Short communication

Synthesis and characterization of $H_5PMo_{10}V_2O_{40}$ deposited Pt/C nanocatalysts for methanol electrooxidation

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A B S T R A C T

Pt/C(a) catalysts are firstly prepared by modified impregnation method. In order to enhance the ability of Pt/C catalysts for methanol electrooxidation, $H_5PMo_{10}V_2O_{40}$ (PMV) is adsorbed on Pt/C catalysts to obtain the PMV-Pt/C catalysts. The Pt/C(a) and PMV-Pt/C are characterized by transmission electron microscopy (TEM) and X-ray diffractometry. It is shown that Pt particles with small average size are uniformly disperesed on carbon. Cyclic voltammetry and chronoamperometry show that the PMV-Pt/C catalysts exhibit excellent catalytic activity and stability for methanol electrooxidation.

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1. Introduction

Direct methanol fuel cells (DMFCs) are commonly considered as candidates for future energy-generating devices due to its high specific energy at low operating temperature and ease of handling clean liquid fuel [1–3]. However, several factors inhibit the commercialization of DMFCs. The poor kinetics of methanol oxidation reactions on conventional anode catalyst materials is one of the major factors. Intense research has been performed on Pt-based multicomponent catalysts to improve the poison tolerance with the ultimate goal of creating cost-effective catalysts in practical fuel cell. It has been shown that metals including ruthenium, osmium, iridium, rhodium, tin, etc. can improve the catalytic activity of Pt either by bifunctional mechanism or by electronic effect. In the bifunctional mechanism, second compound such as ruthenium assists the oxidation of CO or CHO species by adsorption of oxygen-containing species close to the poisoned Pt sites [4,5]. In the electronic effect (or the ligand effect), the alloyed metal modifies the electronic structure of Pt, resulting in a lower bond strength of the adsorbed species on Pt [6–9].

Heteropolyacids (HPAs), because of their unique composition of heteropoly anions and countercations (H^+, H_3O^+, $H_5O_2^+$, etc.), have been utilized both as acids and oxidation catalysts for a number of industrial processes [10]. Izumi and Urabe stated that HPAs had a very strong affinity for active carbon. Even washed with hot water or hot methanol by a Soxhlet extractor, entrapped catalysts with a maximum HPA content of 7.2–13.9 wt.% were obtained [11]. HPAs with Keggin-type structure are particularly attractive because of their ability to adsorb irreversibly on carbon and metal surfaces [11]. Some research groups have explored this phenomenon to modified carbon materials and Pt nanoparticles for oxygen reduction [12–14] and methanol oxidation [15,16]. For example, Chen et al. modified CNT with molybdophosphoric acid ($H_3PMo_{12}O_{40}$) through chemisorption and found that catalysts supported on modified CNTs presented higher performance for methanol oxidation compared with catalysts supported on CNTs [12]. Dumesic et al. found that $H_3PMo_{12}O_{40}$ facilitated the electrooxidation of intermediate species such as CO and diminished the poison of catalysts [17]. Molybdovanadophosphoric acid ($H_{3+x}PMo_{12−x}V_xO_{40}$), obtained by substitution of Mo for V, has been found to possess unique catalytic properties, presumably a result of the redox properties of V and the acidic character of the molybdophosphoric acid [18–20]. Interestingly, it is reported that the employment of transition metals oxides (VO_x and MoO_x) can promote CO oxidation [21–24], and $H_5PMo_{10}V_2O_{40}$ contains these oxides.

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In this work, we prepared Pt/C catalysts by a simple and rapid route (denoted as modified impregnation method). In order to enhance the methanol oxidation ability of Pt/C catalysts, $H_5PMo_{10}V_2O_{40}$ was adsorbed on Pt/C catalysts. The activities of $H_5PMo_{10}V_2O_{40}$ deposited Pt/C catalysts were tested and discussed.

2. Experimental

2.1. Materials

The metal source was aqueous solution of H_2PtCl_6. Vulcan XC-72 carbon black was purchased from Cabot Corporation. $H_5PMo_{10}V_2O_{40}$ was prepared by the literature method [25]. Deionized water (18.23 MΩ) was produced by a Milli-Q ultrapure system from Millipore Ltd., USA.

