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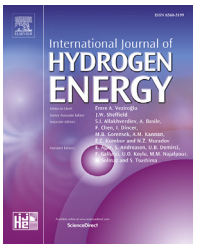

Short Communication

Using PdO and PbO as the starting materials to prepare a multi-walled carbon nanotubes supported composite catalyst (Pd_xPb_y/MWCNTs) for ethanol oxidation reaction (EOR)

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ABSTRACT

For the first time, a novel composite catalyst, namely, a multi-walled carbon nanotubes (MWCNTs) supported palladium and lead catalyst (denoted as Pd_xPb_y/MWCNTs), was prepared through a hydrothermal method using PdO, PbO and MWCNTs as the starting materials. The electrocatalytic activities of the resultant catalysts towards EOR in 1M KOH were examined mainly by using CV, CA and EIS. The electrochemical measurement results indicated that the peak current of EOR in the forward potential scan on the catalyst of Pd_1Pb_1/MWCNTs was almost 9 times larger, plus about 100 mV decrease in the onset potential value of EOR, than that on the Pb-free catalyst. A very simple, cost-effective and scalable way to synthesize Pd and Pb composite electrocatalyst for EOR was presented in this work, which was very meaningful to the further commercialization of EOR.

Introduction

Recently, direct ethanol fuel cells (DEFCs) have been paid much more attentions mainly due to the following reasons [1–4]. (1) The energy density of ethanol as a renewable fuel was about 8030 Wh kg^{-1}, being much higher than that of methanol (6100 Wh kg^{-1}). (2) DEFCs are environmentally-friendly power sources since ethanol has no toxicity as compared to methanol. (3) Ethanol has abundant reserves due to the fact that ethanol can be massively produced from the biomass via a fermentation method. (4) The transportation and storage of ethanol are cheaper and easier especially when compared to that of the hydrogen gas. Very recently, palladium (Pd) was

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demonstrated to have satisfactory electrocatalytic activity towards EOR particularly in alkaline media [5]. Thus, many efforts have been conducted focusing on preparing Pd-based alloys or composites, with an intention to cut down the preparation cost of EOR electrocatalyst while maintaining an acceptable electrocatalytic activity as compared to the pure Pd electrode. Of late, many kinds of Pd-based bimetallic catalysts like Pd–Au [6], Pd–Ir [7], Pd–Co [8], Pd_3M [9] (M = Cu, Ni, Fe) and Pd–Tb [10] have been successfully developed and employed as anode electrocatalysts for EOR. Although many novel kinds of Pd-based bimetallic catalysts have been prepared, seeking for a novel Pd-based EOR catalyst, with simple preparation process and relatively lower preparation cost as well as the satisfactory electrocatalytic ability for EOR, is still the main topic in the research field of EOR catalyst. To the best of our knowledge, except for the works regarding the Pd and Pb composite catalyst [11,12], no paper reporting the preparation of Pd and Pb composite catalyst using PdO and PbO as the starting materials via a hydrothermal method was published so far.

Meanwhile, to our knowledge, lead (Pb) is a rather cheaper material which has been widely employed as a raw material in producing lead acid batteries. Apparently, the successful preparation of Pd and Pb composite catalyst for EOR will significantly lower the preparation cost of EOR catalyst, which is very beneficial to the further commercialization of DEFCs. In the published works of Pd_3Pb [11], K_2PdCl_4 and lead acetate ($Pd(OAc)_2 \cdot 3H_2O$) were employed as the precursors, and $NaBH_4$ was used as the reducing agent. While, in the recent work concerning Pd and Pb composite catalyst [12], $PdCl_2$, $Pb(NO_3)_2$ and $NaBH_4$ were employed as the reactants, and the bifunctional mechanism and d-band theory were utilized to interpret the electrocatalytic activity improvement of the synthesized catalyst compared to the Pb-free catalyst. Although many novel kinds of carbon such as graphene [13], carbon nanodots [14], carbon nanofiber [15] have been successfully fabricated in recent years, carbon nanotubes (CNTs) still hold the dominant position in the carbon application field mainly due to its superior properties (like high specific surface area, higher electric conductivity, good thermal and chemical stability) [16–19]. In this work, MWCNTs, one kind of CNTs, were successfully employed as both carriers for the prepared particle catalysts and reducing agents in the hydrothermal process.

