. It can be seen from curve a of Fig. 6 that oxygen reduction begins at about 0.65 V and the reduction current of oxygen on Pt increases as the potential becomes more negative.

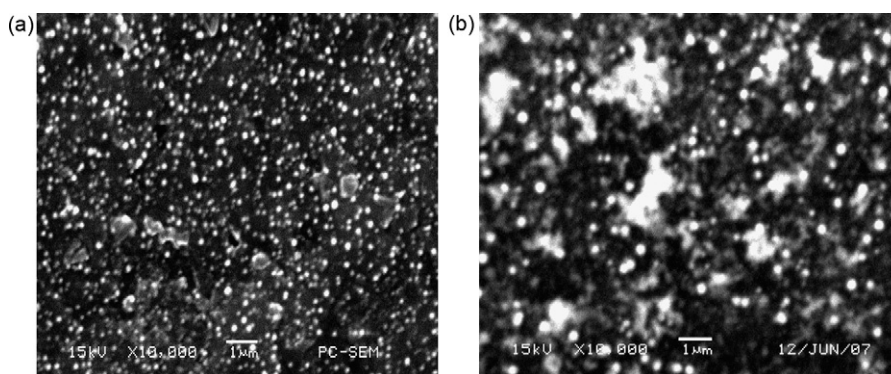
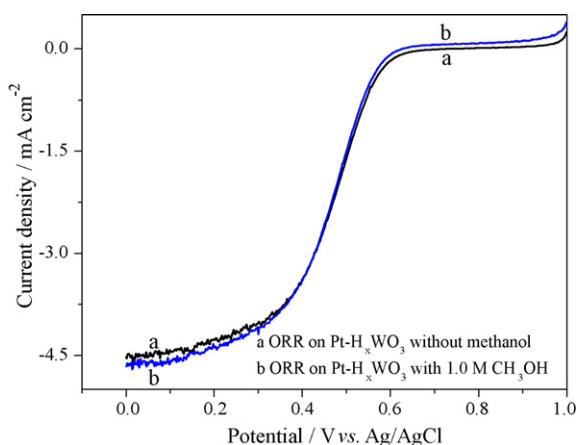


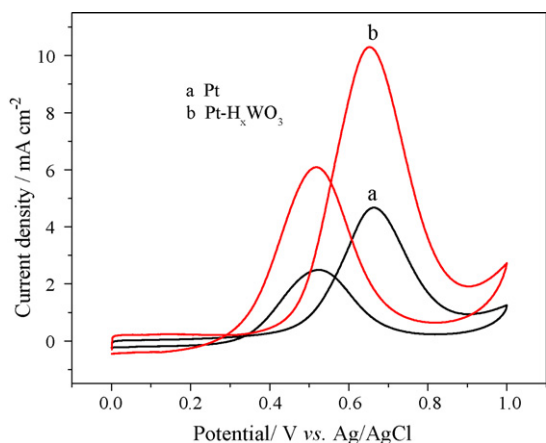
Fig. 5. SEM images of Pt (a) and Pt- $H_xWO_3$  (b).



**Fig. 7.** Linear sweeping voltammograms of Pt-H<sub>x</sub>WO<sub>3</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution saturated with oxygen and without (a) and with (b) 1.0 M CH<sub>3</sub>OH, rotating rate: 600 r min<sup>-1</sup>; scan rate: 5 mV s<sup>-1</sup>.

The oxygen reduction on Pt-H<sub>x</sub>WO<sub>3</sub> has similar voltammetric behavior to that on Pt, as shown by the curve b of Fig. 6. However, it can be seen by comparing curve b with a that the oxygen reduction on Pt-H<sub>x</sub>WO<sub>3</sub> begins at about 0.7 V, 50 mV more positive than that on Pt. The oxygen reduction current on Pt-H<sub>x</sub>WO<sub>3</sub> is larger than that on Pt at the same potential. For example, at 0.4 V, the reduction current of oxygen on Pt-H<sub>x</sub>WO<sub>3</sub> is 3.4 mA cm<sup>-2</sup> but that on Pt is only 2.0 mA cm<sup>-2</sup>. This indicates that the catalytic activity of platinum toward oxygen reduction can be improved by hydrogen tungsten bronze. This is in accordance with the result obtained by Bockris and McHardy [29] group who used H<sub>x</sub>WO<sub>3</sub> as a support and claimed that it can enhance the activity of Pt. The mechanism for the improvement of catalytic activity of platinum toward oxygen reduction by hydrogen tungsten bronze may be ascribed to the proton spillover from hydrogen tungsten bronze. The proton generated from Eq. (2) can be spilled over to Pt-O<sub>2</sub>, thus the oxygen reduction on platinum is catalyzed by hydrogen tungsten bronze. Although proton can be supported by the acid solution, the proton from solution should be different from that in hydrogen tungsten bronze which neighbors platinum. On the other hand, the electronic structure of platinum can be changed and the bond between platinum and oxygen can be weakened by the composite of platinum with other elements or compounds.

Fig. 7 shows the voltammograms of oxygen reduction on Pt-H<sub>x</sub>WO<sub>3</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub> methanol-free and methanol-containing



**Fig. 8.** The cyclic voltammograms of methanol oxidation on Pt (a) and Pt-H<sub>x</sub>WO<sub>3</sub> (b) in 1.0 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Scan rate: 50 mV s<sup>-1</sup>.

solutions saturated with O<sub>2</sub>. It can be seen from Fig. 7 that the oxygen reduction current on Pt-H<sub>x</sub>WO<sub>3</sub> is nearly not influenced by the methanol.

This phenomenon can be ascribed to the surface cleaning that H<sub>x</sub>WO<sub>3</sub> plays for platinum. In the methanol-containing solution saturated with oxygen, the catalyst platinum without composite with H<sub>x</sub>WO<sub>3</sub> will be poisoned by the intermediates from the methanol oxidation by oxygen in the solution, resulting in its poor activity toward oxygen reduction. However, as for the catalyst Pt-H<sub>x</sub>WO<sub>3</sub>, the intermediates can be oxidized further by the oxygen in the solution, thus the platinum surface can be kept clean due to the activity improvement of platinum toward the methanol oxidation by the H<sub>x</sub>WO<sub>3</sub>. Fig. 8 presents the voltammograms of methanol oxidation on Pt and Pt-H<sub>x</sub>WO<sub>3</sub> in 1.0 M CH<sub>3</sub>OH + 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The methanol oxidation current on Pt-H<sub>x</sub>WO<sub>3</sub> is far larger than that on Pt, indicating the activity improvement of platinum toward methanol oxidation by H<sub>x</sub>WO<sub>3</sub>.

#### 4. Conclusion

Pt and hydrogen tungsten bronze can be co-deposited by potentiostat. The co-deposited composite is good for direct methanol fuel cell as cathode catalyst, because the activity of platinum toward oxygen reduction not only can be improved significantly by hydrogen tungsten bronze but also cannot be reduced by the existence of methanol due to the composite of platinum with hydrogen tungsten bronze.

#### Acknowledgements

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