2.2. Preparation of catalysts

2.2.1. The Pt/C(a)
The Pt/C(a) catalysts were prepared by modified impregnation method. First, H_2PtCl_6 was mixed with carbon black suspended in deionized water. The mixture was treated in an ultrasonic bath for 1 h and mechanically stirred for 2 h. When the pH of the mixture solution was adjusted to about 11 with 25% $NH_3 \cdot H_2O$ solution, $PtCl_6^{2-}$ was precipitated due to the formation of $(NH_4)_2PtCl_6$ and the precipitate was adsorbed on carbon black. With dropwise addition of $NaBH_4$ solution, $(NH_4)_2PtCl_6$ was reduced to Pt nanoparticles. After the suspension was filtered and washed, the Pt/C (20 wt.% Pt) catalysts were obtained.

2.2.2. PMV-Pt/C
The Pt/C(a) catalysts obtained was added into 20 mg mL^{-1} PMV solution and kept at room temperature (20 °C) for 24 h with constant shaking. Subsequently, the suspension was filtered and washed with deionized water until the washing solution became colorless and then dried at 80 °C for 6 h to obtain the PMV-Pt/C catalysts.

2.2.3. The Pt/C(b)
H_2PtCl_6 was mixed with carbon black suspended in deionized water. The mixture was treated in an ultrasonic bath for 1 h and mechanically stirred for 2 h. The pH value of the mixture was adjusted to 9 by adding a concentrated solution of Na_2CO_3. Afterward, the excessive $NaBH_4$ solution was added dropwise into the above mixture. After the suspension was filtered and washed, the Pt/C (20 wt.% Pt) catalysts were obtained.

2.3. Physicochemical characterization of catalysts

The size and morphology of PMV-Pt/C catalysts were characterized by TEM (JEOL JEM2010). X-ray diffraction spectra were measured with a Philips PW1700 diffractometer using Cu Kα (λ = 1.5405 Å) radiation source operating at 40 kV and 30 mA. The bulk compositions of the prepared catalysts were evaluated with energy dispersive X-ray analysis in a scanning electron microscope (JEOL JAX-840).

2.4. Electrochemical measurements

Electrochemical measurements were carried out with an EG&G mode 273 potentiostat/galvanostat and a conventional three-electrode test cell. The catalyst ink was prepared by ultrasonically dispersing the mixture of 5 mg catalysts, 1 mL ethanol, and 50 μL 5 wt.% Nafion solutions. 10 μL catalyst inks was pipetted and spread on the glassy carbon disk. The mg Pt cm^{-2} loading of test electrodes is 0.14 mg Pt cm^{-2}. A Pt foil and an Ag/AgCl were used as the counter and reference electrodes, respectively. All electrolyte solutions were deaerated by high-purity nitrogen for 15 min prior to any measurement. For chronoamperometry, the electrode potential was fixed at 0.6 V vs. Ag/AgCl. The special surface area of Pt in the catalysts was measured electrochemically by oxidation of pre-adsorbed CO (CO_{ad}) in the 0.5 M H_2SO_4 solution at a scan rate of 20 mV s^{-1}. CO was purged into the 0.5 M H_2SO_4 solution for 30 min to allow the complete adsorption of CO onto the catalyst when the working electrode was kept at 0 mV vs. Ag/AgCl electrode. Excess CO in the electrolyte was then purged out with N_2 for 10 min. The amount of CO_{ad} was evaluated by integration of the CO_{ad} stripping peak, corrected for the electric double-layer capacitance. The special surface area of Pt metal was estimated assuming a monolayer of linearly adsorbed CO and the coulombic charge necessary for oxidation as 420 μC cm^{-2} [26,27].

