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The enhancement effect of phosphomolybdic acid ($H_3PMo_{12}O_{40}$) on Pd/C catalyst for the electroreduction of hydrogen peroxide

Limei Sun · Liang Xu · Yan Zhao · Yanli Wang

Abstract A Pd/C electrode modified by $H_3PMo_{12}O_{40}$ was prepared and its catalytic performance for H_2O_2 electroreduction in acidic medium was investigated by cyclic voltammograms. Pd nanoparticles supported on Vulcan XC-72 carbon were prepared by chemical reduction of $PdCl_2$ in aqueous solution using $NaBH_4$ as the reducing agent. X-ray diffraction analysis indicated that the particle size of Pd is around 9.7 nm. The modified electrode was prepared by cyclic voltammograms in H_2SO_4 solution containing $H_3PMo_{12}O_{40}$. The results showed that $H_3PMo_{12}O_{40}$ can efficiently enhance the electrocatalytic activity for H_2O_2 electroreduction on Pd/C. The effect of $H_3PMo_{12}O_{40}$ content on the electrocatalytic activity of the catalyst was also investigated by CV. The best results appeared at the concentration of $H_3PMo_{12}O_{40} = 0.5$ mmol L^{-1}.

Keywords Hydrogen peroxide · Electroreduction · Phosphomolybdic acid · Palladium · Fuel cell

1 Introduction

Fuel cells using hydrogen peroxide as oxidant, such as metal semi-fuel cells (MSFCs) and direct borohydride fuel cells (DBFCs), are one kind of novel electrochemical power source with high specific energy being developed for undersea applications. The catalytic electrochemical reduction rate of hydrogen peroxide is a major factor determining the performance of fuel cells. Therefore, the study on electrocatalysts for H_2O_2 reduction has brought public attention in recent years in the fuel cell community. Noble metals, such as Pd [1–3], Ir [3, 4], Ru [5], Ag [6, 7], and Au [8], have been investigated as electrocatalysts for hydrogen peroxide reduction in acidic or basic medium. Among these catalysts, Pd and Pd-based catalysts demonstrated the best performance for hydrogen peroxide reduction.

Heteropolyacids have been used for the activation of both electrooxidation and electroreduction reactions because of their special chemical properties [9]. The glassy carbon electrode modified by adsorption of $P_2Mo_{18}O_{62}^{6-}$ showed catalytic redox activity for H_2O_2 electroreduction and the activity can be greatly enhanced by coating the electrode with multiple layers of polyoxometalate [10]. Hamidi et al. [11] achieved multilayer films on the surface of a gold electrode by alternating deposition of 1:12 phosphomolybdic anion with water soluble polypyrrole. The chemically modified electrode (CME) exhibited an electrocatalytic response for the reduction of hydrogen peroxide. In this study, we prepared carbon-supported Pd catalyst modified by $H_3PMo_{12}O_{40}$ and examined its catalytic activity for hydrogen peroxide electroreduction in H_2SO_4 solution, and found that the modified electrode showed higher catalytic activity than Pd/C.

2 Experimental

2.1 Reagents

$PdCl_2$ was purchased from Shenyang Keda Chemical Engineering Co., Ltd. $H_3PMo_{12}O_{40}$, $NaBH_4$, H_2SO_4, and H_2O_2 (30%) were supplied by Tianjin Tianda Chemical Preparation Co., Ltd. Carbon black powder (Vulcan XC-72, Cabot International) with a specific surface area (BET)

L. Sun (✉) · L. Xu · Y. Zhao · Y. Wang
College of Chemistry and Chemical Engineering, Inner Mongolia University for the Nationalities, TongLiao 028000, People's Republic of China
e-mail: sunlimei2000@163.com

of 250 m^2 g^{-1} was used as the support for the catalysts. All chemicals are analytical grade and were used as-received without further purification. Ultrapure water (Millipore, 18 MΩ cm) was used throughout the study.

2.2 Catalyst preparation

Vulcan XC-72 carbon black (60 mg) was pretreated by dispersing in 65% HNO_3 solution and heating at 60 °C for 4 h. Appropriate amounts of $PdCl_2$ were dissolved in 10 mL ultrapure water, and the treated carbon was then dispersed into the above solution by sonication. Then 1 mol L^{-1} NaOH solution was added to adjust the pH to 7–8. The 10 mL $NaBH_4$ solution was added dropwise to the carbon suspension under vigorous stirring condition at room temperature. The mixture was stirred for another 4 h for the reaction to be completed. The solid particles were separated from the solution by filtration and washed with water thoroughly. The obtained catalysts were dried in a vacuum oven at 80 °C overnight. The sample contained a total metal loading of 20 wt%.