In this work, PdO, PbO and MWCNTs were employed as the reactants, and no other reducing agents were introduced into the reaction system. The effect of atomic ratio of Pd to Pb on both the properties and the electrocatalytic performances of the synthesized catalysts was fully studied.

Experimental details

Fabrication of the Pd_xPb_y/MWCNTs catalyst

The synthesis of the catalyst, i.e., Pd_xPb_y/MWCNTs, was accomplished via a very simple hydrothermal method. In brief, 6 mg PdO, 20 mg MWCNTs and a proper amount of PbO were mixed together with 4 mL bidistilled water, producing a suspension solution. Then, the resultant suspension solution was submitted to 40 min ultrasonic treatment to prepare a more homogeneous suspension solution. Afterwards, the resulting suspension solution was sealed in a home-made reaction vessel and placed in a muffle furnace, and heated in the muffle furnace at 200 °C for 3 h to complete the hydrothermal process. And after the temperature of the muffle furnace was down to the room temperature, the samples were took out and filtrated carefully. After being washed three times with bidistilled water, the samples were dried in air condition for 48 h to harvest the final products. It should be emphasized that in all the experiments, the weights of PdO and MWCNTs were constant, and the amount of added PbO changed correspondingly based on the atomic ratio of Pd to Pb. Therefore, the samples having the Pd to Pb atomic ratio in the starting materials of 0:1, 1:0, 1:0.5, 1:1 and 1:2, were named as catalyst k, o, a, b and c, respectively.

Preparation of Pd_xPb_y/MWCNTs coated glassy carbon (GC) electrodes

1 mg of above produced catalyst was added into 1 mL Nafion ethanol solution (The Nafion mass percentage was 0.1 wt%) generating a suspension solution, which was followed by 20 min ultrasonication. Subsequently, 20 μL of above catalyst ink was dropped on a well-polished and cleaned glassy carbon (GC) electrode (The diameter of the GC electrode used was 3 mm). After a drying in air, a working electrode of Pd_xPb_y/MWCNTs coated GC electrode was prepared successfully. Correspondingly, the GC electrodes modified with catalyst k, o, a, b and c were called as electrode k, o, a, b and c, respectively.

Results and discussion

XRD analysis

Fig. 1 shows the XRD patterns of the prepared catalysts including the standard XRD patterns of PdO, Pd and PbO, desiring to examine the crystal structure and the chemical composition of the obtained catalysts. The broad diffraction peak appearing at about 26° should be originated from the

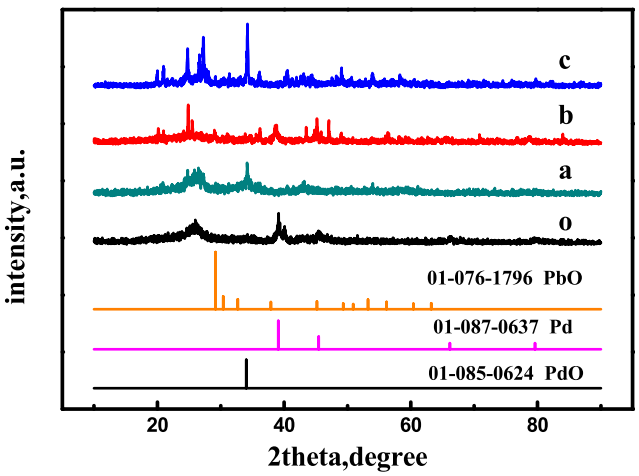

Fig. 1 – XRD patterns for the prepared catalysts including the standard XRD patterns of PdO, Pd and PbO. Pattern o, a, b and c corresponded to the catalyst o, a, b and c.

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