3. Results and discussion

3.1. TEM, XRD and EDX analyses

Fig. 1A and B shows TEM images for Pt/C(a) and PMV-Pt/C catalysts. It is shown that the Pt particles have a small average size and were uniformly dispersed on carbon supports. The average diameter for Pt particles is 2.6 nm for Pt/C(a) catalysts and 2.7 nm for PMV-Pt/C catalysts. Fig. 1C presents the TEM image of the Pt/C(b) catalyst. Comparing with the TEM image of the Pt/C(a) catalyst, the Pt particles in the Pt/C(b) catalyst shows a poor distribution and some Pt particles are severely aggregated. The average diameter for Pt particles is 4.2 nm. It is well known that Pt nanoparticles
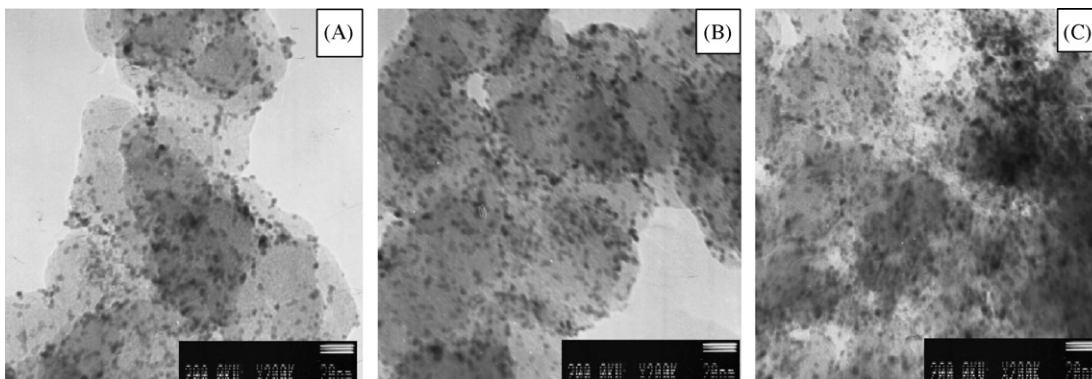

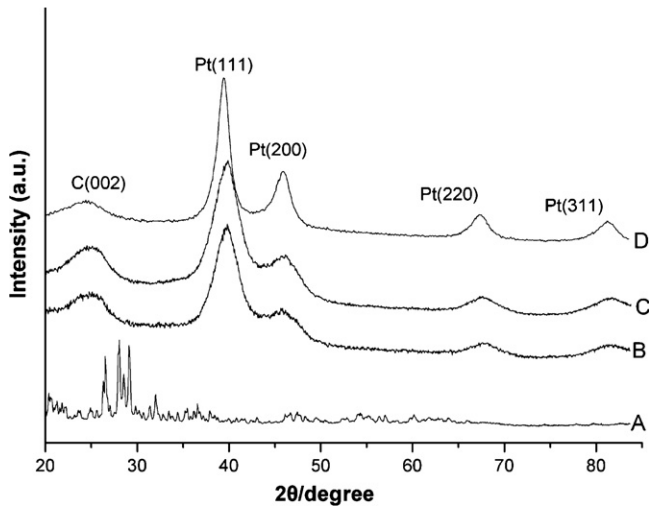**Fig. 1.** TEM picture of (A) Pt/C(a), (B) PMV-Pt/C, and (C) Pt/C(b) catalysts.

Fig. 2. XRD patterns of (A) PMV, (B) the PMV-Pt/C, (C) Pt/C(a) and (D) Pt/C(b).

Fig. 3. EDX spectra of PMV-Pt/C catalyst.