2.3 Catalyst characterizations

X-ray powder diffraction (XRD) patterns of the Pd/C catalysts were recorded with a Rigaku D/Max-3B diffractometer (Shimadzu) using Cu Kα radiation ($\lambda = 1.5406$ A°). The 2θ angle was scanned from 10° to 90°.

2.4 Electrochemical measurements

Electrochemical measurements were carried out in a standard three-electrode electrochemical cell with saturated calomel electrode (SCE) as the reference and glassy carbon rod behind a D-porosity glass frit as the counter electrode. The working electrode was prepared as follows: 5 mg of the catalyst was suspended in 1 mL ultrapure water by sonicating for about 30 min to obtain the catalyst ink, and 15 μL of the ink was spread on the surface of a glass carbon disk electrode ($d = 5$ mm, PARSTAT2273) with a micropipette and dried in atmosphere, named Pd/C. The electrode modified by $H_3PMo_{12}O_{40}$ was prepared by cyclic voltammetry (CV) that was conducted in 0.1 mol L^{-1} H_2SO_4 containing different concentration $H_3PMo_{12}O_{40}$ from 0.7 V to −0.5 V, named PMA-Pd/C. The electrochemical activity of the catalysts was also measured by CV in a 0.1 mol L^{-1} H_2SO_4 solution. Chronoamperometry (CP) was performed in 0.1 mol L^{-1} H_2SO_4 containing 0.5 mol L^{-1} H_2O_2. The electrolyte solution was deaerated by bubbling ultra-high-purity nitrogen for 20 min before each experiment. The potential scan rate for all tests is 50 mV s^{-1}, and the working temperature is room temperature. Electrochemical measurements were performed using a computer-controlled

potentiostat (EG&G, PAR2273). All potentials in this study were referred to the SCE.

3 Results and discussion

3.1 Catalyst characterizations

The XRD pattern of the Pd/C catalyst is shown in Fig. 1. The peak located at about 25.5° is associated with the carbon support. The Pd catalyst displayed the characteristic patterns of face-centered cubic (fcc) diffraction clearly. The average particle size of the catalyst is about 9.7 nm, which is calculated from broadening of the (220) diffraction peak using Scherrer's equation.

3.2 Electrochemical measurements

In order to optimize the content of $H_3PMo_{12}O_{40}$ in catalysts, a series of PMA-Pd/C catalysts with different $H_3PMo_{12}O_{40}$ concentration were measured in 0.1 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} H_2O_2 aqueous solution, as shown in Fig. 2. It can be seen that the highest current density are obtained when the $H_3PMo_{12}O_{40}$ concentration is 0.5 mmol
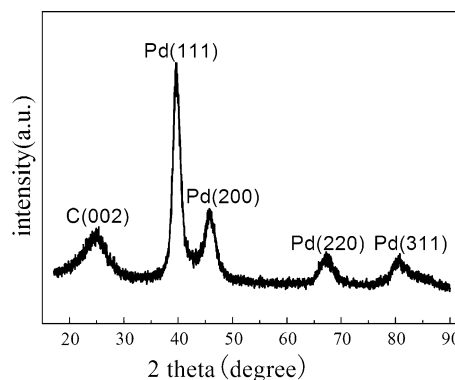

Fig. 1 XRD pattern of Pd/C catalyst

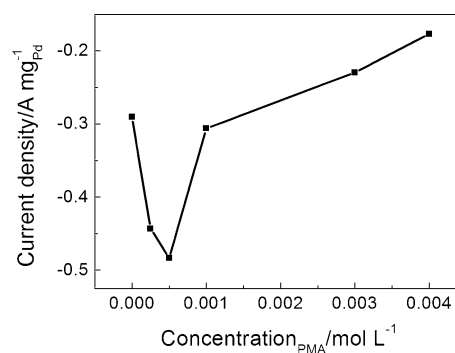**Fig. 2** The effect of the $H_3PMo_{12}O_{40}$ concentration on the peak current density (A mg^{-1} $_{Pd}$) in 0.1 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} H_2O_2, scan rate: 50 mV s^{-1}

L^{-1} in the electrolyte during the preparation and its current density is increased by 71.4% than Pd/C. The significantly highest peak current density indicates that this catalyst proportion has the best electrocatalytic activity for the hydrogen peroxide electroreduction. The following cyclic voltammograms and CP are compared and shown between the pure Pd/C catalyst and PMA-Pd/C catalyst prepared in 0.5 mmol L^{-1} $H_3PMo_{12}O_{40}$ + 0.1 mol L^{-1} H_2SO_4 solution.

