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Regular Article

Simple fabrication of pineapple root-like palladium-gold catalysts as the high-efficiency cathode in direct peroxide-peroxide fuel cells

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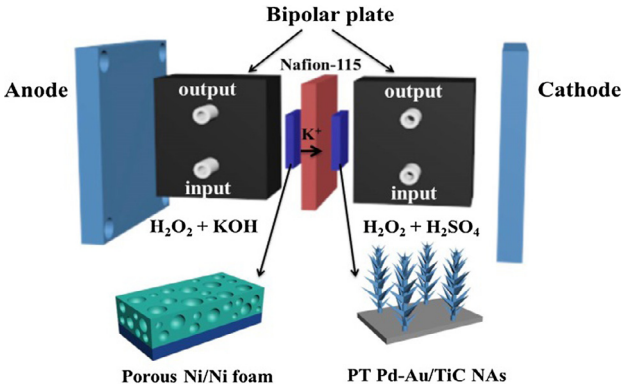
GRAPHICAL ABSTRACT

The direct peroxide-peroxide fuel cells using special 3D pineapple root-like Pd-Au/TiC cathode shows a peak power density of 56.5 mW cm^{-2} at 20 °C.



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ABSTRACT

Pd-Au/TiC electrodes with various three-dimensional structures are obtained by the pulsed potential electro-deposition in $PdCl_2/HAuCl_4$ electrolytes. The morphologies of Pd-Au/TiC composite catalysts are significantly dependent on the component of deposited solutions. The surface appearance of Pd-Au catalysts changes from rime-shaped structure, to feather-like construction, then to pineapple root-like structure and finally to flower-like configuration with the increase of $PdCl_2$ content in electrolytes. These particular three-dimensional structures may be very suitable for H_2O_2 electro-reduction, which assures a high utilization of Pd-Au catalysts and provides a large specific surface area. The electrocatalytic activities of H_2O_2 reduction on the Pd-Au/TiC electrodes improve as increasing the Pd content in Pd-Au alloy catalysts. The pineapple root-like Pd_5Au_1/TiC electrode reveals remarkably excellent electrochemical property and desirable stability for catalyzing H_2O_2 reduction in acid media. The direct peroxide-peroxide fuel cells with a 10 cm^3 min^{-1} flow rate display the open circuit voltage (OCV) of 0.85 V and the peak power density of 56.5 mW cm^{-2} at 155 mA cm^{-2} with desirable cell stability, which is much higher than those previously reported.

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1. Introduction

Nowadays, direct liquid fuel cells are regarded as appropriate electrical energy for portable devices because of their simple fuel-feed operation at ambient temperature [1–6]. H_2O_2 is usually studied as the oxidant of direct liquid fuel cells that applied in the space and underwater power source fields without air atmosphere because of its simpler storage and transportation and faster reduction kinetics than O_2 gas (Eqs. (1) and (3)) [7,8]. H_2O_2 is also able to be employed as the fuel since the electro-oxidation of H_2O_2 can be occurred (Eqs. (2) and (4)) [7]. Recently, H_2O_2 is able to be simultaneously applied as an oxidizer and a fuel in direct peroxide-peroxide fuel cells (DPFCs) [1–4,7]. S. Yamazaki's group investigated a hydrogen peroxide fuel cell adopting H_2O_2 as both an oxidant and a fuel. The fuel cell used 1 M NaOH as electrolyte and had a one-compartment structure without membranes separating the anode and cathode. This cell obtained the open circuit voltage (OCV) of ~0.1 mV and maximum current density of 2.9 mA cm^{-2} [9]. S.A.M. Shaegh and N.T. Nguyen studied a single-chamber membraneless hydrogen peroxide fuel cell using H_2O_2 as both fuel and oxidant. The electrolyte was H_2O_2 containing HCl. This cell showed the OCV of 0.6 V and maximum power density of 1.55 mW cm^{-2} [2]. Distinctly, the cell performance of one-compartment H_2O_2 fuel cell in onefold acidic or alkaline media is very low [1,2,9]. After that, A.E. Sanli improved the cell performance of H_2O_2 fuel cell using a two-compartment construction with the separation of anodic and cathodic parts, which is the same as the conventional fuel cell structure. The fuel cell achieved the OCV of ~0.9 V and maximum power density of 10 mW cm^{-2} through using acidified peroxide ($H_2SO_4 + H_2O_2$) as oxidant and alkalized peroxide ($KOH + H_2O_2$) as fuel [10]. In addition, the combination of cathodic reaction in acidic electrolyte (Eq. (1)) and anodic reaction in alkaline electrolyte (Eq. (4)) can obtain the highest theoretical output potential (1.63 V). Thus, the two-compartment DPFCs are superior to the one-compartment cell. However, the current cell performance is also not high, so the DPFCs urgently need to improve for the sake of competing with other fuel cells.