dispersed in solution are susceptible to aggregation. When the H_2PtCl_6 solution is mixed with carbon black, most of H_2PtCl_6 was in the solution, some H_2PtCl_6 is adsorbed onto the carbon black. Therefore, after H_2PtCl_6 in the solution is reduced, most of the Pt particles obtained are suspended in the solution. Thus, they are easily aggregated before they are dispersed onto the surface of the carbon black. This is the main reason why the large Pt particles are
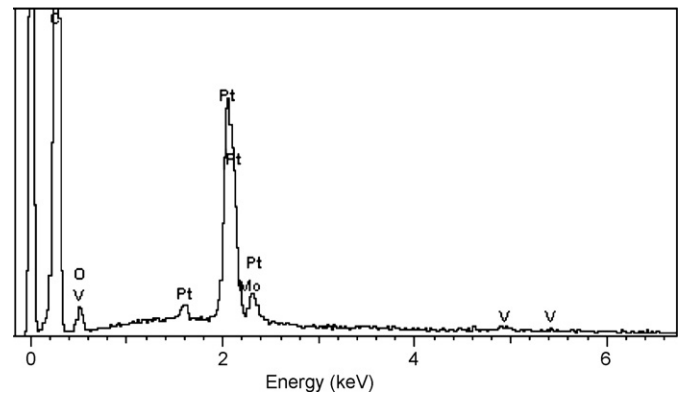
obtained with the conventional impregnation method. Whereas with the modified impregnation method, $PtCl_6^{2-}$ in the solution was firstly precipitated in the form of $(NH_4)_2PtCl_6$ and then the precipitates were adsorbed on carbon supports. After the precipitates were reduced, the resulted Pt nanoparticles were anchored to carbon supports and thus inhibited aggregating.

Typical XRD patterns of PMV, PMV-Pt/C, Pt/C(a) and Pt/C(b) are shown in Fig. 2. For PMV-Pt/C, Pt/C(a) and Pt/C(b) catalysts, the diffraction peaks at 2θ about 39°, 46°, 68°, and 81°, are due to the Pt (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes, respectively,
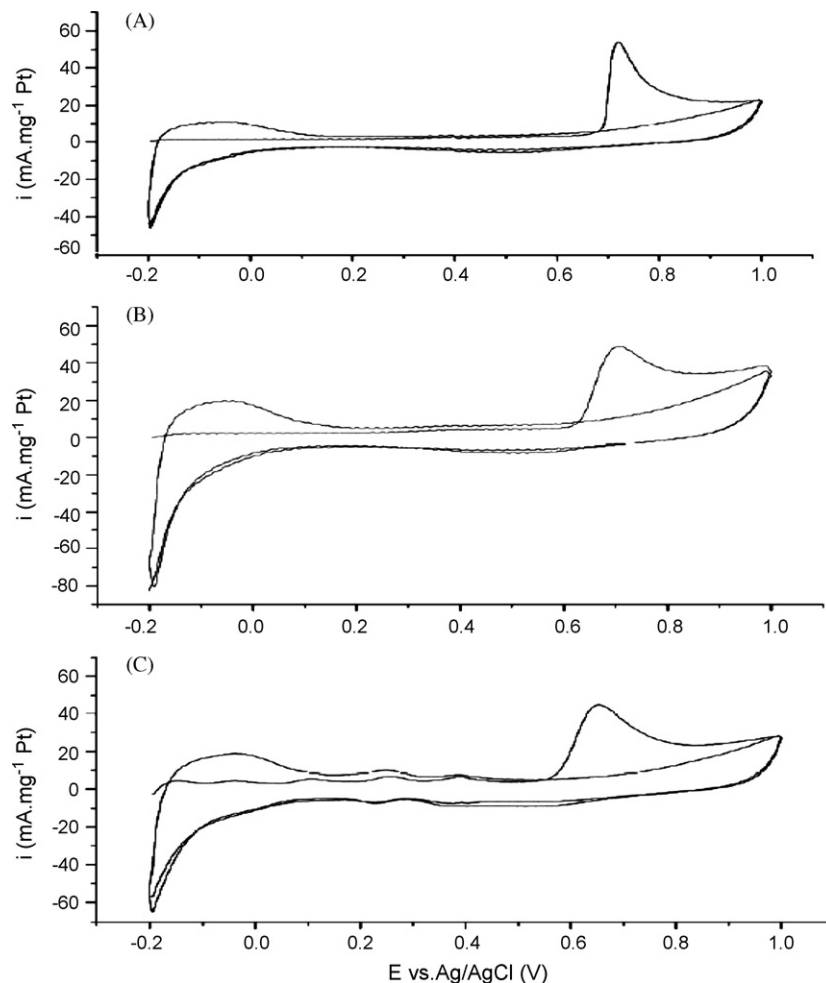

