



Preparation of porous palladium nanowire arrays and their catalytic performance for hydrogen peroxide electroreduction in acid medium



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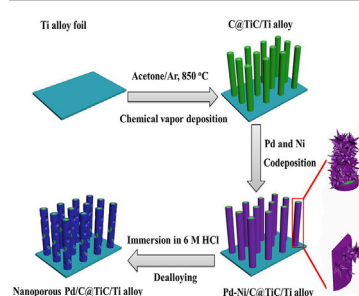
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HIGHLIGHTS

- The electrode shows unique 3D porous nanoarrays structure with a large surface area.
- The electrode exhibits superior catalytic activity and stability for H₂O₂ reduction.
- The reduction current density reaches 3.47 A mg⁻¹ at the potential of 0.2 V.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 August 2015

Received in revised form

1 November 2015

Accepted 3 November 2015

Available online 14 November 2015

Keywords:

Palladium catalyst

Nanopore

Nanowire arrays

Hydrogen peroxide

Electroreduction

ABSTRACT

Nanoporous palladium supported on the carbon coated titanium carbide (C@TiC) nanowire arrays (Pd NP/C@TiC) are successfully prepared by a facile chemical vapor deposition of three-dimensional (3D) C@TiC substrate, followed by electrochemical codeposition of Pd–Ni and removal of Ni via dealloying. The structure and morphology of the obtained Pd NP/C@TiC electrodes are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), field-emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Cyclic voltammetry (CV), linear sweep voltammetry (LSV), chronoamperometry (CA) and electrochemical impedance spectroscopy (EIS) are used to examine the catalytic performances of the electrodes for H₂O₂ electroreduction in H₂SO₄ solution. The Pd NP/C@TiC electrode exhibits a largely effective specific surface area owing to its open nanoporous structure allowing the full utilization of Pd surface active sites. At the potential of 0.2 V in 2.0 mol L⁻¹ H₂O₂ and 2 mol L⁻¹ H₂SO₄ solutions, the reduction current density reaches 3.47 A mg⁻¹, which is significantly higher than the catalytic activity of H₂O₂ electroreduction achieved previously with precious metals as catalysts.

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1. Introduction

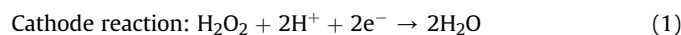
Fuel cells that are used in air-free environments require liquid or compressed oxygen as oxidant. While the bulky tank for carrying oxygen significantly reduces the energy density and safety standard

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of fuel cell systems [1–5]. Recently, hydrogen peroxide (H_2O_2) has been investigated as an alternative oxidant in replacing of oxygen for using in air-free environments (space and underwater). There are two important reasons: (1) H_2O_2 is in liquid state, which is easier for the fuel cell design, assembly and operation. (2) H_2O_2 has faster reduction kinetics than oxygen and also has none of the environmental problems associated with most of other chemical oxidizers [6–9]. Thus, H_2O_2 can be used as a strong oxidant in the polymer electrolyte fuel cells (PEFCs) [10–13]. For the cathode part of PEFC, H_2O_2 is electroreduced in acid media to release H_2O (Eq. (1)) [10,13].



The electrochemical reduction rate of H_2O_2 at the cathode catalysts has great impact on the performance of fuel cells [14–18]. The research of electrocatalysts has a long history. They can be divided into the following categories: (1) metals and alloys (Pd, Au, Ag, Cu, Pd–Ir, Pd–Pt, Pd–Ru, Pd–Ag) [16,19–24], (2) macrocycle complexes of transition metals (Fe- and Co-porphyrin, Cu-triazine) [25–27], (3) metal oxides (Co_3O_4 , NiCo_2O_4 , $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$) [28–30].

Fuel cells using H_2O_2 as oxidant in acid solution could achieve higher cell performance than that in basic medium [20,21,31,32]. For example, the theoretical open circuit voltage (OCV) of direct borohydride fuel cells (DBFCs) with the electroreduction of H_2O_2 in acid is as high as 3.016 V, which is 0.9 V higher than that in basic medium. Walsh et al. [33–35] exploited a basic-acidic bipolar electrolytes DBFC configuration, with NaBH_4 electrooxidation in NaOH and H_2O_2 electroreduction in HCl. A high cell performance with the OCV of 1.9 V and peak power density of 34 mW cm^{-2} was successfully obtained. Direct peroxide–peroxide FCs also use H_2O_2 as oxidant in acid solution to get a high cell performance [10,13,20,21]. Thus, in order to further improve the cell performance using H_2O_2 as oxidant, the electrocatalysts with high performance for H_2O_2 electroreduction in acid are imperious demands.

Based on the instability of base metal in acid condition, noble metal catalysts (e.g. palladium) were selected in harsh acid condition and usually show high activity for H_2O_2 electroreduction. Pd is a more economic and plentiful metal than Pt, which is one of the most used noble metals having outstanding catalytic activity [21]. In order to take in account of the catalysts' cost and improve the fuel cell performance, how to reduce the usage of the noble metals and improve the efficiency is the hot topic of the current research. The morphology of electrode also has direct influence on the electrochemical properties of electrodes, how to prepare novel morphology of the electrode is also the focus of our research.