In acid media

$$\text{Cathodic reaction } 1: \ H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \quad E^o_{c1} = 1.78\ \text{V} \tag{1}$$

$$\text{Anodic reaction } 1: \ H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \quad E^o_{a1} = 0.69\ \text{V} \tag{2}$$

In alkaline media

$$\text{Cathodic reaction } 2: \ HO_2^- + H_2O + 2e^- \rightarrow 3OH^- \quad E^o_{c2} = 0.87\ \text{V} \tag{3}$$

$$\text{Anodic reaction } 2: \ HO_2^- + OH^- \rightarrow O_2 + H_2O + 2e^- \quad E^o_{a2} = 0.15\ \text{V} \tag{4}$$

Elevating the cathodic characteristic is the critical factor for DPFCs to obtain a desirable cell property. The selection and usage of cathodic electro-catalysts have a large influence on the electro-catalytic rate of H_2O_2 reduction in acidic solutions. Recently, precious metals and their alloys have been studied as effective catalysts on account of the excellent stability and good activity in harsh ambient media [11–16]. Palladium, which has similar characters to platinum, is an active electro-catalyst and less costly than platinum. Gold is also another efficient catalyst, but usually reveals not so high catalytic property as a result of the feeble chemisorption nature. In addition, the electronegativity of gold is stronger than that of palladium and platinum [17,18], which can improve the surface adsorption intensity of palladium-based electro-catalysts, so as to speed up the electrochemical reaction rate. Lately, gold has been proved to play a significant role in relatively enhancing the catalytic stability of palladium and platinum [19,20].

For the sake of gaining the synergistic effects of palladium and gold, palladium (Pd) electro-catalysts combined with gold (Au) were investigated in many literatures and caught much attention [11–13,21–25]. The two phase structures of Pd-Au electrocatalysts, such as core-shell and composite structure, generally exhibit better catalytic properties than the mono precious metal. Guo et al. [21] reported that the catalytic performance of toluene oxidation can be boosted by the usage of $1.95Au_1Pd_2$ instead of Pd or Au nanoparticles, which was resulted from their high adsorbed oxygen ability and powerful interaction between Au and Pd nanoparticles. Gudarzi and co-workers [22] synthesized the bimetallic Pd–Au catalysts through the co-impregnation method and showed that all the obtained Pd–Au catalysts were more efficient than the monometallic Pd. Tabakova et al. [23] prepared a series of mono-Au, mono-Pd and Au–Pd bimetallic catalysts towards benzene oxidation. They found that the electrocatalytic activity of Au–Pd catalysts was better than the single Au and Pd metal.

Therefore, precious metals Au and Pd composite materials may be an ideal catalyst for H_2O_2 electro-reduction in DPFCs. Besides, with the purpose of reducing the catalyst price and enhancing the DPFCs performance, what way to decrease the loading of precious metals and increase the catalytic efficiency is a currently hot spot. The morphologies of catalytic electrodes have remarkable effects on their electrochemical activity as well, how to design the neoteric three-dimensional (3D) morphologies of catalytic electrodes is the concentration of our study. Firstly, the employment of current collector with 3D structure is the essential and important requirement for the preparation of 3D electrodes. At present, nanowire arrays (NAs) structure for current collector has been extensively applied in many fields, since NAs generally own large specific surface area with open architecture and outstanding mass transfer features [4,26–29]. Secondly, the morphologies of electrocatalyst itself should also be reasonably and controllably designed as a 3D structure.

In this work, we put forward a research on the synthesis of Pd-Au catalysts with different morphologies directly deposited on titanium carbide (TiC) NAs substrate without any conductive agent and binder. The highly conductive TiC NAs were elected in the present study by reason of their excellent stability in acidic H_2O_2 media. Pineapple root-like (PT), rime-shaped (RM) and feather-like (FT) Pd-Au/TiC NAs composite electrodes were easily obtained by a pulsed potential electro-deposition. The morphologies of Pd-Au catalysts can be simply adjusted and controlled by the electrochemical deposition conditions. The PT Pd-Au/TiC NAs electrode presented markedly better catalytic performance than the RM and FT Pd-Au/TiC NAs electrodes towards H_2O_2 electro-reduction in sulfuric acid electrolyte. The DPFCs with using the PT Pd-Au/TiC NAs electrode as cathode materials demonstrated dramatically higher performance than that reported in the previous literatures [3,4,30].

2. Experimental

The Pd-Au/TiC NAs composite electrodes were fabricated via the facile pulsed potential electro-deposition of pineapple root-like (PT), rime-shaped (RM) and feather-like (FT) Pd-Au catalysts on the TiC nanowire arrays (NAs), as shown in Scheme 1a. The TiC NAs on Ti substrate ($10 \times 10 \times 1$ mm) were produced according to our previous studies [31]. Afterwards, the Pd-Au/TiC NAs composite electrodes with different composition and morphologies were electrochemically deposited on TiC NAs substrate in the