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Phosphorictungstenic Acid-Pt/C Cathodic Catalyst in Direct Methanol Fuel Cell

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Abstract: *It was reported that the carbon supported Pt and phosphorictungstenic acid (PWA) (Pt-PWA/C) catalysts were prepared with mixing the carbon supported Pt (Pt/C) catalyst and PWA solution. It was found that because PWA covered on the Pt surface possesses the oxygen affinity and the ability for inhibiting the permeation of methanol the Pt-PWA/C catalyst can increase the electrocatalytic activity for the oxygen reduction reaction (ORR) and inhibit the electrooxidation of methanol comparing with the Pt/C catalyst. When the weight ratio of PWA and Pt/C in the PWA-Pt/C catalyst is 1, the composite catalyst showed the best performance. Comparing with the Pt/C catalyst, the reduction current of oxygen is increased by about 38% and the oxidation current of methanol is decreased by about 76% at the Pt-PWA/C electrode with the best weight ratio. Therefore, the Pt-PWA/C with the suitable weight ratio can be used as a cathodic catalyst in the direct methanol fuel cell (DMFC).*

Key words : Oxygen reduction reaction, Phosphorictungstenic acid, Pt, Direct methanol fuel cell

1. INTRODUCTION

DMFC has been demonstrated to be the most promising fuel cell for portable power devices due to the high energy density, convenient fuel management and low system complexity, etc. However, there are several problems that prevent DMFC from commercial applications. One of them is that the methanol crossover from anode through the solid polymer electrolyte to the cathode, leading the decrease in the fuel utilization, the induction of a mixed potential due to the electrocatalytic oxidation of methanol at the Pt cathode and even poisoning of the cathodic Pt catalyst [1-3]. In addition, similar to the proton exchange membrane fuel cell (PEMFC), ORR also proceeds at a very low kinetic rate in DMFC. The exchange current density of ORR at the Pt electrode is as low as 10^{-10} A/cm^2, whereas for the hydrogen oxidation reaction, it is as large as 10^{-4}A/cm^2 [4,5]. Therefore, obtaining a cathodic catalyst with high electrocatalytic activity for ORR and the excellent methanol tolerance is of key significance in the DMFC development.

Some non-noble metal catalysts, such as metalophthalocyanines, metaloporphyrines [6-11] and chalcogenides [12-16] are of the high methanol tolerance. However, the electrocatalytical activities of these catalysts for ORR are lower than that of Pt catalyst and not stable. Our group [17] found that the composite catalyst of metalophthalocyanine and Pt/C showed the high methanol tolerance ability with the good electrocatalytical activity for ORR. Recently, it was found that some Pt-based binary alloys, such as $Pt_{0.7}Ni_{0.3}$ exhibit high catalytic activity for ORR and good methanol tolerance ability [18]. Savadogo et al. [19, 20] reported firstly that the Pd-Co catalyst demonstrated an improvement of at least 250mV in the overpotential for ORR comparing with the Pt catalyst. Savadogo et al. [21-26] also invented the composite catalysts suitable for the use as the cathodic catalysts. A composite catalyst consists of at least one metal selected from Pd, Pt, Ru, Rh, Ir or Os and at least a compound selected from tungstic acid, molybdic acid, ammonium tungstate, ammonium molybdate, sodium tungstate and sodium

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molybdate. PWA as one member of the heteropolyacid family with the high proton conductivity and pseudo-liquid behavior has been mostly used in catalyzing many kinds of reactions and also been used in fuel cells as the catalysts, electrolytes and membranes [24,27-45]. For example, Pt-heteropolyacid catalysts, such as Pt-PWA catalysts were used as the cathodic catalysts for ORR in phosphoric acid fuel cell [24]. This kind of the catalyst was firstly fabricated by dispersing Pt from H_2PtCl_6 onto the carbon supporter and then, adding different quantities of PWA to the carbon-supported Pt catalyst. The performance of various 2%Pt-x%PWA catalysts for the ORR was investigated. These catalysts were prepared with mixing Pt/C catalyst with PWA was dissolved in Nafion solution. The purpose of this work is to evaluate performance of the Pt-PWA/C catalyst used as the cathodic catalyst in DMFC. It was found that Pt-PWA/C composite catalyst with the suitable weight ratio of PWA and Pt/C exhibits the high electrocatalytic activity for ORR and methanol tolerant ability.

