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# Dispersed platinum supported by hydrogen molybdenum bronze-modified carbon as electrocatalyst for methanol oxidation

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**Abstract** A new electrocatalyst, $Pt/H_xMoO_3$-C, for methanol oxidation, was prepared by dispersing platinum nano-particles on Vulcan XC-72 modified by hydrogen molybdenum bronze ($H_xMoO_3$, $0 \leq x \leq 2$). The modification of Vulcan XC-72 with $H_xMoO_3$ on was accomplished by reducing the adsorbed molybdic acid and the platinum nano-particles were dispersed on the modified carbon by reducing chloroplatinic acid, with formaldehyde as the reductant. The prepared $Pt/H_xMoO_3$-C was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersion spectrometer, cyclic voltammetry (CV), chronoamperometry (CA), and single-cell test, with a comparison of the electrocatalyst, carbon-supported platinum (Pt/C) prepared under the same condition but without the modification. The results obtained from XRD and SEM showed that the modification of Vulcan XC-72 with $H_xMoO_3$ reduced the platinum particle size and improved distribution uniformity of platinum on carbon. The results, obtained from CV, CA, and the single-cell test, showed that $Pt/H_xMoO_3$-C exhibited better electrocatalytic activity toward methanol oxidation than Pt/C.

**Keywords** Platinum · Nano-particle · Modification ·
Hydrogen molybdenum bronze · Carbon ·
Methanol oxidation

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## Introduction

Direct methanol fuel cell (DMFC) transforms chemical energy into electric energy directly with liquid fuel, which is believed to be one of the most possible commercialized fuel cells because of its many advantages, including rich and cheap resources and easy operation. However, there are several problems that limit the application of DMFC. Among these problems, the most important is the use of noble metal platinum as catalyst, whose amount needs to be reduced and activity toward methanol oxidation should be improved [1, 2]. Thus considerable efforts have been devoted to develop new catalysts with low amount of platinum and higher electrocatalytic activity. The activity of platinum toward methanol oxidation can be improved, and its amount can be reduced by the combination of platinum with one or more other elements such as Ru [2–7], Mo [8–10], and Sn [11–15], or oxides such as $TiO_2$ [16], $MoO_x$ [17], and $WO_x$ [18, 19].

In our previous reports [20–22], it has been found that the composite of platinum with hydrogen molybdenum bronze ($H_xMoO_3$, $0 \leq x \leq 2$) can improve significantly the activity of platinum toward methanol oxidation, and several Pt-$H_xMoO_3$ composite electrocatalysts have been prepared for methanol oxidation with the aim at the improvement of electrocatalytic activity of platinum and the reduction of platinum amount. In this paper, we developed a new composite of platinum with $H_xMoO_3$ by dispersing platinum nano-particles on the carbon modified with $H_xMoO_3$ and obtained a new electrocatalyst, dispersed platinum supported by hydrogen molybdenum bronze-modified carbon (Pt/ $H_xMoO_3$-C), for methanol oxidation. The modification was accomplished by reducing the adsorbed molybdic acid on Vulcan XC-72 and the platinum nano-particles were dispersed on the modified carbon by reducing chlor-

oplatinic acid, with formaldehyde as reductant. It was found that the modification of Vulcan XC-72 with $H_xMoO_3$ reduced the platinum particle size and improved distribution uniformity of platinum on carbon, and the modified electrocatalyt exhibited better electrocatalytic activity toward methanol oxidation than that without modification.

