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Electrocatalytic activity of carbon supported Pt–Mn–Rh tri-metallic nanoparticles for ethanol oxidation

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ABSTRACT: *Carbon supported Pt, Pt-Mn-Rh (1:1:1)and Pt-Mn-Rh (1:3:1) electrocatalysts were synthesized by impregnation method using $NaBH_4$ as a reducing agent, and their effects on electrocatalytic activity for ethanol oxidation were investigated using cyclic voltammetry. In comparison to Pt, Pt-Mn-Rh (1:1:1) and Pt-Mn-Rh (1:3:1) nanoparticles demonstrate better catalytic characteristics for ethanol oxidation, such as forward peak current density, resistance to carbon monoxide poisoning and peak potential for oxidation. This work indicates that Pt-trimetallic nanoparticles could be desirable catalyst candidates for direct ethanol fuel cells.*

KEYWORDS: *Fuel cell, Ethanol, Cyclic voltammetry*

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I. INTRODUCTION

In recent years, developing non-toxic and renewable energy technologies have been receiving increased attention due to the seriousness of environmental pollution and the depletion of fossil fuels. Direct ethanol fuel cells (DEFCs) are the most promising alternatives to conventional power sources due to their high energy density(8.0 kW h kg-1), low toxicity, low operating temperature, ease of handling liquid fuel and natural availability from biomass [1-3].

However, the slow kinetics of ethanol oxidation reaction (EOR) and the poor selectivity of ethanol complete oxidation to CO_2 diminish the overall performance of DEFC, and hamper its commercialization [4,5]. Carbon-supported Pt catalyst is commonly used as anode catalyst in low temperature fuel cells; however, pure platinum itself is known to be rapidly poisoned on its surface by strongly adsorbed species coming from the dissociative adsorption process of ethanol, especially by absorbed CO [6-10].

One strategy that could be employed to enhance catalytic activity and reduce the demand of Pt-based catalysts is to explore the use of novel carbon materials to effectively disperse catalyst particles, such as carbon nanotubes and graphene [11-13]. Another possibility is to develop Pt-based bimetallic or multi-metallic catalysts to resist carbon monoxide poisoning and to reduce the catalyst price, such as Pt–Sn [14], Pt–Ru [15], and Pt–Sn–Rh [16]. In this study, we investigated electrocatalytic activity of Pt and Pt-trimetallic (Pt–Mn–Rh) nanoparticles for ethanol oxidation.

II. EXPERIMENTAL

Materials.

All materials are purchased from the indicated suppliers and used without any further pretreatment（purification）: Hexachloroplatinicacid（$H_2PtCl_6\cdot 6H_2O$，Alfa Aesar, 98%), manganese(II) chloride tetrahydrate（$MnCl_2\cdot 4H_2O$， Aladdin,99%), rhodium chloride ($RhCl_3$, MERCK), ethylene glycol (EG, Aladdin, 98%), Sodium borohydride ($NaBH_4$，Aladdin,99%)，sodiumhydroxide (NaOH, Sinopharm Chemical Reagent Co. Ltd., 97%) and carbon black (Vulcan XC-72R，Cabot Corp.). 5wt.% Nafion solution was purchased from Dupont. All the solutions were prepared with ultrapure water (Millipore, 18.2 MΩ cm^{-1}).

Preparation of catalysts.

The carbon-supported Pt/C, $Pt_1Mn_1Rh_1/C$ and $Pt_1Mn_3Rh_1/C$ (molar ratio) eletrocatalysts were prepared by the impregnation method using $NaBH_4$. The total metal loading of catalyst was controlled at 20 wt.% for all the catalysts. The carbon black was ultrasonically dispersed in 30 mL of ultrapure water for 30 min. The calculated amounts of $H_2PtCl_6·6H_2O$, $MnCl_2·4H_2O$ and $RhCl_3$ precursors were added into the ink with further 30 min of ultrasonication. The suspension was stirred for 1 h and then was added 1mol L^{-1} NaOH solution to adjust the pH to 8. The temperature of suspension was raised to 80℃ and then 20mL of 0.1mol L^{-1} solution of $NaBH_4$ was added drop-wise into the ink under argon (Ar) atmosphere, and the bath was stirred for 1 h. The suspension was cooled, filtered and washed with ultrapure water thoroughly, and finally dried in a vacuum oven at 80℃ for 6h.

