



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

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

Investigation of the effect of carbonaceous supports on the activity and stability of supported palladium catalysts for methanol electro-oxidation reaction

Roya Kiyani ^a, Mohammad Javad Parnian ^{a,b}, Soosan Rowshanzamir ^{a,b,*}

^a School of Chemical Engineering, Iran University of Science and Technology, Tehran, Iran

^b Fuel Cell Laboratory, Green Research Center, Iran University of Science and Technology, Tehran, Iran

ARTICLE INFO

Article history:

Received 1 April 2017

Received in revised form

9 July 2017

Accepted 16 July 2017

Available online xxx

Keywords:

Nitrogen-doped graphene

Multi-walled carbon nanotubes

Palladium nanoparticles

Methanol oxidation reaction

ABSTRACT

In this study, nitrogen doped graphene (NG) and multi-walled carbon nanotubes (MWCNT) were used as supporting materials for palladium active phase to investigate their performance in direct methanol fuel cells (DMFCs). The facile and low temperature solvothermal method was used for the synthesis of NG. Palladium nanoparticles were deposited on the surface of NG and MWCNT by a modified polyol reduction method. The morphologies and microstructures of the prepared catalysts were characterized by scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction. Also, cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy were carried out to evaluate the electrocatalytic activity and the durability of the obtained catalysts towards methanol oxidation reaction. Pd/NG catalyst had a better activity and durability of methanol electrocatalytic oxidation rather than Pd/MWCNT catalyst, which is related to good dispersion of Pd nanoparticles on the surface of nitrogen doped graphene and the physicochemical characteristics of NG.

© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Direct methanol fuel cells (DMFCs) are considered as promising energy conversion devices during the last decade due to some important advantages, like high energy density, high energy conversion efficiency, low pollution emission, low operating temperature, and easy handling and transportation of renewable liquid fuel [1–6]. However, the commercialization of DMFCs has been faced with numerous obstacles, such as low rate of methanol oxidation reaction (MOR) at the anode, incomplete oxidation of intermediate carbon species, insufficient catalytic activity and poisoning of the anode

electrocatalysts [7]. Therefore, significant efforts should be made in order to enhance the catalytic efficiency of the electrocatalyst for methanol oxidation at the anode side [8–10]. In DMFCs, methanol is directly oxidized to CO₂ and H₂O by platinum-based catalyst. Typically, Pt and its alloys have been considered as the most promising catalyst for methanol oxidation in acidic environment. However, some challenges such as the high cost of Pt, its rare sources, and poisoning by the intermediate species like CO, that was formed during the methanol oxidation reaction in acidic media, restricted the widespread use of Pt [11–13]. Some literature reported that in alkaline media, higher activity of alcohols oxidation can be achieved compared with acidic media because of the

* Corresponding author. Iran University of Science and Technology, P.O. Box: 16846-13114, Tehran, Iran.

E-mail addresses: mjparnian@iust.ac.ir (M.J. Parnian), rowshanzamir@iust.ac.ir (S. Rowshanzamir).

<http://dx.doi.org/10.1016/j.ijhydene.2017.07.113>

0360-3199/© 2017 Hydrogen Energy Publications LLC. Published by Elsevier Ltd. All rights reserved.

formation of further hydroxide ions species. Importantly, to reduce the cost, non-Pt catalysts could be used as potential catalysts in the anode side, therefore, a wide range of electrode materials can be selected [11,14–16]. Also, the corrosion restrictions are less significant in alkaline media in comparison to acidic medium [15,17]. For this purpose, a variety of non-platinum-based catalysts have been suggested. Nowadays, palladium (Pd) and Pd-based catalysts have attracted more attention towards methanol oxidation reaction (MOR) in alkaline electrolyte, because of its similar properties with Pt, (like the same group in a periodic table and the same fcc crystal structure), and significant advantages compared to Pt (like lower cost, greater availability, and more resistant to poisoning by carbon species in alkaline media) [18–25]. However, in general, it suffers from the lower electroactivity for oxidation of methanol in alkaline medium. Also, according to the easy accumulation of naked Pd nanoparticles, the control of particle size and good distribution of them, has been difficult. Therefore, the main key to achieving the commercialization of palladium is the preparation of Pd-based catalysts with controllable nanostructures and improvement of catalyst's properties [21,26]. Introducing a suitable substrate for a good distribution of metal nanoparticles is very important [27]. Various approaches to nanoparticle synthesis were implemented to improve the catalytic performance, the nanoparticles dispersion, and support properties of the different catalysts in the different applications [28,29]. Sun et al. [30] synthesized single-crystalline BaTiO₃ nanoparticles with controlled morphologies by a thermohydrolysis route that an excellent distribution in aqueous solution was reached for the nanoparticles under the presence of hydrazine. Many efforts have been made to disperse Pd nanoparticles on different supports with high surface area, good electrical conductivity, strong adsorption of metal nanoparticles, as well as low cost to improve their electrocatalytic activity. The ideal support demonstrates the ability to enhance the distribution of nanoparticles and then the maximum portion of the active phase can participate in the electrocatalytic reaction [31–33]. It is obvious, that the structure of support material, can influence the activity and durability of the catalyst [34–36]. Various carbon materials such as carbon black, carbon nanofibers, and carbon nanotubes have been used as support in DMFCs. Among them, graphene is considered to be the ideal support due to its superior physical and chemical properties such as high surface area, low construction cost, good thermal and chemical stability, high electrical conductivity, and mechanical strength [14,37–44]. It should be noted that graphene has different applications in industry, for example, to prepare thermoplastic polyurethane (TPU) based conductive polymer composites (CPCs) [45]. In another study, Liu et al. [46] prepared lightweight conductive porous graphene/thermoplastic polyurethane (TPU) foams by using the thermal induced phase separation (TISP) technique. Also, carbon based materials such as graphene and carbon nanotubes have wide applications in the sensor, catalyst support, and etc [47–50]. Theoretically, Pd nanoparticles can be well dispersed over graphene, however, the restacking property of graphene can influence the performance of the composite because of the huge surface energy [22]. Also, the aggregation of metal nanoparticles on the surface of pristine graphene because of

