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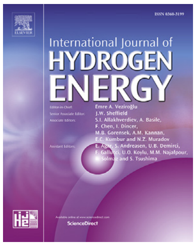

Monodisperse Pd nanoparticles assembled on reduced graphene oxide-Fe_3O_4 nanocomposites as electrocatalysts for borohydride fuel cells

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ARTICLE INFO

Article history:
Received 21 July 2017
Received in revised form
20 December 2017
Accepted 23 December 2017
Available online xxx

Keywords:
Palladium nanoparticles
Iron oxide nanoparticles
Reduced graphene oxide
Nanocomposite
Oxygen reduction reaction
Borohydride oxidation reaction

ABSTRACT

5 nm palladium nanoparticles (Pd NPs) are synthesized and assembled on reduced graphene oxide-iron oxide nanocomposite (rGO-Fe_3O_4) to be used in oxygen reduction reaction (ORR) and borohydride oxidation reaction (BOR) studies in alkaline media. The structure and morphology of the resulting Pd/rGO-Fe_3O_4 hybrid material are evaluated by X-ray diffraction (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray spectroscopy (EDS) analyses. The electrochemical behavior of Pd/rGO-Fe_3O_4 hybrid material for the ORR and BOR is investigated by voltammetry with rotating disk and rotating ring disk electrode and electrochemical impedance spectroscopy, enabling evaluation of the number of exchanged electrons, Tafel slope, exchange current density and activation energy. The results reveal that ORR at Pd/rGO-Fe_3O_4 proceeds as a 2-electron process with Tafel slope of 0.133 V dec^{-1}, while BOR proceeds as a 5.6-electron process with Tafel slope of 0.350 V dec^{-1} and exchange current density of 1.38 mA cm^{-2}. The BOR activation energy was found to be 12.4 kJ mol^{-1}. Overall, this study demonstrates the good efficiency of Pd/rGO-Fe_3O_4 hybrid material for BOR.

Introduction

Low-temperature alkaline fuel cells (LTAFCs) are a group of electrochemical energy conversion devices that deliver energy with high efficiency and low emissions. Direct borohydride fuel cells (DBFCs), as a type of LTAFC, produce electricity by oxidation of borohydride anion (BH_4^-) at the anode and oxygen reduction at the cathode [1]. Direct oxidation of BH_4^- (BOR) results in 8 exchanged electrons along with nontoxic environmentally friendly products and theoretical energy density of 9.3 kW h kg^{-1}, which is higher than that of provided by other fuels [2–4]. The aforementioned advantages of BH_4^- as a fuel have not been fully utilized up to now. The low standard electrode potential represents a thermodynamic value that cannot be achieved in practice. Furthermore, BOR proceeds

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https://doi.org/10.1016/j.ijhydene.2017.12.155

Please cite this article in press as: Martins M, et al., Monodisperse Pd nanoparticles assembled on reduced graphene oxide-Fe_3O_4 nanocomposites as electrocatalysts for borohydride fuel cells, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2017.12.155

via complex mechanisms determined by the electrode material and potential [5]. The main side reaction is BH_4^- hydrolysis to generate $H_{2(g)}$ that reduces faradaic efficiency of BOR. In this respect, BOR electrocatalysts are generally divided into two categories, hydrolyzing (e.g., Pt, Pd) and non-hydrolyzing (e.g., Au) [1]. On the other hand, oxygen (O_2) might be reduced through a direct 4-electron process to OH^-or through a sequence of 2-electron processes to HO_2^- and then to OH^-. The HO_2^- formed in the 2-electron processes may also disproportionate to OH^- and O_2.

Pd is regarded as the most promising substitute of Pt as electrocatalyst for fuel cells as it enables fast reaction kinetics comparable to that of Pt along with its higher abundance and lower price. Therefore, intensive research involving Pd-based catalysts with high electrochemical activity and stability is being carried out [6]. For instance, Pd shows better BOR electrocatalytic activity than Au with 0.2 V lower onset potential despite being active for the hydrolysis of BH_4^- as well [1,5,7].