2. EXPERIMENTAL

2.1 Catalyst preparation

3.2g Vulcan-XC 72 active carbon was mixed with 200 ml of the de-ionized water and iso-propanol with the volume ratio of 2:1 and stirred for one hour at 60~70^{o}C. Then, 155mL 12.6mM H_2PtCl_6 solution was added dropwise to the active carbon slurry and stirred for another hour. After the pH of the above solution was adjusted to 8-9 with the Na_2CO_3 solution, the $NaBH_4$ solution as the reducing agent was dropped into the solution with stirring for 6 hours. Then, the solution was filtered, washed with the de-ionized water until no Cl-can be detected in the filtrate. After the precipitate obtained was dried at 80^{o}C under vacuum overnight, the Pt/C catalyst with 20wt.% Pt was obtained. Finally, 5mg of the Pt/C catalyst was mixed with 0.4ml of 5wt.% Nafion solution and sonicated for 15 minutes and mixed with 1, 3, 5, 7 or 10mg PWA dissolved in the 0.4mL of 5wt.% Nafion solution. After the mixture was sonicated for 15 minutes, the slurry of the Pt-PWA/C catalysts was obtained and called as Pt-PWA-1/C, Pt-PWA-3/C, Pt-PWA-5/C, Pt-PWA-7/C and Pt-PWA-10/C catalyst, respectively.

2.2 Electrochemical measurements

All electrochemical measurements were performed using a Princeton Applied Research Model 273A potentiostat/Galvanostat and a conventional three-electrode electrochemical cell. Ag/AgCl electrode was used as the reference electrode and all potentials are quoted with respect to Ag/AgCl electrode. The auxiliary electrode is a platinum foil. The rotating disc electrode (RDE) with the glassy carbon disc (5 mm in diameter) was used as the substrate of the working electrode. Before use, RDE was polished successively with the slurry of 0.5 and 0.03μ m aluminia powders (Buchler Co.) to a mirror-finish and sonicated in the de-ionized water. Then, ca. 5μl of the catalyst slurry prepared above was transferred via a syringe onto the glassy carbon disc. After evaporating the solvent under air, the working electrode was ready to be used.

For the electrochemical measurements, 0.5M H_2SO_4 solution without or with 1M CH_3OH was used. The solutions were deaerated with bubbling the highly purified nitrogen or pure oxygen for 15mintues before the experiments according to the experimental requirements. The rotation speed of the working electrode was controlled in the range of 600-2500 rpm with an analytical rotator and ASR speed control system, EG & G Princeton Applied research model 636. All the experiments were carried out at the room temperature (~25^{o}C).

3. RESULTS AND DISCUSSION

Figure 1 shows the linear sweeping voltammograms of oxygen saturated in 0.5 M H_2SO_4 solution at the Pt/C catalyst electrode for the different rotating speeds. It can be observed from Figure 1 that the onset potential of ORR is approximately 0.7V. When the potential is scanned to the negative direction, the current increases until it reaches a limiting current. The result is similar to that reported in literature [11].

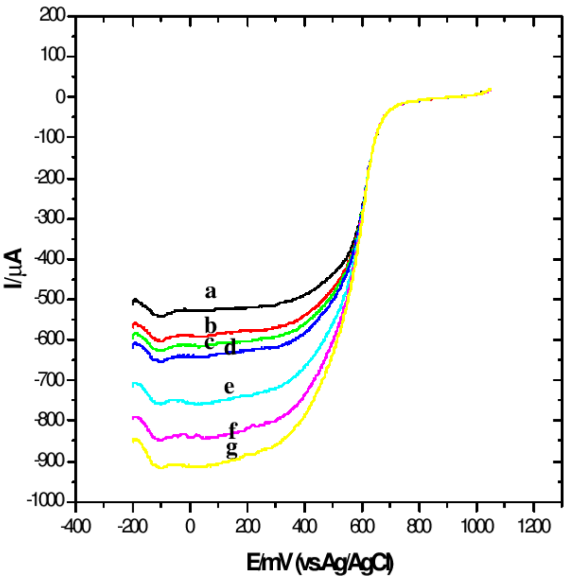

Figure 1: The linear sweeping voltammograms of oxygen saturated in the 0.5 M H_2SO_4 solution at the Pt/C electrode. Rotating speeds: (a) 600, (b) 800, (c) 900, (d) 1000, (e) 1500, (f) 2000 and (g) 2500 rpm.

Figure 2 shows the linear sweeping voltammograms of oxygen saturated in the 0.5 M H_2SO_4 solution at the Pt-PWA-1/C electrode for the different rotating speeds. Comparing with Figure

1, it can be found that the onset potential of ORR at the Pt-PWA-1/C electrode is almost the same as that at the Pt/C electrode.

