

Pt and Pd Supported on Carbon Microspheres for Alcohol Electrooxidation in Alkaline Media

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Pt and Pd supported on carbon microspheres (CMS) are used as electrocatalysts for alcohol (methanol, ethanol and ethylene glycol) electrooxidation in alkaline media. The results show that Pt and Pd supported on carbon microspheres give better performance for all alcohols electrooxidation than that supported on carbon black. The activity order of alcohol oxidation on Pt/C and Pt/CMS is ethylene glycol (EG) > methanol > ethanol. The EG shows the highest activity and ethanol shows the lowest activity. However, the activity order of alcohol oxidation on Pd/C and Pd/CMS is ethanol > EG > methanol and the ethanol gives the best performance. The results show that Pt is a good electrocatalyst for EG oxidation and Pd is a good electrocatalyst for ethanol oxidation. The increased magnitude order of alcohol oxidation on catalysts supported on carbon microspheres to catalysts supported on carbon black is ethanol > methanol > EG. The results show that carbon microspheres are good support for ethanol oxidation and not good support for EG oxidation.

Keywords: Fuel cells; Carbon microspheres; Palladium; Alcohol electrooxidation

1. INTRODUCTION

Direct methanol fuel cells (DMFCs) are recognized to be promising power source for portable electronic devices and electric vehicles [1,2]. However, it is well known that methanol is volatile and relatively toxic. Therefore, other alcohols are being considered as alternative fuels. Ethanol is less toxic compared to methanol, and can be easily produced in great quantity by fermentation of sugar-containing raw material. Thus, direct ethanol fuel cells (DEFCs) have attracted more and more attention [3,4]. Polyhydric alcohols such as ethylene glycol (EG) have high boiling points and are much less volatile. They have higher theoretical energy density than that of methanol and can be electrochemically oxidized [5,6]. The application of EG electrooxidation on direct alcohol fuel cells (DAFCs) has attracted increased interests [7,8]. The fuel cells based on EG fuel show certain advantages such as low fuel cross-over and high power density [9,10].

Pt-based catalysts are recognized as the best electrocatalysts for low temperature fuel cells [11]. However, the limitation of the usage of Pt-based catalysts comes from high cost and limited Pt resources. One effective approach to the cost reduction is to reduce the usage of the Pt catalysts or to replace the Pt catalysts [12]. Our previous work has focused on Pd electrocatalysts in alkaline media [13-15]. The usage of Pd is interesting as it is at least fifty times abundant on the earth than Pt. The electrochemical oxidation of methanol and ethanol on Pd electrocatalysts has been extensively investigated in our previous works, however there is little information on EG oxidation on Pd electrocatalysts in alkaline media. Here we report a complete study of Pt and Pd supported on carbon microspheres for the direct electrochemical oxidation of methanol, ethanol and EG in alkaline media.

The effect of the supporting material on the activity of electrocatalysts for alcohol oxidation is of continued interest. It is well known that carbon materials such as carbon nanotubes, carbon nanocoils, carbon nanofibers, hollow graphitic nanoparticles and ordered nanoporous carbon have been used as catalyst support for DAFCs [16-19]. The carbon spheres have been used as support for Pt for methanol electrooxidation in acid media [20-22]. In this paper, carbon microspheres were prepared with a simple method from sucrose by a hydrothermal method and used as support for Pt and Pd for alcohol electrooxidation in alkaline media.

2. EXPERIMENTAL PART

Carbon microspheres were prepared from sucrose by a hydrothermal method [13]. In a typical procedure, sucrose (6 g) was dissolved in water (40 ml), which was placed in a sealed 50 ml stainless-steel autoclave. The autoclave was then put into an electronic furnace. The temperature of the furnace was increased to 600°C from ambient temperature at a rate of 10°C min⁻¹ and maintained at 600°C for 10 hours. It was cooled down to room temperature. The resulted product in the autoclave was dried under vacuum at 60°C.