On the other hand, the type and structure of support material have considerable effects on the catalytic performance of the electrocatalysts used for the fuel cells [8]. In this regard, a variety of carbon materials with high specific surface area, good electrical conductivity, mechanical robustness and stability have been used as support material for the fuel cell electrocatalysts, which increases the electrocatalytically active surface area and leads to higher currents [8]. Among them, graphene or its derivate reduced graphene oxide (rGO) appears to be an exceptional support material for electrocatalyst applications owing to its intrinsic high specific surface area and superior electrical features [9]. Wet chemical synthesis of rGO allows the decoration of rGO nanosheets with surface functional groups that prevent agglomeration of metal nanoparticles (NPs). Furthermore, the functional groups (–COOH, –OH and –O–) are reactive species assisting the heterogeneous nucleation of metal NPs. Recently, magnetite NPs (Fe_3O_4 NPs) have attracted attention in several fields, including biotechnology/biomedicine, magnetic resonance imaging, environmental remediation, catalysis, materials science, electrochemical and bio–electrochemical sensing, and as electrode for supercapacitors and lithium ion batteries [10]. For instance, Fe_3O_4 NPs anchored on multi-walled carbon nanotubes exhibited high electroactivity for hydrogen peroxide sensing [11]. Moreover, Fe_3O_4 NPs has been also reported as an effective catalyst support in several reactions [12–15]. For instance, Zhang et al. describe the excellent performance of PdFe/Fe_3O_4 in organic reactions [14]. Padilla et al. report the high electrocatalytic activity and stability of Pt/Fe_3O_4 for the oxygen reduction reaction (ORR) in acid media [13]. In the study performed by Li et al. the enhanced electrocatalytic activity of Pd for methanol oxidation in alkaline media is demonstrated by the use of Fe_3O_4 as support material [15]. These magnetic NPs have a small size and high surface area that lead to a substantial improvement of catalytic activity. However, the drawbacks associated with their superparamagnetic property, oxygen sensitivity, tendency to agglomerate and low electrical conductivity limits their use in electrocatalysis [8]. Electrocatalysts morphology, particle size distribution, density of surface active sites and their catalytic activity are determined by the synthesis route. Several chemical procedures have been employed to obtain these Fe_3O_4 NPs such as coprecipitation, thermal decomposition, microemulsion and hydrothermal methods [16]. Alternatively, Fe_3O_4 NPs can be obtained by chemical synthesis which involves the precipitation of these NPs from the solution. Comparing with other synthetic routes, thermal decomposition and hydrothermal synthesis reveal the best results in terms of the control of size and morphology [16]. To enhance the stability and the conductivity of Fe_3O_4, magnetic nanocomposites have been synthesized with various carbon materials, including graphene, carbon nanotubes, conducting polymers and other inorganic materials [8,17–20]. Hazhir et al. reported the synthesis of rGO-Fe_3O_4 nanocomposite for electrochemical sensing with excellent electronic, mechanical and thermal properties [17].

In this work, we describe preparation of a novel hybrid material consisting of ex-situ synthesized Pd NPs assembled on rGO-Fe_3O_4 nanocomposite, abbreviated as Pd/rGO-Fe_3O_4, and for the first time the evaluation of their electrocatalyst performance for ORR and BOR in alkaline conditions for potential use in DBFCs. Examples of Pd-rGO or Fe_3O_4-rGO electrocatalysts can be found in literature but the electrocatalyst presented herein is the first case of combining the advantageous properties of Pd NPs, Fe_3O_4 NPs and rGO in one structurally-defined nanocomposite for the ORR and BOR. Indeed, it is experimentally proved that Pd/rGO-Fe_3O_4 nanocomposites showed higher performance than their monometallic counterparts. Moreover, this work comprises a comprehensive study on the ORR and BOR kinetic parameters that are determined by using cyclic voltammetry (CV) and linear scan voltammetry (LSV) with rotating disk (RDE) and rotating ring disk (RRDE) electrode, and electrochemical impedance spectroscopy (EIS) measurements.

Experimental

Preparation of Pd/rGO-Fe_3O_4 hybrid material

Pd NPs were synthesized by using the surfactant-mediated synthesis protocol that is reported elsewhere [21]. Subsequently, Fe_3O_4 NPs were synthesized by the thermal decomposition of Fe $(acac)_3$ in the presence of oleylamine and benzyl ether at 300 °C [22]. Reduced graphene oxide (rGO) was prepared using well-known synthesis protocol including the modified Hummer's method to produced graphene oxide (GO) and the reduction of GO by DMF refluxing. To prepare Pd/rGO-Fe_3O_4 hybrid material, Fe_3O_4 NPs were first assembled on rGO via liquid-phase self-assembly method that yielded rGO-Fe_3O_4 nanocomposite. Next, as-synthesized Pd NPs were assembled on rGO-Fe_3O_4 nanocomposite by using the liquid self–assembly method again and Pd/rGO-Fe_3O_4 hybrid material was obtained. The yielded hybrid material was washed with ethanol several times and dried under vacuum.

Structural and morphological characterization

Structural and morphological properties as well as chemical composition of Pd/rGO-Fe_3O_4 hybrid material were examined by transmission electron microscopy (TEM) along with the associated energy dispersive X-ray spectroscopy (EDS), X-ray

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