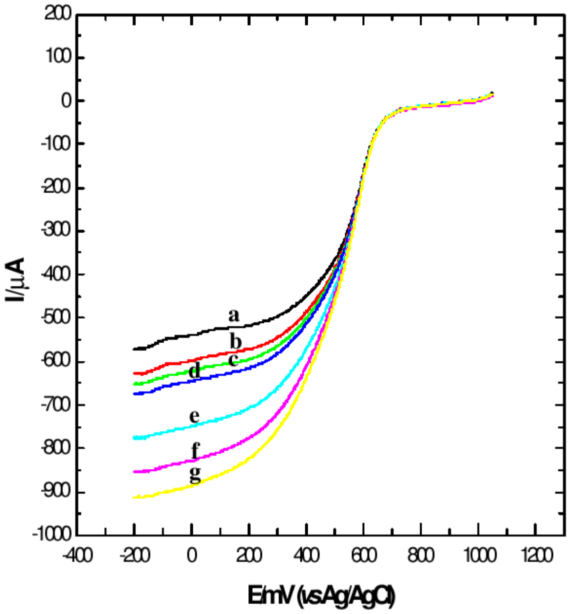

Figure 2: The linear sweeping voltammograms of oxygen saturated in the 0.5 M H_2SO_4 solution at the Pt-PWA-1/C electrode. Rotating speeds: (a) 600, (b) 800, (c) 900, (d) 1000, (e) 1500, (f) 2000 and (g) 2500 rpm.

The linear sweeping voltammograms of oxygen saturated in the 0.5 M H_2SO_4 solution at the Pt-PWA-3/C, Pt-PWA-5/C, Pt-PWA-7/C or Pt-PWA-10/C electrodes for the different rotating speeds are similar to those in Figure 2. The onset potential of ORR is almost the same as that in Figure 1 and 2, but the limiting currents are different at the different electrodes.

Figure 3 shows the linear sweeping voltammograms of oxygen saturated in 0.5 M H_2SO_4 solution at the Pt/C, Pt-PWA-1/C, Pt-PWA-3/C, Pt-PWA-5/C, Pt-PWA-7/C and Pt-PWA-10/C electrodes at the rotating speed of 1000rpm. It can be clearly observed from Figure 3 that the onset potentials of ORR at the different electrodes are almost the same. However, the limiting currents at the Pt-PWA-3/C and Pt-PWA-5/C electrodes are larger than that at the Pt/C electrode. In turns, the limiting current at the Pt/C electrode is larger than that at Pt-PWA-1/C, Pt-PWA-7/C and Pt-PWA-10/C electrodes. The limiting current at the Pt-PWA-5/C electrode is largest among all the electrodes. The limiting current at the Pt-PWA-5/C electrode is about 800mA at -0.2V, which is about 38% larger than that at the Pt/C electrode. It is illustrated that when the weight ratio of PWA and Pt/C is 1 in the experimental conditions, the best promotion effect of the Pt-PWA/C catalyst for ORR was obtained.

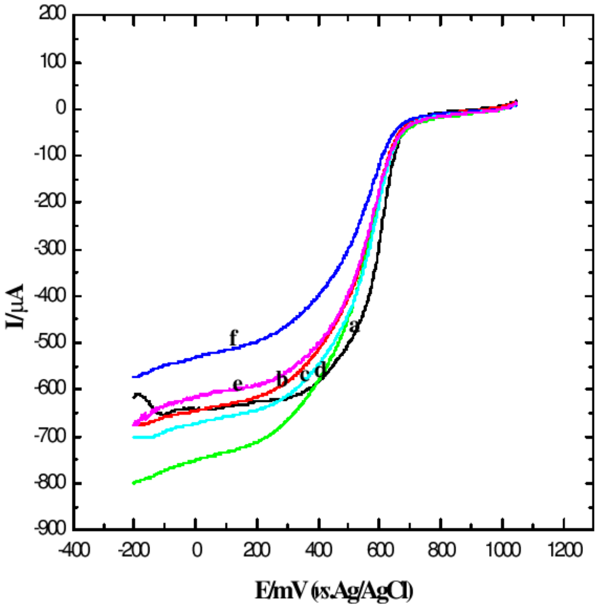

Figure 3: The linear sweeping voltammograms of oxygen saturated in the 0.5 M H_2SO_4 solution at the (a) Pt/C, (b) Pt-PWA-1/C, (c) Pt-PWA-3/C, (d) Pt-PWA-5, (e) Pt-PWA-7/C and (f) Pt-PWA-10 electrodes. The rotating speeds: 1000rpm.