its inefficient binding sites, can decrease the active sites of the electrocatalyst. Therefore, various methods have been developed to improve the properties of graphene by chemical functionalization and chemical doping with heteroatoms. Up to now, studies have proved that the physical, chemical, and electronic properties of graphene can be modified by chemical doping of heteroatoms such as nitrogen, boron, fluorine, phosphorus, and sulfur in its structure [34,51]. It is noteworthy, nitrogen doping can effectively improve the physicochemical properties of graphene [34,41,52]. Interestingly, the doping of carbon materials with heteroatoms like nitrogen and sulfur has attracted as a suitable adsorbent for heavy metals to decrease the environment pollution [53,54].

It has been shown that nitrogen atoms due to the high electron affinity can improve the nucleation and growth rate of metal nanoparticles, and lead to better dispersion of metal nanoparticles on the surface of graphene, resulting in improved electrochemical activity and stability of the synthesized catalysts [15,55]. The introduction of the nitrogen leads to anchor the metal nanoparticles onto the support homogeneously, and thereby increase the electrocatalytic activity and utilization of the catalyst. The studies show that the presence of nitrogen atoms on the surface of graphene can control the shape and size of metal nanoparticles [41,52]. It has been recognized that nitrogen doping makes defects in the structure of graphene and these defects provide good sites to deposit the metal nanoparticles on the surface [15,56].

Up to now, various methods for nitrogen doped graphene synthesis mainly include thermal annealing of graphene oxide in ammonia, chemical vapor deposition (CVD) with ammonia and methane, and nitrogen plasma treatment of graphene [15,41]. It is remarkable that these methods are complex and expensive for laboratory scale, also using the various precursors of carbon and nitrogen sources, leads to uncontrollable doping of nitrogen in the structure of graphene. Lately, a facile method has been used to prepare NG in a large scale. The solvothermal method is a simple approach to controlling the amount of nitrogen doping in the structure of carbon, in addition, this synthesis method produces low pollution [11]. A simple synthesis method for preparation of nitrogen doped graphene was proposed by Sun et al. [57]. Other researchers have shown that Pt nanoparticles distributed more uniformly on the surface of nitrogen-doped carbon nanotubes than pristine carbon nanotubes because of the additional surface structure defects that created by nitrogen doping [27,58,59]. Wang et al. [16] investigated Pd catalysts, Pt catalysts, and bimetallic Pt–Pd catalysts supported on nitrogen doped graphene for methanol oxidation in alkaline media. The results showed that Pt–Pd/NG has better catalytic activity and stability than Pd/NG and Pt/NG. In another study, Guohai Yang et al. [60] synthesized Pd/MWCNT, Pt/MWCNT, and Pt–Pd/MWCNT and studied their activities towards methanol oxidation. It has demonstrated that Pt–Pd alloys nanoparticles were uniformly dispersed on MWCNT and Pt–Pd/MWCNT had higher electrocatalytic activity towards methanol oxidation in alkaline media than the commercial catalysts, which could be attributed to the alloying effect of Pt–Pd and the synergistic interaction between the support and nanoparticles. Awashti et al. [61] prepared 40 wt%Pd-x wt.% Ru (where x = 0, 1, 3, 5, 6 and 10) nanoparticles (NPs) supported

Download English Version:

<https://daneshyari.com/en/article/5145295>

Download Persian Version:

<https://daneshyari.com/article/5145295>

[Daneshyari.com](https://daneshyari.com)