## Experimental

### Preparation of catalysts

Vulcan XC-72 (Johnson Matthey Company) was dispersed uniformly in de-ionized water by ultrasonication, and then $Na_2MoO_4$ solution and $H_2SO_4$ solution were added under magnetic stirring to form the adsorbed molybdic acid on carbon. The mixture was heated to 80 °C and excessive formaldehyde as reductant was added and the solution was kept at 80 °C for 1 h to form $H_xMoO_3$-modified carbon. The superfluous formaldehyde in the solution was driven out by heating. Platinic chloride solution was added and the mixture was heated for 1 h for the adsorption of platinum precursor on the $H_xMoO_3$-modified carbon, and then excessive formaldehyde, also as reductant, was added and the mixture was kept heated at 80 °C for 1 h. $Pt/H_xMoO_3$-C was obtained by washing, filtrating, and drying the precipitate. For a comparison, carbon-supported platinum (Pt/C) was prepared by the reduction of platinum precursor on carbon without modification and $H_xMoO_3$-C was prepared without further addition of platinum.

### Characterization of catalysts

X-ray diffraction (XRD) measurements were carried out on a Rigaku D/max 2200 vpc diffractometer operated at 30 kV and 20 mA with Cu $K_\alpha$ radiation. The morphology of samples was observed with a scanning electron microscope (JSM-6380, Japan). The composition of catalysts was analyzed by energy-dispersion spectrometer (EDS; thermal field emission environmental scanning electron microscopy (SEM)-EDS-EBSD, Model Quanta 400F). The contents of platinum and molybdenum were given in standard deviation, which was obtained through three measurements by EDS.

The cyclic voltammetric and chronoamperometric measurements were conducted in a three-electrode cell at room temperature on a Solartron Analytical 1480 Multistat (England), with an Ag/AgCl/saturated KCl electrode as the reference electrode and a platinum sheet as the counter electrode. The working electrode was a rotating glassy carbon (GC) disk electrode with a diameter of 3 mm on a rotating disc electrode (RDE, Model ATA-1B). The
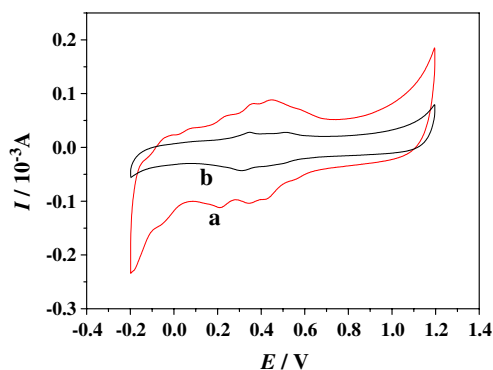


Fig. 1 Cyclic voltammagrams of $H_xMoO_3$-C (a) and C (b) electrodes in 0.5 mol $L^{-1}$ $H_2SO_4$ solution, scan rate: 50 mV $s^{-1}$

prepared electrocatalysts were ultrasonically dispersed in 0.5% Nafion+$C_2H_5OH$ solution to generate a homogeneous black ink with a content of 0.4 mg $mL^{-1}$ Pt. 5 µL of this ink was pipetted onto the GC electrode surface and dried at room temperature. Before the catalyst was coated, the GC electrode was polished with 2400 mesh sand paper, cleaned by ultrosonication in distilled water successively.

A single DMFC was set up to confirm the electrocatalytic activity of $Pt/H_xMoO_3$-C toward methanol oxidation. The membrane electrode assemble was prepared as reference [23]. Nafion 117 was used as the membrane and a commercial carbon supported catalyst (20 wt.% Pt, Johnson Matthey Company) was used as cathode catalysts with a platinum loading of 0.2 mg $cm^{-2}$. The prepared $Pt/H_xMoO_3$-C was used as anode catalyst with a platinum loading of 0.2 mg $cm^{-2}$. The effective area of the membrane electrode assemble was 4 $cm^2$. The single DMFC using the prepared Pt/C as anode catalyst with the same platinum loading was also set up for comparison. In the determination of the cell performance, 1 mol $L^{-1}$ methanol solution was used as the anolyte with a flow rate of 1 mL $min^{-1}$ at room temperature, and pure oxygen was used as the cathodic reactant with a flow rate 250 mL $min^{-1}$.
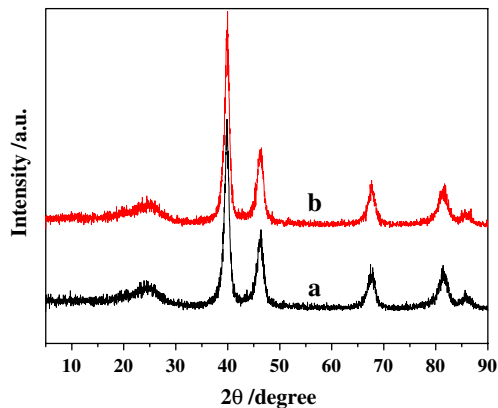