Fig. 4. CO_{ad} stripping voltammograms for Pt/C(b), Pt/C(a) and PMV-Pt/C catalysts at room temperature.
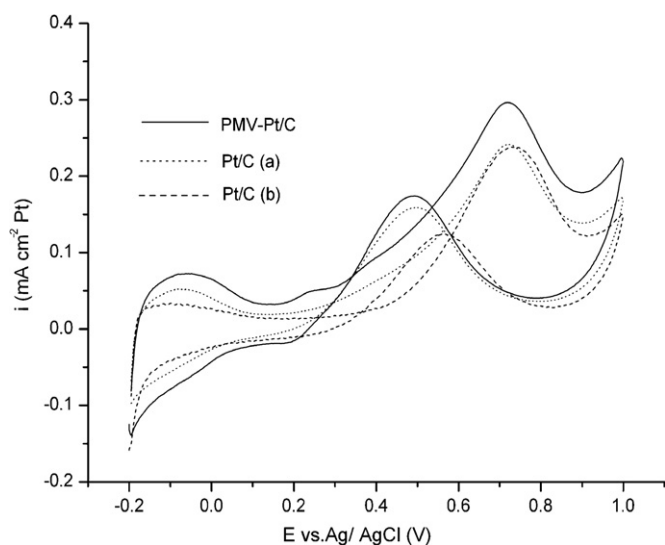
Fig. 5. Cyclic voltammograms recorded at $20\,mV\,s^{-1}$ in 1 M $CH_3OH + 0.5$ M H_2SO_4 solution at room temperature (the current density is current per Pt electroactive surface area).

Fig. 6. Polarization current vs. time plots measured at room temperature in 1 M $CH_3OH + 0.5$ M H_2SO_4 solution (the current density is current per Pt electroactive surface area).

which represents the typical character of a crystalline Pt face centered cubic (fcc) pattern. The diffraction peaks for PMV-Pt/C and Pt/C(a) are much broader than those for Pt/C(b), which indicates that the PMV-Pt/C and Pt/C(a) catalysts have smaller particle size. The diffraction peak at about $24°$ observed is attributed to the hexagonal graphite structure (0 0 2), which can reflect the graphite degree of the carbon material. For PMV-Pt/C catalysts, no other diffraction peaks are observed except for the diffraction peaks of Pt and carbon support. Thus, it can be concluded that PMV are adsorbed in a highly dispersed manner on the Pt/C catalysts with no agglomeration.

The composition of the bulk catalysts was determined by energy dispersive X-ray (EDX) analysis (Fig. 3). The Pt/Mo atomic ratio is estimated to be 2.96, corresponding to 6.3 wt.% of PMV in the PMV-Pt/C composite. The Mo/V atomic ratio is estimated to be 5.53. This value is slightly higher than the value expected for $H_5PMo_{10}V_2O_{40}$, and possibly due to the presence of a small quantity of $H_4PMo_{11}V_1O_{40}$.

3.2. Electrochemical analysis

The electrochemically active specific surface area of catalysts can reflect the intrinsic catalytic activity of the catalysts. Usually, it can be measured with the H_{ad} stripping or CO_{ad} stripping method. Here, the CO_{ad} stripping method was used. Fig. 4 shows the CO_{ad} stripping voltammograms for PMV-Pt/C, Pt/C(a) and Pt/C(b) catalysts. It can be found from Fig. 4 that the peak potential for the CO_{ad} oxidation at the PMV-Pt/C, Pt/C(a) and Pt/C(b) catalysts electrodes are 0.65, 0.69 and 0.71 V, respectively. The peak potential of the CO_{ad} oxidation on PMV-Pt/C catalyst is lower than that on Pt/C(a) and Pt/C(b) catalysts, indicating that PMV-Pt/C catalyst is more active for CO_{ad} oxidation than Pt/C(a) and Pt/C(b) catalysts. In addition, electrochemically active specific surface area (ECSA) of Pt for all the catalysts can be calculated by using the CO oxidation charge after subtracting the background current. They are 70.4, 77.1 and $58.6\,m^2\,g^{-1}$ for PMV-Pt/C, Pt/C(a) and Pt/C(b) catalysts, respectively.