Pt and Pd supported on carbon black (VulcanXC-72, Cabot) and carbon microspheres was synthesized at room temperature by chemical reduction using NaBH₄. Excess 0.01 M NaBH₄ solution was mixed with the 0.1 M H₂PtCl₄ or PdCl₂ solution with HCl solution containing carbon black or carbon microspheres under stirring. The resulted material was washed with deionized water and dried at 40°C in vacuum. The working electrode was fabricated by casting PTFE (polytetrafluoroethylene) impregnated catalyst ink onto a 0.50 cm² carbon rod electrode. The PTFE, Pt and Pd loading on electrode was 0.10 mg cm⁻². The Pt and Pd percentage loading was controlled as 27 wt% in electrocatalysts.

Electrochemical experiments were performed on a CHI 680b electrochemical workstation (CH Instrument, Inc.). A standard three-electrode cell was used and controlled at 25°C using a water bath during the experiment. A platinum foil (3.0 cm²) and Hg/HgO (1.0 M KOH) were used as counter and reference electrode, respectively. X-ray diffraction (XRD) was carried out on a D/MAX2200 diffractometer employing Cu K α radiation ($k = 0.15418$ nm). Scanning electron microscopic (SEM) analysis was performed with a Philips XL-30 and transmission electron microscopy (TEM) was performed with a Philips CM-300 high resolution system operating at 20 keV.

3. RESULTS AND DISCUSSION

Fig.1a shows the typical SEM micrograph of platinum particles immobilized on carbon microspheres (Pt/CMS). Fig.1b shows the typical TEM micrograph of palladium particles immobilized on carbon microspheres (Pd/CMS). It can be observed that the diameter of carbon microspheres is about 1500-2000 nm. Platinum and palladium particles are immobilized in a well-dispersed way on the outer surface of those carbon microspheres. The Pt and Pd nanoparticles supported on carbon black and carbon microspheres exhibit an XRD pattern of a typical face-centered-cubic (fcc) lattice structure as shown in Fig.2. The Pt(111) and Pd(111) peaks were used to calculate the particle size of Pt and Pd according to the Scherrer's equation. The average Pt nanoparticle sizes in Pt/C and Pt/CMS electrocatalysts are 10.1 nm and 8.3 nm. The average Pd nanoparticle sizes in Pd/C and Pd/CMS electrocatalysts are 10.4 nm and 7.6 nm. The results indicate that Pt and Pd particles are better dispersed on carbon microspheres than that on carbon black.

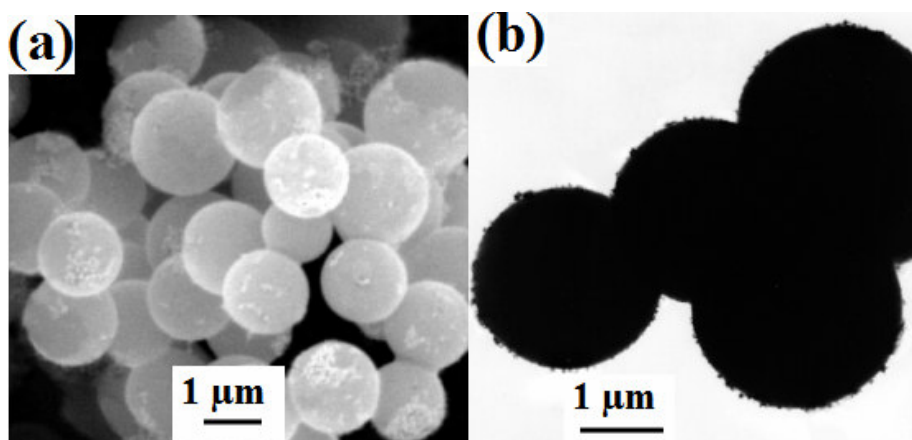


Figure 1. (a) SEM of platinum particles immobilized on carbon microspheres (Pt/CMS); (b) TEM of palladium particles immobilized on carbon microspheres