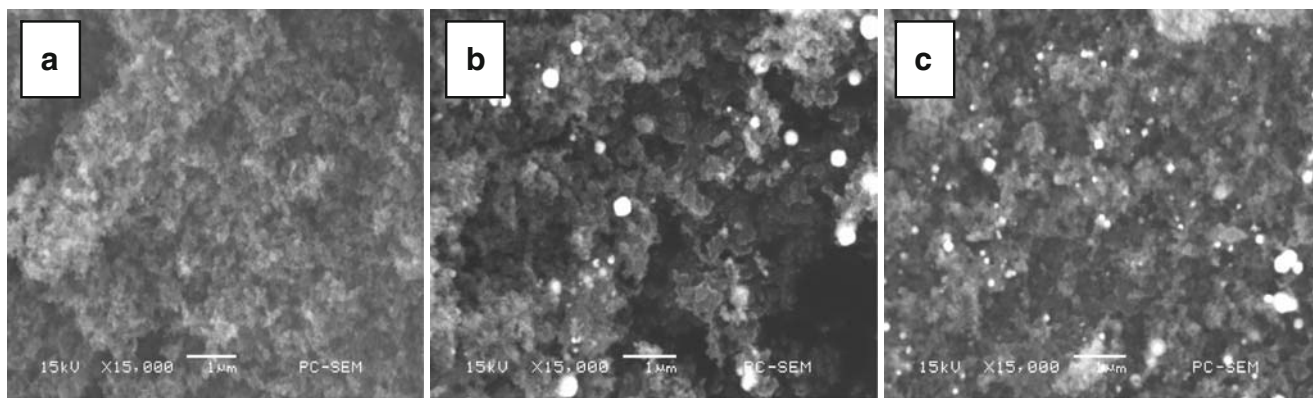Fig. 2 XRD patterns of Pt/C (a) and $Pt/H_xMoO_3$-C (b)

**Fig. 3** The SEM images of $H_xMoO_3$-C (**a**), Pt/C (**b**), and Pt/$H_xMoO_3$-C (**c**)

## Results and discussion

### Cyclic voltammogram of $H_xMoO_3$-modified carbon

Figure 1 shows the cyclic voltammograms of $H_xMoO_3$-C and C (Vulcan XC-72) electrodes in 0.5 mol $L^{-1}$ $H_2SO_4$ solution. It can be seen from Fig. 1 that there are no other reactions take place on carbon except the formation and reduction of hydroxylation of carbon at the potentials between 0 and 0.6 V (curve b of Fig. 1). $H_xMoO_3$-C exhibits larger currents (curve a of Fig. 1) than Vulcan XC-72, indicating that the carbon has been modified with $H_xMoO_3$. The larger currents of $H_xMoO_3$-C electrode corresponds to the reactions of redox $H_xMoO_3$/$H_yMoO_3$ ($0 \leq y < x \leq 2$) [22].

