Electrochimica Acta 203 (2016) 91–98

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Manganese Dioxide Coated Graphene Nanoribbons Supported Palladium Nanoparticles as an Efficient Catalyst for Ethanol Electrooxidation in Alkaline Media

Qi Liu[a], Kun Jiang[b], Jinchen Fan[a], Yan Lin[a], Yulin Min[a], Qunjie Xu[a,*], Wen-Bin Cai[b,*]

[a] *Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, PR China*
[b] *Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, Fudan University, Shanghai 200433, PR China*

ARTICLE INFO

Article history:
Received 29 January 2016
Received in revised form 31 March 2016
Accepted 5 April 2016
Available online 6 April 2016

Keywords:
Palladium
Manganese dioxide
Graphene nanoribbons
Ethanol oxidation reaction
Alkaline media

ABSTRACT

Design of appropriate supporting materials is an alternative route to yield efficient Pt-free catalysts for ethanol oxidation reaction, which in practice may determine the conversion efficiency of direct alkaline ethanol fuel cells. In this work, graphene nanoribbons (GNRs) coated with MnO_2 are used as a unique supporting material for loading and dispersing Pd nanoparticles. XRD, TEM and XPS are applied to characterize the structure of as-synthesized Pd/MnO_2/GNRs nanocomposite catalyst, revealing a good dispersion as well as a modification of electronic property of Pd nanoparticles. Electrochemical measurements demonstrate that the as-synthesized nanocomposite displays largely enhanced electrocatalytic activity and durability toward ethanol oxidation in alkaline media as compared to the other tested Pd-based catalysts with various supports.

1. Introduction

Recently, new sustainable energy sources and technologies have become the focus of frontier research all over the world stimulated by the increasing demand for fossil fuel alternatives [1–4]. In that context, direct ethanol fuel cells (DEFCs) have attracted enormous attention not only because they have a theoretically high energy density (given the C1 pathway with complete oxidation of ethanol to form CO_2) but also become the biomass fuel ethanol can be widely available [5–7]. In fact, the design and synthesis of efficient catalysts for ethanol oxidation reaction (EOR) is of great importance for boosting the conversion efficiency of DEFCs [8,9]. Pt is the mostly used precious metal for electro-catalyzing EOR [10,11]. Nevertheless, due to high cost and scarcity of Pt, in number of efforts are recently shifted to the investigation of Pd-based catalysts [6,12]. Notably, Pd displays much lower electrocatalytic activity for EOR in acidic media, and yet a higher EOR activity in alkaline media, as compared to Pt [13]. With the technical progress of alkaline anion-exchange membranes, direct alkaline ethanol fuel cells (DAEFCs) promise a greater development. Accordingly, new efficient Pd-catalysts are under intensive investigation [14]. Even though the oxidation of ethanol to form acetate (i.e., the parallel C2 pathway) is so far predominant, which may compromise the actual energy density output, the facile electron transfer at lower anode overpotentials and the large-scale and low cost biomass nature of ethanol make DEFCs competitive for portable power sources.

It is well known that the activity and durability of a catalyst is highly dependent on the structure and composition of the support in addition to those of metallic nanoparticles (NPs) [15]. Supported catalysts decrease the usage of noble metals and expose more surface active sites due to their higher dispersion state, moreover, a synergistic effect between the metals and the supports may be enabled owing to their electronic interaction [16,17]. So far, carbon-based materials including carbon black [18], carbon microspheres [19], carbon nanotubes [20] and graphene [21], have widely been employed as supporting materials. Specifically, multi-walled carbon nanotubes (MWCNTs) have drawn a significant attention in electrocatalysis since they possess a larger surface area and a higher electrical conductivity compared to commercial Vulcan XC-72R carbon black, and a much lower cost compared to SWCNTs and graphene [22]. However, due to strong π-π interactions and high aspect ratio, it is very difficult to achieve uniform deposition of

---

* Corresponding authors.
E-mail addresses: xuqunjie@shiep.edu.cn (Q. Xu), wbcai@fudan.edu.cn (W.-B. Cai).

http://dx.doi.org/10.1016/j.electacta.2016.04.021
0013-4686/

metal NPs on MWCNTs as well as to disperse the MWCNTs-supported catalysts in solvents to make catalyst inks, as a result, the use of MWCNTs as the support was strongly restricted [23].

Fortunately, a report by Tours indicated that MWCNTs can be lengthwise cut and unraveled into graphene nanoribbons (GNRs) [24]. Compared to MWCNTs, GNRs can provide oxy-groups to facilitate uniform deposition of metallic NPs and facile dispersion of the GNRs-supported catalysts in aqueous solvents, and thus are a new type of supporting carbon materials for novel electro-catalysts [25]. Up to now, the reported Pt/GNRs [26] and Pd/GNRs [27] are only limited to catalyze the electrooxidation of methanol and formic acid in acidic media, respectively.

On the other hand, metal oxides are alternatively used as supporting materials for catalysts. Metal oxides such as CeO_2 [28], V_2O_5 [29], TiO_2 [30], WO_3 [31], NiO [32], MoO_x [33] and MnO_2 [34] with Pd can decrease the onset potential for the EOR because of the facile formation of the adsorbed hydroxide at the active surfaces, which is one of key steps for ethanol oxidation in alkaline media. The addition of an oxide promotes the formation of the Pd surface hydroxide due to a spillover of the primary oxide and/or the partial electron transfer [35]. Among these metal oxides, MnO_2 is one of the promising candidates given its low-cost, good electrochemical behavior and high CO tolerance [34,36,37]. Nevertheless, the low conductivity of MnO_2 should be compensated by incorporating a highly conductive nanomaterial. Notably, GNRs charge carriers create an energy gap near the charge neutrality point, which is tightly contacted with MnO_2, hence electronic transport can be greatly enhanced in a composite [38].