Electrochemical measurements.

The electrochemical measurements were performed in a conventional three-electrode cell by using CHI760E electrochemical workstation controlled at 25°C. A piece of Pt foil(1㎠) was used as counter electrode. In this work, all the potentials were versus the Hg/Hg_2SO_4 reference electrode (-0.70 V relative to the reversible hydrogen electrode, RHE).The activation of the electrocatalyst was carried out in 0.1 M $HClO_4$ supporting electrolyte and the ethanol oxidation reaction (EOR) was investigated in 0.1 M $HClO_4$+ 0.1 M EtOH. The glassy carbon electrode with 4mm of diameter was used as a working electrode. Working electrode was prepared as follows: the ink was prepared by ultrasonically dispersion a mixture including of 5.0 mg of electrocatalyst, 2.0 mL compound of ethanol and water (V/V=1:1) for 30min. Next, 7.5μL of this ink was transferred onto a polished glassy carbon disk, and onto which 10mL of a 5 wt.% Nafion® solution in order to form a homogeneous thin catalyst layer (39.8 $\mu g_{metal} cm^{-2}$). Cyclic voltammograms (CVs) were recorded within a potential range of -0.65~0.5 V at 50 mV s^{-1}.For the sake of comparison, the electrochemical results expressed hereafter are normalized by the Pt mass at the working electrode.

III. RESULTS AND DISCUSSION

The cyclic voltammograms in $HClO_4$ solution for the Pt/C and Pt-Mn-Rh/C electrocatalysts are shown in Fig.1, in which H_2 adsorption/desorption peaks, an electrochemical double-layer region, and peaks for the formation and reduction of Pt oxide can be observed [17]. Compared with the CV curves, the peaks corresponding to hydrogen adsorption/desorption of Pt-Mn-Rh/C (1:1:1) and (1:3:1) become clearly higher than that of Pt/C. The increase in peak area (or peak heights) of the catalysts with high Mn content on the surface has to be ascribed to MnO_x dissolution.

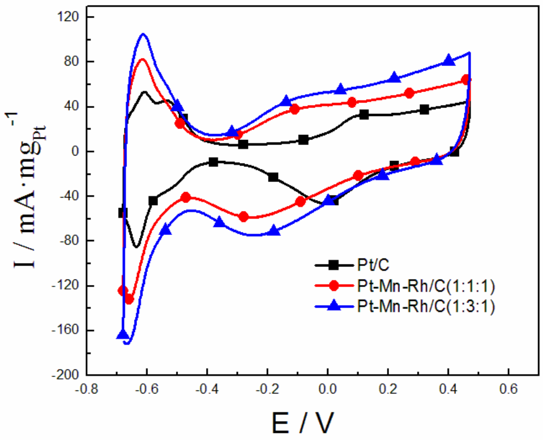

Fig. 1. Cyclic voltammograms in 0.1 M $HClO_4$ solution for the Pt/C, Pt-Mn-Rh/C(1:1:1) , Pt-Mn-Rh/C(1:3:1) electrocatalysts.

The ECSA of different catalysts can be calculated according to the following equation [18, 19];

$$ESCA = \frac{Q_H}{0.21 \times M_{Pt}}$$

where Q_H (mC) is the charge due to the hydrogen adsorption/ desorption in the hydrogen region of the CVs, 0.21mC/cm^2 is the electrical charge associated with monolayer adsorption of hydrogen on Pt, and M_{Pt} is the loading of Pt metal on the working electrode. The electrochemical active surface area (ECSA) and mass activity (MA) of all the catalysts calculated by CV measurements are reported in Table 1. The calculated ECSA of Pt-Mn-Rh/C (1:1:1) and (1:3:1) were 105.87 m^2/g$_{Pt}$ and 83.72 m^2/g$_{Pt}$, higher than that of Pt/C (75.4 m^2/g$_{Pt}$). This fact indicates that the addition of Mn and Rh maybe produce many more accessible Pt active sites by bifunctional mechanism.