### Effect of supports on crystal structure and particle size of platinum

Figure 2 presents the XRD patterns of Pt/C and Pt/$H_xMoO_3$-C. It can be seen from the curve a of Fig. 2 that both Pt/C and Pt/$H_xMoO_3$ have diffraction peaks at about 24.7°, 39.9°, 46.5°, 67.8°, 81.2°, and 86.0°, which correspond to (002) crystal plane of carbon and (111), (200), (220), (311), and (222) crystal planes of platinum [24, 25]. Pt/$H_xMoO_3$-C has similar diffraction (curve b of Fig. 2) with Pt/C except for the small shifts of the diffraction peaks to the smaller angles, suggesting that the modification of carbon with $H_xMoO_3$ does not affect the crystal structure of the platinum loaded on the supports. There is not any diffraction peak of $H_xMoO_3$ for Pt/$H_xMoO_3$-C, suggesting that the $H_xMoO_3$ in Pt/$H_xMoO_3$-C is amorphous.

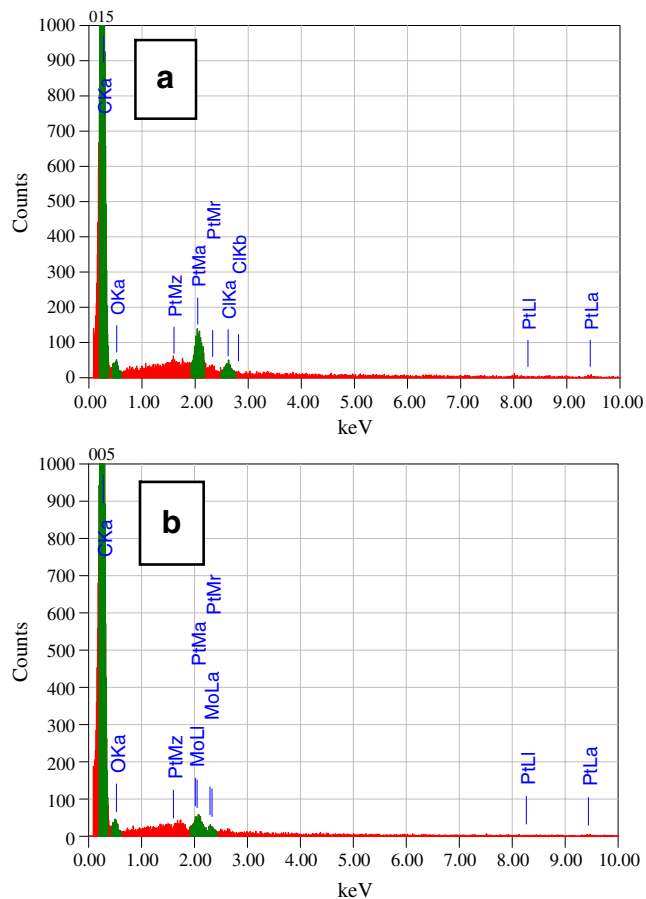Figure 3 presents the SEM images of $H_xMoO_3$-C, Pt and Pt/$H_xMoO_3$-C. It can be seen from Fig. 3 that the
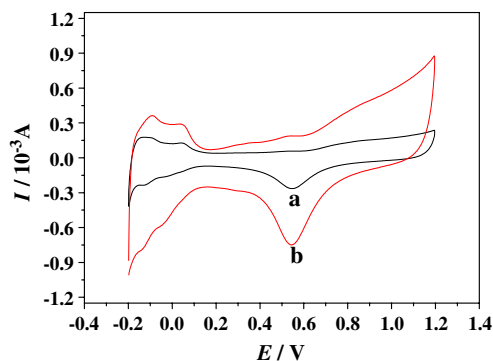