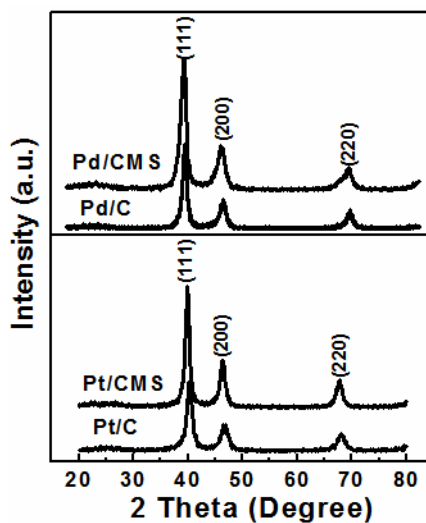


Figure 2. XRD pattern of Pt/C, Pt/CMS, Pd/C and Pd/CMS catalysts

Fig.3 shows the cyclic voltammograms of alcohol oxidation in 1.0 M alcohol + 1.0 M KOH on Pt/C, Pt/CMS, Pd/C and Pd/CMS electrodes. The cyclic voltammetry was carried out at a scan rate of 5 mV s^{-1} in the potential range from -0.8 to 0.3 V. By comparing with the cyclic voltammograms in the absence of alcohol, an alcohol oxidation peak can be clearly observed in the cyclic voltammograms on all electrocatalysts in the presence of 1.0 M alcohol. The electrooxidation of alcohols was characterized by two well-defined current peaks on the forward and reverse scans. In the forward scan, the oxidation peak is corresponding to the oxidation freshly chemisorbed species coming from alcohol adsorption. The reverse scan peak is primarily associated with removal of carbonaceous species not completely oxidized in the forward scan than the oxidation of freshly chemisorbed species [23,24]. The magnitude of the peak current on the forward scan indicates the electrocatalytic activity for the oxidation reaction of the alcohols. The electrochemical performances of the oxidation reaction for all alcohols on all electrodes were given in Table 1 and Table 2. The electrocatalytic activity for alcohol oxidation on catalysts supported on carbon microspheres is higher than that supported on carbon black.