Table 1. Electrocatalytic activity parameters of Pt/C and Pt-Mn-Rh/C catalysts

electrode	ECSA (electrochemical active surface area) [m^2/g$_{Pt}$]	MA (mass activity) [mA/mg$_{pt}$]
Pt/C	75.4	221.5
Pt-Mn-Rh/C(1:1:1)	83.72	253.63
Pt-Mn-Rh/C (1:3:1)	105.87	321.85

The electrocatalytic activities of the Pt/C and Pt-Mn-Rh/C electrocatalysts for EOR were measured by cyclic voltammetry between -0.65V and +0.5 V (vs. Hg/Hg_2SO_4) at 50 mV/s in an Ar-purged 0.1 M $HClO_4$+ 0.1 M C_2H_5OH solution at room temperature (Fig.2).

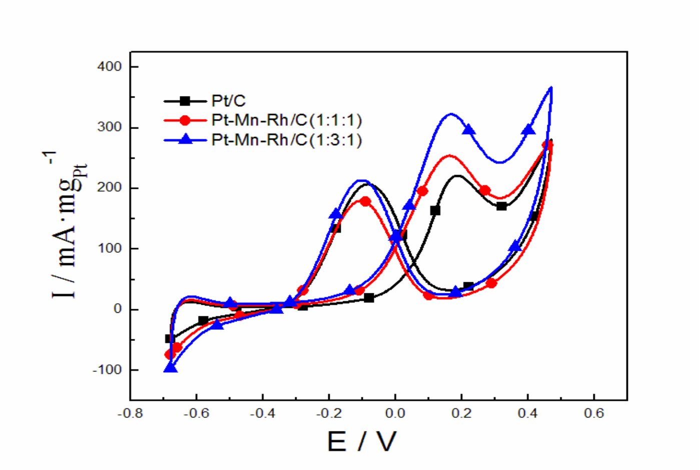

Fig. 2. Cyclic voltammograms in 0.1 M $HClO_4$+0.1 M EtOH solution for the Pt/C, Pt-Mn-Rh/C(1:1:1) , Pt-Mn-Rh/C(1:3:1) electrocatalystsat 50 mV/s between -0.65V~0.5 V vs.Hg/Hg_2SO_4.

Results were compared in terms of forward peak current density and the ratio of forward peak current density to reverse peak current density (Table 2). Usually, a higher I_F/I_R value implies a better tolerance of catalyst to carbonaceous species, and vice versa [20, 21]. The forward peak current density of the catalysts for ethanol oxidation followed the order of Pt-Mn-Rh/C (1:3:1)>Pt-Mn-Rh/C (1:1:1)>Pt/C. For Pt/C electrode, the peak potential for ethanol oxidation was 0.185 V and the forward peak current density was 221.5 mA/mg$_{Pt}$. In comparison, Pt-Mn-Rh/C electrodes had a higher peak potential than Pt/C, and a slightly higher forward peak current density. The I_F/I_R ratio of the catalysts for ethanol oxidation also followed the order of Pt-Mn-Rh/C (1:3:1) >Pt-Mn-Rh/C (1:1:1)>Pt/C. That is, the tolerance of the Pt-Mn-Rh/C catalysts to carbonaceous species were enhanced than that of Pt/C catalyst.

Table 2. Comparison of electrocatalytic activity of Pt/C and Pt–Mn-Rh/C catalysts for ethanol oxidation

Sample	Forward sweep		Reverse sweep		I_F/I_R
	I_F[mA/mg$_{pt}$]	E[v]	I_R[mA/mg$_{pt}$]	E[v]	
Pt/C	221.5	0.185	207.0	-0.082	1.07
Pt-Mn-Rh/C(1:1:1)	253.6	0.161	179.3	-0.103	1.41
Pt-Mn-Rh/C (1:3:1)	321.8	0.167	213.7	-0.101	1.50

IV. CONCLUSIONS

For ethanol oxidation, Pt-Mn-Rh/C (1:1:1) and (1:3:1) demonstrated larger ratio of forward peak current density to reverse peak current density, lower peak potential of oxidation, and slightly higher forward peak current density for ethanol oxidation in comparison to Pt/C. On the other hand, Pt-Mn-Rh/C exhibited much better oxidation characteristics than Pt/C. Considering the high cost of Pt, our experimental results clearly demonstrate that Pt-Mn-Rh/C catalysts are desirable catalyst candidates for direct ethanol fuel cells.

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