**Fig. 4** EDS of Pt/C (**a**) and Pt/$H_xMoO_3$-C (**b**)



**Fig. 5** Cyclic voltammograms of Pt/C (**a**) and Pt/$H_xMoO_3$-C (**b**) in 0.5 mol $L^{-1}$ $H_2SO_4$ solution, scan rate: 50 mV $s^{-1}$
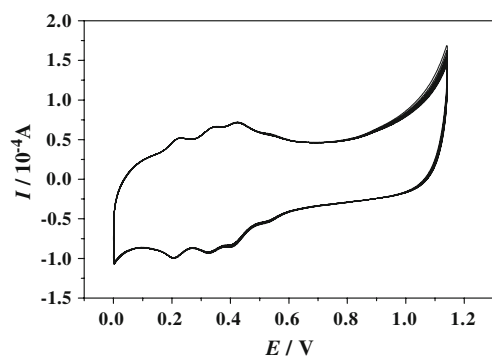
Fig. 6 Cyclic voltammogram of $H_xMoO_3$-C electrode in 0.5 mol $L^{-1}$ $H_2SO_4$+0.5 mol $L^{-1}$ $CH_3OH$ solution, scan rate: 50 mV $s^{-1}$

morphology of the $H_xMoO_3$ cannot be distinguished by SEM (Fig. 3a) but it affects the platinum particle sizes (Fig. 3b and c). The average platinum particle size is about 100 nm (Fig. 3b) and about 10 nm (Fig. 3c) on C and $H_xMoO_3$-C, respectively, indicating that the platinum particle size can be significantly reduced by the modification of carbon with $H_xMoO_3$. Furthermore, the distribution of the platinum particles on $H_xMoO_3$-C is more uniform than that on C. This is important for the loading reduction and the electrocatalytic activity improvement of platinum.

Effect of supports on loaded amount of platinum

Figure 4 presents the EDS of Pt/C and Pt/$H_xMoO_3$-C. It can be seen from Fig. 4 that Pt/C contains Pt and C, and Pt/$H_xMoO_3$-C contains Pt, Mo and C. The loaded amount of platinum is 21±1 wt.% and 6±1 wt.% for Pt/C and Pt/$H_xMoO_3$-C, respectively, suggesting that the reaction kinetics for the formation of platinum on carbon during the preparation of Pt/$H_xMoO_3$-C is slowed down by $H_xMoO_3$, which results in more uniform distribution and smaller size of platinum particles in Pt/$H_xMoO_3$-C than in Pt/C. Although Pt/$H_xMoO_3$-C has lower loaded amount of platinum, it has larger electrochemical active surface area of platinum than Pt/C due to its smaller size of the platinum particles, as indicated by
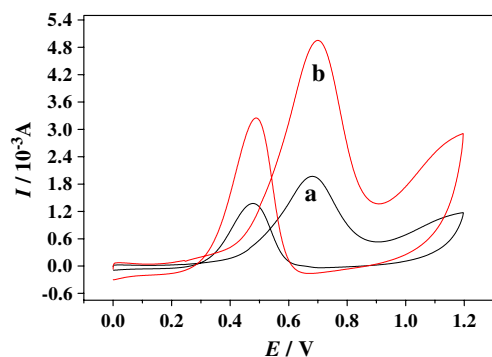


Fig. 7 Cyclic voltammograms of Pt/C (a) and Pt/$H_xMoO_3$-C (b) in 0.5 mol $L^{-1}$ $H_2SO_4$+0.5 mol $L^{-1}$ $CH_3OH$, scan rate: 50 mV $s^{-1}$
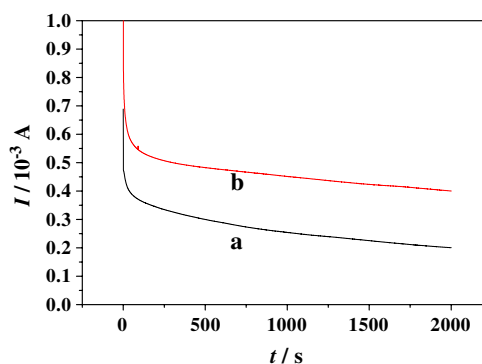


Fig. 8 Chronoamperometric curves of Pt/C (a) and Pt/$H_xMoO_3$-C (b) electrodes in 0.5 mol $L^{-1}$ $H_2SO_4$+0.5 mol $L^{-1}$ $CH_3OH$ solution at 0.6 V

the hydrogen adsorption/desorption currents of Fig. 5. The currents of Fig. 5 at the potentials between −0.2 and 0.1 V correspond to the adsorption and desorption of hydrogen on platinum, which are determined by the electrochemical active surface area of platinum. The coulomb for the hydrogen adsorption is 753.48 and 1,558.65 μC for Pt/C and Pt/$H_xMoO_3$-C, respectively, indicating that the electrochemical active platinum surface area of Pt/$H_xMoO_3$-C is two times that of Pt/C.