Based on the above discussion, it is expected that a new efficient Pd-based catalyst for EOR in alkaline media may be created if we combine highly conductive GNRs and CO-tolerant MnO_2 to form a unique composite support. In the present work, Pd/MnO_2/GNRs with Pd NPs uniformly dispersed on MnO_2-coated GNRs were synthesized and tested as an electrocatalyst for EOR in alkaline media. Pd/MnO_2/GNRs exhibited the highest electrocatalytic activity and stability among all the samples examined, including Pd/MnO_2/RGO, Pd/MnO_2/MWCNTs, Pd/GNRs, Pd/MWCNTs and Pd/C catalysts.

2. Experiment section

2.1. Materials

MWCNTs (purity >95%, length: 10–30 μm and OD: 20–30 nm) were purchased from Chengdu Organic Chemicals Co. Ltd. (Chengdu, China). EDTA, K_2PdCl_4, H_2O_2 were supplied by Aladdin Co. Ltd. (Shanghai, China). Ethylene glycol, $KMnO_4$, Na_2CO_3, $NaBH_4$, NaOH and ethanol were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). 5 wt.% Nafion® solution was provided by DuPont Co. Ltd (Wilmington, DE, USA). All reagents were of analytical reagent grade and used without further purification. Milli-Q water (18.2MΩ·cm) was used throughout all experiments.

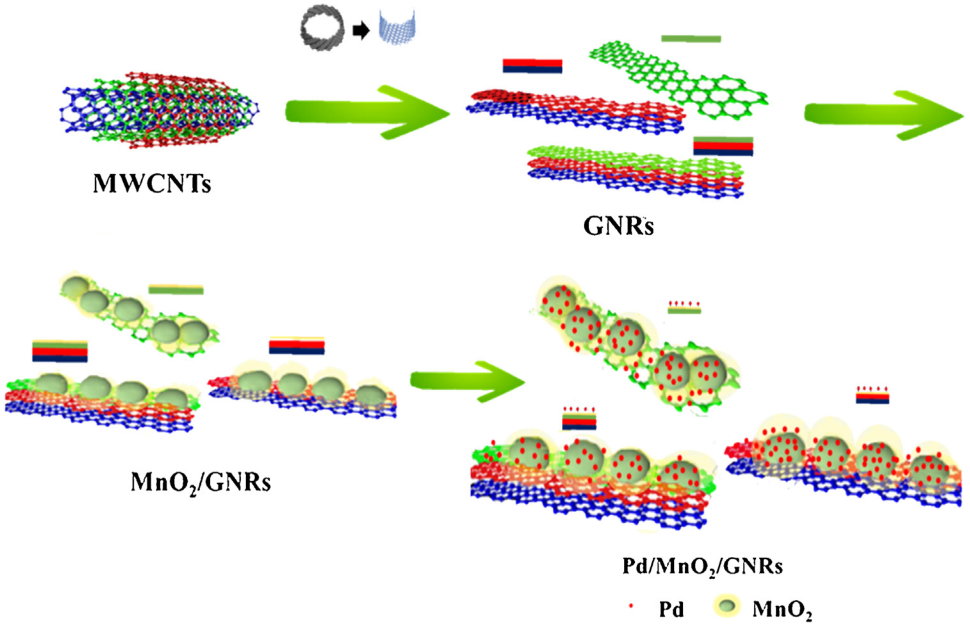
2.2. Materials Synthesis

2.2.1. Preparation of GNRs

The GNRs were synthesized by step-oxidation unzipping of MWCNTs according to the method reported by Tour's group [24]. In brief, 1.0 g of MWCNTs was firstly dispersed in 100 mL of concentrated sulfuric acid under stirring for 2 h. Then, 5.0 g of $KMnO_4$ was slowly added into above MWCNTs/sulfuric acid mixture in an ice bath as oxidizing agent. Afterward, the mixture was stirred and allowed to react for 1 h at room temperature and another 1 h at 70 °C. After that, the mixture was poured into ice water, followed by adding 20 mL of 30 wt.% H_2O_2 aqueous solution. The GNRs were collected by centrifugation and rinsed with a hydrochloric acid solution (10% (v/v)) and Milli-Q water in sequence. Finally, as-prepared GNRs were freeze-dried for use.

2.2.2. Preparation of MnO_2/GNRs

Using $KMnO_4$ as the precursor, MnO_2/GNRs were prepared with reduction of ethylene glycol. 50 mg of GNRs were firstly dispersed in 25 mL of Milli-Q water by sonication for 2 h. By then, 80 mg of $KMnO_4$ was added into the GNRs aqueous solution. After magnetic stirring for 2 h, 30 mL of ethylene glycol was added into the suspension through a peristaltic pump under magnetic stirring, and then, the mixture solution was reacted for about 3 h at 60 °C.



Scheme 1. Schematic illustration of fabrication for Pd/MnO_2/GNRs.