It has been known that the relationship between the oxygen reduction current (I) at a thin catalyst layer on RDE and its rotation speed (ω) is given by Koutecky-Levich equation[46,47]:

$$1/I = 1/I_k + 1/B\omega^{1/2} \tag{1}$$

where I is the oxygen reduction current, Ik is the kinetic current, ω=2πf/60 (f in rpm), B is the Levich slope.

$$B = 0.62nFAcD^{2/3}\nu^{-1/6} \tag{2}$$

Where n is the number of electrons transferred per oxygen molecule, F is the Faraday constant (96486.7C mol^{-1}[48]), A is the apparent surface area of the electrode ($0.196cm^2$), c is the bulk concentration of oxygen dissolved in the solution (1.22×10^{-6} mol cm^{-3}[11]), D is the diffusion coefficient of oxygen in the solution (1.9×10^{-5} cm s^{-1}[49]), andν is the kinematic viscosity of the solution (0.987×10^{-2}cm s^{-1}[50]).

Figure 4 shows the Koutecky-Levich plots for the reduction of oxygen saturated in the 0.5 M H_2SO_4 solution at the different electrodes at -0.2V. The linearity of the plots in Figure 4 confirmed that the above equations are suitable to analysis the behavior of ORR at the catalysts and suggests that the values of ω used in this research are large enough to obtain the values of n independent of ω using equation(1) and (2)[51-53]. Therefore, the values of n calculated from the slopes of the Koutecky-Levich lines in Figure 4 using the above parameters can be obtained and are listed in Table 1. The n value at Pt/C electrode is in well accordance with that reported in the literatures [46, 47, 54-56]. It can be seen that at the Pt-PWA/C electrodes, the values of n do not change significantly, illustrating that the addition of PWA into the Pt/C catalyst does not alter the ORR pathway.

Table 1: The electron numbers involved in ORR per molecule

Catalyst	n
Pt/C	3.7
Pt-PWA-1/C	4.4
Pt-PWA-5/C	4.3
Pt-PWA-10/C	4.0

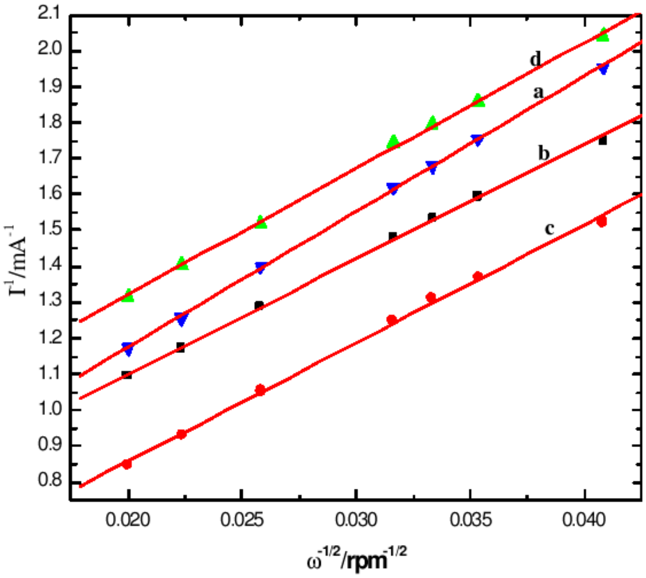

Figure 4: The Koutecky-Levich plots for the reduction of oxygen saturated in the 0.5 M H_2SO_4 solution at the (a) Pt/C, (b) Pt-PWA-1/C, (c) Pt-PWA-5/C and (d) Pt-PWA-10/C electrodes. The fixed potential: -0.2V.

Ik can be calculated from the intercepts of the Koutecky-Levich lines in Figure 4. The rate constant *K* for ORR can be obtained from Ik using Equation 3.

$$K = Ik/nFAC\Gamma \tag{3}$$

Where K is the rate constant ($M^{-1}\ S^{-1}$). Γ (mol cm^{-2}) is the quantity of the catalyst in the electrode, which participates in ORR. However, the real amount of the active catalyst could not been determined. Thus, only $K\Gamma$ can be calculated and the results are listed in Table 2. It can be observed from Table 2 that I_k and $K\Gamma$ at the Pt/C electrode are slightly larger than that at the Pt-PWA-1/C and Pt-PWA10/C electrodes, but much less than that at the Pt-PWA-5/C electrode.