The PMV-Pt/C catalyst was characterized at room temperature by cyclic voltammetry (CV) in electrolytes of 0.5 M H_2SO_4 and 1 M CH_3OH at a scan rate of $20\,mV\,s^{-1}$, which is shown in Fig. 5. The current density in Fig. 5 is current per Pt electroactive surface area.
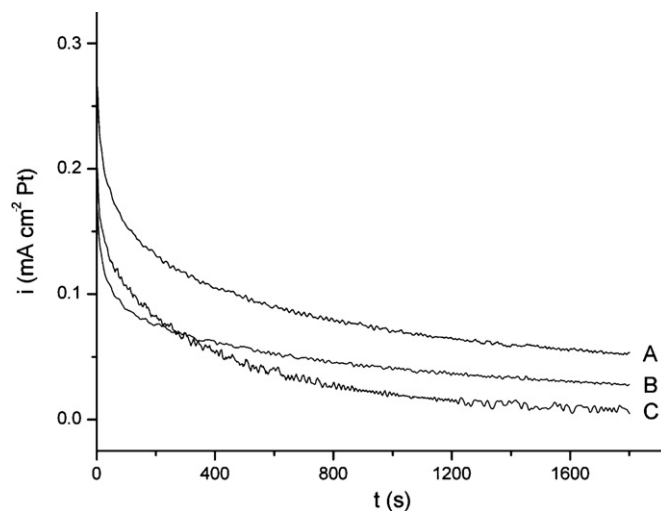
For comparison, the Pt/C(a) and Pt/C(b) catalysts were also studied under the same experimental conditions. It can be observed from Fig. 5 that there are similar peak potentials (at about 0.72 V vs. Ag/AgCl) for three kinds of catalysts, however, the oxidation peak for PMV-Pt/C catalysts is $0.296\,mA\,cm^{-2}$ Pt, which is much higher than the other samples (i.e. $0.242\,mA\,cm^{-2}$ Pt for Pt/C(a) and $0.235\,mA\,cm^{-2}$ Pt for Pt/C(b) catalysts). In other words, the PMV-Pt/C catalysts have a higher specific activity than the Pt/C(a) and Pt/C(b) catalysts.

Chronoamperometry (CA) curves for the three catalysts are shown in Fig. 6. The current density in Fig. 6 is current per Pt electroactive surface area. These curves reflect the activity and stability of the three catalysts to catalyze methanol oxidation. Obviously, the decay in the methanol oxidation current with time was different. The PMV-Pt/C catalyst shows the highest initial current density and limiting current density, which indicates the best catalytic activity and stability.

This significant improvement in the catalytic performance may be attributed to two aspects: firstly, the Pt particles supported on carbon prepared by our modified impregnation have uniform distribution and small average size; secondly, PMV deposited on Pt/C may facilitate the electrooxidation of intermediate species such as CO and diminish the poison of catalysts.

4. Conclusion

To summarize, Pt/C(a) catalysts are firstly prepared by modified impregnation method. Compared with the catalysts prepared using the conventional impregnation method, the catalysts prepared using modified impregnation methods have smaller average size and more uniform distribution. In order to enhance the ability of Pt/C(a) catalysts for methanol electrooxidation, $H_5PMo_{10}V_2O_{40}$ (PMV) is adsorbed on Pt/C catalysts to obtain the PMV-Pt/C catalysts. The resultant PMV-Pt/C catalysts exhibit excellent catalytic activity and stability for methanol electrooxidation. This significant improvement in the catalytic performance may be attributed to two aspects: firstly, the Pt particles supported on carbon prepared by our modified impregnation have uniform distribution and small average size; secondly, PMV deposited on Pt/C may facilitate the proton transfer during methanol oxidation and the electrooxidation of intermediate species such as CO.

Acknowledgements

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