Electrocatalytic activity toward methanol oxidation

Figure 6 shows the cyclic voltammogram of $H_xMoO_3$-C electrode in 0.5 mol $L^{-1}$ $H_2SO_4$+0.5 mol $L^{-1}$ $CH_3OH$ solution. It can be found by comparing Fig. 6 with the curve a of Fig. 1 that the cyclic voltammogram of $H_xMoO_3$-C in the methanol-containing solution is similar to that in the methanol-free solution, indicating that $H_xMoO_3$ itself has no electrocatalytic activity toward methanol oxidation.

Different from the $H_xMoO_3$-C electrode, Pt/C and Pt/$H_xMoO_3$-C electrodes exhibit electrocatalytic activity
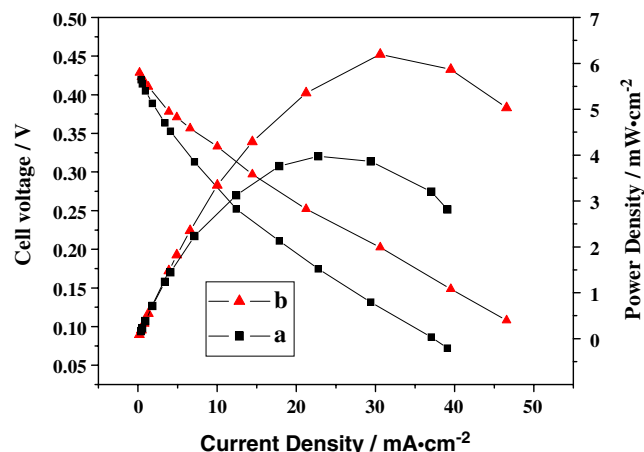


Fig. 9 Performances of DMFCs with Pt/C (a) and Pt/$H_xMoO_3$-C (b) as anode catalysts

toward the methanol oxidation, as shown in Fig. 7. It can be seen from Fig. 7 that the methanol oxidation current on Pt/H$_x$MoO$_3$-C electrode is larger than that on Pt/C, indicating that Pt/H$_x$MoO$_3$-C has better electrocatalytic activity toward methanol oxidation than Pt/C. It is certain that the better electrocatalytic activity of Pt/H$_x$MoO$_3$-C is related to its smaller particle size of platinum. Considering the ratio of oxidation peak currents for Pt/H$_x$MoO$_3$-C (4.95 mA) to Pt/C (1.97 mA) is 2.5, larger than the ratio of electrochemical active surface area of platinum (2.1), there should be a contribution of H$_x$MoO$_3$ to the improvement in electrocatalytic activity of platinum in Pt/H$_x$MoO$_3$-C. This contribution can be ascribed to the reduction of charge transfer resistance caused by the proton spillover effect between platinum and H$_x$MoO$_3$. The redox couple H$_x$MoO$_3$/H$_y$MoO$_3$ ($0 \leq y < x \leq 2$) is reversible. The hydrogen molybdenum bronze with high amount of hydrogen (H$_x$MoO$_3$) is easily oxidized on the platinum to form the hydrogen molybdenum bronzes with less hydrogen (H$_y$MoO$_3$). The latter plays a role as proton acceptors, which help the oxidation of adsorption intermediates CH$_z$O$_{ads}$($0 \leq z \leq 4$) on platinum. The electrocatalytic process can be formulated as [22]:

$$[H_xMoO_3]_{ads} \rightleftarrows [H_yMoO_3]_{ads} + (x-y)\,e^- + (x-y)\,H^+$$

$$0 \leq y < x \leq 2$$

$$Pt + CH_3OH \rightleftarrows Pt - [CH_zO]_{ads} + (4-z)e^- + (4-z)H^+$$

$$0 \leq z \leq 4$$

$$Pt - [CH_zO]_{ads} + n\,Pt - [H_yMoO_3]_{ads} + H_2O \rightleftarrows CO_2 + Pt$$
$$+ n\,Pt - [H_xMoO_3]_{ads}$$

$$n\,Pt - [H_xMoO_3]_{ads} \rightleftarrows n\,Pt - [H_yMoO_3]_{ads} + n(x-y)e^-$$
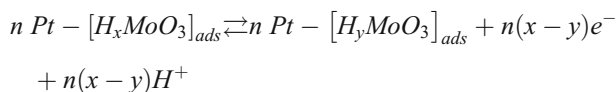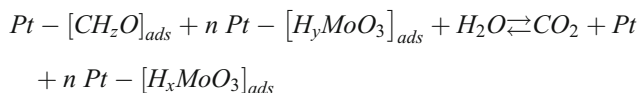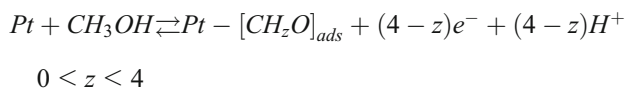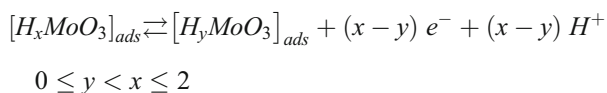$$+ n(x-y)H^+$$

Figure 8 presents the chronoamperometric curves of Pt/C and Pt/H$_x$MoO$_3$-C electrodes in 0.5 mol L$^{-1}$ H$_2$SO$_4$+ 0.5 mol L$^{-1}$ CH$_3$OH solution at 0.6 V. It can be seen from Fig. 8 that the current of methanol oxidation on Pt/H$_x$MoO$_3$-C is always larger than that on Pt/C. The current is 0.37 and 0.54 mA at 100 s, and 0.20 and 0.40 mA at 2,000 s, for Pt/C and Pt/H$_x$MoO$_3$-C, respectively, corresponding to a current decaying of 46% and 26% for Pt/C and Pt/H$_x$MoO$_3$-C, respectively. The higher current for the methanol oxidation indicates the higher electrocatalytic activity of Pt/H$_x$MoO$_3$-C, which is in agreement with the results obtained from cyclic voltammetry. The less current decaying suggests that

Pt/H$_x$MoO$_3$-C has better antipoisoning ability to intermediates of methanol oxidation than Pt/C. The current decaying is related to the decrease of methanol concentration as the experiment proceeds, but it results mainly from the poisoning of platinum from the intermediates of methanol oxidation, because the working electrode surface is small (about 7 mm$^2$).

Figure 9 presents the performance of the single DMFC using Pt/H$_x$MoO$_3$-C as the anode catalyst with a comparison of the single cell using Pt/C as the anode catalyst. It can be seen from Fig. 9 that, under the same current density, the cell using Pt/H$_x$MoO$_3$-C as the anode catalyst has less polarization and larger power output than the cell using Pt/C as the anode catalyst. This confirms the better electrocatalytic activity of Pt/H$_x$MoO$_3$-C toward methanol oxidation than Pt/C.

## Conclusions

Carbon can be modified with hydrogen molybdenum bronze and the modified carbon can be used as the support for platinum. On this support, platinum can be loaded uniformly and with small particle size. The platinum supported with hydrogen molybdenum bronze-modified carbon exhibits better electrocatalytic activity toward methanol oxidation than the platinum supported with carbon without modification. The improved electrocatalytic activity is ascribed not only to the smaller particle size but also to the proton spillover effect between platinum and hydrogen molybdenum bronze.

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