Figure 3 shows cyclic voltammograms of the PMA-Pd/C and Pd/C catalysts in 0.1 mol L^{-1} H_2SO_4. It can be clearly seen that the Pd/C catalyst displayed the main characteristics of polycrystalline Pd in acid solution [12], two pairs of anodic and cathodic peaks observed in the potential region of −0.3 V ∼ 0 V were hydrogen adsorption and desorption. For the PMA-Pd/C catalyst, the hydrogen adsorption and desorption peaks shifted to lower potentials, indicating a weakened adsorption strength of hydrogen on the Pd surface, which may be attributed to the hydrogen spillover effect of MoOx [13]. Furthermore, the cyclic voltammograms for the PMA-Pd/C catalyst indicate that there is a pair of redox peaks between 0.2 and 0.35 V, as seen in the inset magnification. These peaks could be attributed to the intermediate oxidation states of Mo, between III and IV [14, 15]. The peak was not apparent, which may be due to the lower $H_3PMo_{12}O_{40}$ content.

Figure 4 shows Cyclic voltammograms of PMA-Pd/C and Pd/C catalysts in 0.1 mol L^{-1} H_2SO_4 containing 0.5 mol L^{-1} H_2O_2. It can be seen that PMA-Pd/C catalyst has the higher electrocatalytic current density and higher onset potential for the hydrogen peroxide electroreduction. The current density for H_2O_2 electroreduction on PMA-Pd/C catalyst are about 200 mA mg_{Pd}^{-1} higher than that on Pd/C within the whole potential range tested. This high activity of PMA-Pd/C catalyst demonstrated the promotion effect of $H_3PMo_{12}O_{40}$ to Pd for hydrogen peroxide electroreduction.

In order to further compare the electrocatalytic performance of PMA-Pd/C and Pd/C towards the hydrogen peroxide electroreduction, CP tests were conducted in 0.1 mol
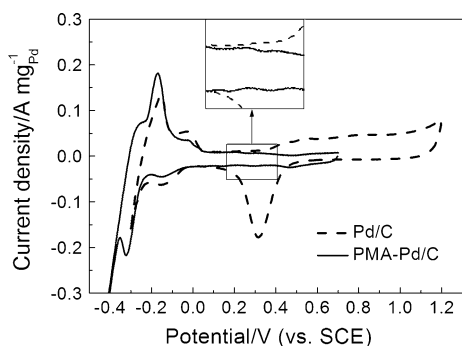

Fig. 4 Cyclic voltammograms of PMA-Pd/C and Pd/C catalysts in 0.1 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} H_2O_2, scan rate: 50 mV s^{-1}

Fig. 5 Chronoamperometry curves of PMA-Pd/C and Pd/C catalysts in 0.1 mol L^{-1} H_2SO_4 + 0.5 mol L^{-1} H_2O_2 at 0 V for 1800 s, scan rate: 50 mV s^{-1}

L^{-1} H_2SO_4 + 0.5 mol L^{-1} H_2O_2 at the constant potential of 0.0 V. The results are given in Fig. 5. Both current densities for H_2O_2 electroreduction on the two catalysts remained stable throughout. However, the current density after holding the potential at 0.0 V for 30 min were about 500 mA mg_{Pd}^{-1} for PMA-Pd/C and 270 mA mg_{Pd}^{-1} for Pd/C. Clearly, the former is more active than the latter for hydrogen peroxide electroreduction.

4 Conclusion

A Pd/C electrode modified by $H_3PMo_{12}O_{40}$ was prepared using the electrochemical method and its catalytic performance for H_2O_2 electroreduction in acidic medium was investigated by cyclic voltammograms. In the optimized measurements, the highest peak current density of PMA-Pd/C was obtained when the concentration of $H_3PMo_{12}O_{40}$ in the electrolyte during the preparation is 0.5 mmol L^{-1}. The results of CVs show that the PMA-Pd/C catalyst has better electrocatalytic activity and stability for H_2O_2 electroreduction than Pd/C. All the measurements described that the adding of $H_3PMo_{12}O_{40}$ can efficiently enhance the electrocatalytic activity of Pd/C catalyst in acidic medium.

Fig. 3 Cyclic voltammograms of PMA-Pd/C and Pd/C catalysts in 0.1 mol L^{-1} H_2SO_4 with a scan rate of 50 mV s^{-1}

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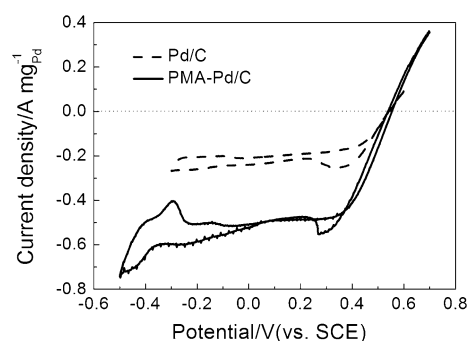1. Yang W, Yang S, Sun W et al (2006) Electrochim Acta 52:9
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