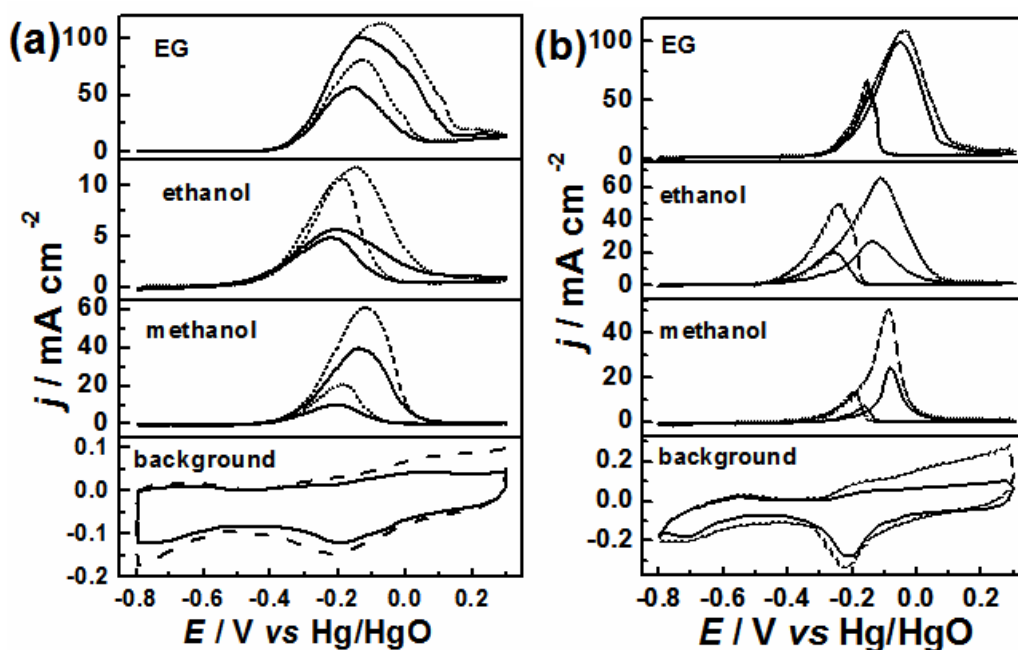


Figure 3. Cyclic voltammograms for alcohol electrooxidation on (a) Pt/C (the solid line), Pt/CMS (the dotted line) and (b) Pd/C (the solid line), Pd/CMS (the dotted line) electrodes in 1.0 M alcohol +1.0 M KOH with a platinum and palladium loading of 0.10 mg cm^{-2} and a scan rate of 5 mV s^{-1}

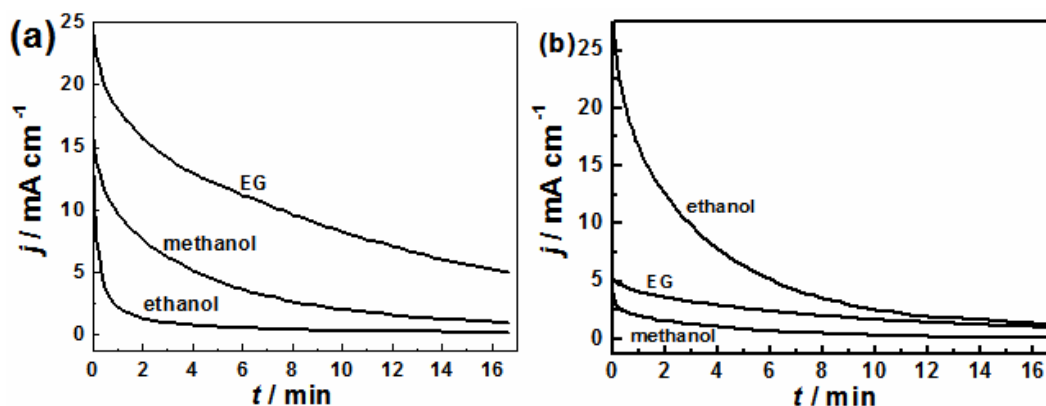
From the Fig.3a and Table1 we can find that the activity order of alcohol oxidation on Pt/C and Pt/CMS is EG > methanol > ethanol. The EG shows the highest activity and ethanol shows the lowest activity. The results is same as the literature [25,26].The stability of Pt/CMS electrocatalysts for alcohol oxidation has been investigated with current–time curves in 1.0 M alcohol + 1.0 M KOH and the results are shown in Fig. 4a. In this experiment, a potential step from -0.6 V to -0.3 V. The results show that the stability order is EG > methanol > ethanol. The results show that Pt is a good electrocatalyst for EG oxidation but not good electrocatalyst for ethanol oxidation.

Table 1. Comparison of electrochemical performance of alcohol oxidation on Pt/C and Pt/CMS electrodes with a platinum and palladium loading of 0.10 mg cm^{-2} and a scan rate of 5 mV s^{-1}

Alcohol	E_s / V		E_p / V		$j_p / \text{mA cm}^{-2}$		$j \text{ at } -0.3 \text{ V} / \text{mA cm}^{-2}$	
	Pt/C	Pt/CMS	Pt/C	Pt/CMS	Pt/C	Pt/CMS	Pt/C	Pt/CMS
methanol	-0.52	-0.51	-0.13	-0.12	39	61	9.4	11.4
ethanol	-0.51	-0.51	-0.18	-0.18	6	12	4.0	6.8
EG	-0.43	-0.43	-0.14	-0.07	101	113	22.8	22.8

Table 2. Comparison of electrochemical performance of alcohol oxidation on Pd/C and Pd/CMS electrodes with a platinum and palladium loading of 0.10 mg cm^{-2} and a scan rate of 5 mV s^{-1}