Table 2: I_k and $K\Gamma$ calculated from the intercepts in Figure 4

Catalyst	Intercept	I_k	$K\Gamma$
	mA^{-1}	mA	$10^{-2}cm\ s^{-1}$
Pt/C	0.420	2.381	2.580
Pt-PWA-1/C	0.462	2.165	2.346
Pt-PWA-5/C	0.198	5.051	5.473
Pt-PWA-10/C	0.619	1.616	1.751

Figure 5 shows the cyclic voltammograms of the different electrodes in the 0.5M H_2SO_4 solution with 1M CH_3OH and saturated oxygen. Two strong peaks for the methanol oxidation in the positive and negative scan directions were observed at the Pt/C electrode (Figure 5, Curve a). However, the oxidation peaks of methanol at the Pt-PWA-1/C, Pt-PWA-5/C and Pt-PWA-10/C electrodes (Figure 5, Curve b, c and d) are much weaker than that at the Pt/C electrode. The peak current at the Pt-PWA-5/C electrode is about 76% less than that at the Pt/C electrode. Especially, the oxidation peaks of methanol at the Pt-PWA-10/C electrode almost disappear. It is illustrated that PWA can significantly inhibits the oxidation of methanol at the Pt/C electrode.

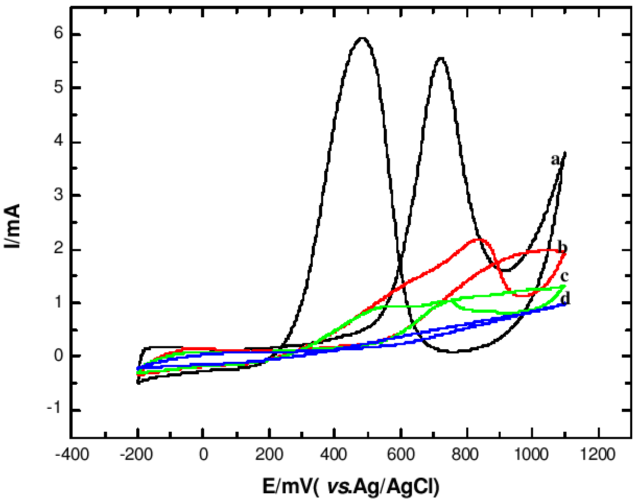

Figure 5: The cyclic voltammograms of the (a) Pt/C, (b) Pt-PWA-1/C, (c) Pt-PWA-5/C and (d) Pt-PWA-10/C electrodes in the 0.5M H_2SO_4 solution with 1M CH_3OH and saturated oxygen. Scan rate: 100mv/s.

The reason for that the Pt-PWA/C catalyst with the suitable weight ratio of PWA and Pt/C has the high electrocatalytical activity for ORR and methanol-tolerance is not very clear so far. The composite catalyst was prepared after the Pt/C catalyst mixed with PWA. Thus, the Pt surface is covered with PWA in some degree. PWA possesses the pseudo-liquid behavior, high oxygen affinity and high proton conductivity and keggin-type-structrue [57]. The high electrocatalytic ability of the Pt-PWA/C composite catalyst with the suitable weight ratio of PWA and Pt/C is attributed to the high oxygen affinity of PWA. However, when the weight ratio of PWA and Pt/C is low, the oxygen affinity of PWA is not enough to display. When the weight ratio is too high, the permeability rate of oxygen trough PWA layer is lowed. Therefore, only the composite catalysts with the suitable range of the weight ratio of PWA and Pt/C can show the high electrocatalytic activity for ORR. Furthermore, it is clearly seen from Figure 5 that the peak current of the methanol oxidation decreases with increasing the weight ration of PWA and Pt/C in the Pt-PWA/C catalysts. For example, at the Pt-PWA-10/C electrode, the methanol oxidation current almost disappears. It is may be due to that the Pt surface is covered with PWA in the Pt-PWA/C catalyst and methanol as the relatively large molecule is difficult to permeate through PWA to the Pt surface. Therefore, the Pt-PWA/C catalyst possesses methanol-tolerant ability.

4. CONCLUSION

From the above results, it can be concluded that the Pt-PWA/C catalyst with the suitable weight ratio of PWA and Pt/C can increase the electrocatalytic activity for ORR and inhibit the electrooxidatio n of methanol comparing with Pt/C catalyst because PWA covered on the Pt surface possesses the oxygen affinity and the ability for inhibiting the permeation of methanol. When the weight ratio of PWA and Pt/C in the PWA-Pt/C catalyst is 1, the composite catalyst showed the best performance.

5. ACKNOWLEDGMENTS

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