In general, the most used electrodes for fuel cells are binder-dependent ones produced by the traditional slurry-coating technique [36]. Such obtained electrodes usually suffer drawbacks of low catalyst utilization because some catalysts are unable to contact with the current collector or are inaccessible to the electrolyte. Furthermore, the existence of binder will greatly decrease the electronic conductivity of the electrode materials, reducing their electrochemical performance. To overcome these issues, preparation of electrodes via direct deposition of electrocatalysts onto a current-collecting substrate has attracted much attention [37–43]. Recently, highly conductive nanowire arrays directly grown on the substrate have been used in various applications, such as catalysts, electrochemical capacitors, lithium ion batteries and solar cells, because nanowire arrays with the open structure usually possess a larger electrochemical active surface area, a higher utilization efficiency of the active materials, and a superior mass transport property [20,21].

In this study, nanowire arrays consisting of carbon coated titanium carbide (C@TiC) by means of a thermal evaporation method

without any template were used as the high conductive nano-skeleton for Pd–Ni deposits using a codeposition. The Ti alloy and C@TiC nanoarrays were selected in this work because it is very stable in the harsh acidic H_2O_2 solution. In addition, C@TiC nanoarrays with open structures were used both as the support and current collector enable the electrode to have good mass transport property. Nanoporous palladium supported on C@TiC nanowire arrays were prepared by electrochemical codeposition of precious metal (Pd) and transition metals (Ni) on the C@TiC, followed by removal of the Ni metal via dealloying. The as-prepared electrode has higher activity and superior stability in harsh acid electrolyte for H_2O_2 electroreduction due to its 3D open porous structure and high specific surface area.

2. Experimental

2.1. Reagents

Palladium chloride (PdCl_2), sulfuric acid (H_2SO_4), hydrogen peroxide (H_2O_2), acetone (CH_3COCH_3), isopropanol ($(\text{CH}_3)_2\text{CHOH}$), ethanol ($\text{C}_2\text{H}_5\text{OH}$), nitric acid (HNO_3), hydrochloric acid (HCl), nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), boric acid (H_3BO_3) and ammonium chloride (NH_4Cl) were obtained from Enterprise Group Chemicals Reagent Co. Ltd China. $\text{Ti}_6\text{Al}_4\text{V}$ alloy foil (thickness: 1 mm) was purchased from Baoji Yiyuan titanium industry Co., Ltd. All chemicals are analytical grade and were used as-received without further purification. Ultrapure water (Millipore, $18 \text{ M}\Omega \text{ cm}$) was used throughout the study.

2.2. Preparation and characterization of nanoporous Pd/C@TiC electrode

The schematic illustration for the synthesis of nanoporous Pd/C@TiC (Pd NP/C@TiC) electrode is shown in Fig. 1. The C@TiC nanowire arrays on Ti alloy substrate was prepared by Cui's method [44]. In brief, $\text{Ti}_6\text{Al}_4\text{V}$ foils ($10 \times 10 \times 1 \text{ mm}$) were ultrasonically degreased in acetone, isopropanol and ethanol sequentially, and rinsed with deionized water. The cleaned $\text{Ti}_6\text{Al}_4\text{V}$ foils were placed in the center of an alumina tube inside a horizontal tube furnace and heated to $850 \text{ }^\circ\text{C}$ under Ar (99.9999%) atmosphere. Acetone was then introduced into the chamber by Ar at a flow rate of 150 SCCM (SCCM denotes standard cubic centimeter per minute at STP). After 90 min reaction, the samples were cooled down to room temperature under Ar gas to obtain the nanowire array substrate. The Pd–Ni/C@TiC electrode was fabricated by the electrochemical co-deposition of Pd and Ni directly on the C@TiC nanowire arrays in a 50 mL aqueous solution containing $0.5 \text{ mmol L}^{-1} \text{ PdCl}_2$, $2 \text{ mmol L}^{-1} \text{ NiCl}_2$, $0.016 \text{ mol L}^{-1} \text{ H}_3\text{BO}_3$ and $0.093 \text{ mol L}^{-1} \text{ NH}_4\text{Cl}$ at a constant potential of -0.8 V (vs. Ag/AgCl) for 600 s. The co-deposition was carried out in a standard three-electrode electrochemical cell controlled by computerized potentiostat (Autolab PGSTAT302, Eco Chemie). A piece of C@TiC substrate was employed as the working electrode, and a platinum foil ($10 \times 10 \text{ mm}$) was served as the counter electrode. A saturated Ag/AgCl ($3 \text{ mol L}^{-1} \text{ KCl}$) electrode was used as the reference electrode, and all potentials in this work were referred to this reference electrode. Before electrodeposition, the C@TiC substrate was first immersed in HNO_3 solution for 30 min. The electrolyte was kept stirring under flowing nitrogen during the electrodeposition. After the electrochemical co-deposition, the Pd–Ni/C@TiC electrode was removed from the solution and immersed in $6 \text{ mol L}^{-1} \text{ HCl}$ solution for 12 h to dissolve Ni element for forming nanopores within Pd. Finally, the electrode was washed with ultrapure water thoroughly and air-dried prior to use.

The morphology of the electrodes was characterized by a

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