Alcohol	E_s / V		E_p / V		$j_p / \text{mA cm}^{-2}$		$j \text{ at } -0.3 \text{ V} / \text{mA cm}^{-2}$	
	Pd/C	Pd/CMS	Pd/C	Pd/CMS	Pd/C	Pd/CMS	Pd/C	Pd/CMS
methanol	-0.38	-0.49	-0.08	-0.09	25	50	0.2	2.5
ethanol	-0.52	-0.58	-0.14	-0.14	27	65	5.6	17.0
EG	-0.32	-0.35	-0.05	-0.04	100	110	2.6	3.6

**Figure 4.** Current-time curves for alcohol oxidation at -0.3 V on (a) Pt/CMS and (b) Pd/CMS electrodes in 1.0 M alcohol + 1.0 M KOH solution with a platinum and palladium loading of 0.10 mg cm^{-2}

The alcohol oxidation on Pd has attracted more and more attention because Pd gives better performance than Pt for ethanol oxidation in alkaline media [13,14]. Here, we can find that the activity order of alcohol oxidation on Pd/C and Pd/CMS is ethanol > EG > methanol from Fig.3b and Table2. The ethanol oxidation gives the best performance. It is different from alcohol oxidation on Pt/C and Pt/CMS. The stability of Pd/CMS electrocatalysts for alcohol oxidation has been investigated with current–time curves in 1.0 M alcohol + 1.0 M KOH and the results are shown in Fig. 4b. The results show that the stability order is ethanol > EG > methanol. The results show that Pd is a good electrocatalyst for ethanol oxidation which has a very bad performance on Pt.

The increased magnitude of alcohol oxidation on catalysts supported on carbon microspheres to carbon black is different from different alcohol oxidation. Hence, the ratio value of the peak current density on catalysts supported on carbon microspheres (j_{CMS}) to carbon black (j_C) can be used to describe the increased magnitude of alcohol oxidation. A high ratio value of j_{CMS} / j_C indicates that the alcohol oxidation on catalysts supported on carbon microspheres has higher increased magnitude to that on carbon black. The order for ratio value of j_{CMS} / j_C on Pt/C and Pt/CMS is ethanol (2.0) > methanol (1.6) > EG (1.1). The order for ratio value of j_{CMS} / j_C on Pd/C and Pd/CMS is ethanol (2.4) > methanol (2.0) > EG (1.1). The increased magnitude is highest for ethanol oxidation and lowest for EG oxidation. Larger three-phase interface formed on Pt/CMS and Pd/CMS due to formation of porous structure by carbon microspheres. The micrometer sized carbon microspheres act as structure units to form pores and channels that significantly reduced liquid sealing effect [22,27]. It makes liquid fuel diffuse into the inside and gaseous product (CO_2) evolve out of the catalyst layer much easier. The increased magnitude is low, which may be due to the low diffusion ability. The results show that carbon microspheres are good support for ethanol oxidation and not good support for EG oxidation.

4. CONCLUSIONS

This study investigated the applying carbon microspheres as support for Pt and Pd used as electrocatalysts for direct electrochemical oxidation of methanol, ethanol and EG in alkaline media. The results show that platinum and palladium particles are immobilized in a well-dispersed way on the outer surface of those carbon microspheres and better dispersed on carbon microspheres than that on carbon black. The electrocatalytic activity for alcohol oxidation on catalysts supported on carbon microspheres is higher than that supported on carbon black. The activity and stability order of alcohol oxidation on Pt/C and Pt/CMS is EG > methanol > ethanol. The results show that Pt is a good electrocatalyst for EG oxidation but not good electrocatalyst for ethanol oxidation. The activity and stability order of alcohol oxidation on Pd/C and Pd/CMS is ethanol > EG > methanol. The results show that Pd is a good electrocatalyst for ethanol oxidation.

The increased magnitude supported on carbon microspheres to carbon black is highest for ethanol oxidation and the lowest for EG oxidation. The results show that carbon microspheres are good support for ethanol oxidation but not good support for EG oxidation. The results show that carbon microspheres is a good support for ethanol oxidation and not good support for EG oxidation.

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