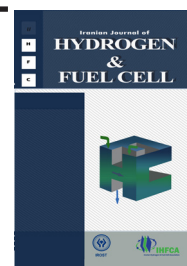Iranian Journal of Hydrogen & Fuel Cell

IJHFC

Journal homepage://ijhfc.irost.ir

One–step synthesis of Pd₃Co alloy nanoparticles deposited on reduced graphene oxide as an electro-catalyst for the oxygen reduction reaction in passive direct methanol fuel cells

Karim Kakaei[*,1], Hussein Gharibi[2], Soheyla Abbaspour[1]

[1]Department of Physical Chemistry and Nano Chemistry, Faculty of Science, University of Maragheh, P.O. Box. 55181-83111, Maragheh, Iran
[2] Department of Chemistry, Faculty of Science, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran

Article Information

Abstract

We reported on a Pd-Co (3:1)/graphene oxide (Pd₃Co /GO) catalyst through a one-step strategy. GO is synthesized from graphite electrodes using ionic liquid-assisted electrochemical exfoliation. Controllable GO-supported Pd₃Co electrocatalystis then was reduced by ethylene glycol as a stabilizing agent to prepare highly dispersed PdCo nanoparticles on carbon graphene oxide to be used in an oxygen reduction reaction in passive direct methanol fuel cell (DMFC) catalysts. The performance of these electrodes in the ORR was measured with cyclic voltammetry (CV), linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), chronoamperometry (CA), inductive coupled plasma (ICP), X-ray diffraction (XRD) and scanning electron microscopy coupled to energy dispersive X-ray (SEM–EDX). Since the Pd₃Co/GO alloy electrocatalysts are inactive for the adsorption and oxidation of methanol, it can act as a methanol-tolerant ORR catalyst in a direct methanol fuel cell (DMFC). A membrane-electrode assembly (MEA) has been prepared by employing of the Pd₃Co/GO as a cathode for a passive direct methanol fuel cell and characterized by polarization curves and impedance diagrams. A better performance was obtained for the cell using Pd₃Co/RGO ($3.56\,\mathrm{mW\,cm^{-2}}$) compared to Pd/RGO ($1.75\,\mathrm{mW\,cm^{-2}}$) and Pt/C-Electrochem ($1.9\,\mathrm{mW\,cm^{-2}}$) as a cathode in the DMFC.

1. Introduction

In recent years, environmental pollution and the energy crisis are both severe challenges faced by human society because of the rapidly growing energy demand and massive combustion of fossil fuels. Scientists believe that the conventional notions of energy generation and conversion are not suitable for sustainable development in the world [1-3]. Fuel cells have become a promising power source due to their

*Corresponding author. Tel.: +98-41-37276068, fax: +98-41-37276066
E-mail address: kakaei@maragheh.ac.ir , k_kakaei56@yahoo.com (Karim Kakaei)

high energy conversion efficiency and environmental affinity. Recently, great attention has been paid to the proton exchange membrane fuel cells (PEMFCs) fueled by H_2 or liquid fuels such as alcohols [1, 4-7]. In comparison with hydrogen-fed fuel cells, direct methanol fuel cells (DMFCs) are promising candidates for electrochemical power generation in portable electronic devices and electric vehicles owing to their high energy density, low pollutant emission, high energy conversion efficiency, and the simplicity in handling and processing of liquid fuel [8-9]. However, several critical problems should be solved before DMFCs are widely used, such as catalyst poisoning, slow oxidation kinetics, and the high cost and low abundance of both anode and cathode Pt-based electro-catalysts. Among noble metals, Pd is similar to Pt in catalytic efficiency for alcohol oxidation. However, Pd has higher availability, lower cost, and better resistance to poisoning by carbonaceous species in alkaline medium [10]. A possible bimetallic structure has been studied by adding other elements, such as Ag [11], Ni [12], Ru [13], Co [14-15], etc. into Pd-based catalysts and has proved to be an effective way to further improve the electrocatalytic performance and tolerance to poisoning intermediates.

In this work we have synthesized GO by an electrochemical method and then reduced GO in the presence of Pd and PdCo nanoparticles to produce a new Pt_3Co/RGO catalyst. Compared to the Pd/RGO electrocatalyst, the obtained Pt_3Co/RGO catalyst showed significant catalytic activity toward ORR and methanol tolerance in passive DMFCs.

2. Experimental

2.1. Graphene and GO generation

Recently, we reported a facile electrochemical approach for the large scale preparation of GO in [5, 16], but we shall briefly repeat the main features here. A graphite rod electrode was inserted as the anode and cathode into the ionic liquid (IL)/water solution with a separation of 1 cm. The ionic liquid Urea choline chloride was mixed with water at a 1:1 ratio. Static potentials of 5 V were used to the two electrodes using a DC power supply. Three stages occurred in the electrochemical exfoliationwhich represent the beginning of electrochemical reaction and the end of reaction in the process of electrochemical oxidation, intercalation, and corrosion of the graphite anode. In the first stage there is an induction period before visible signs of exfoliation can be detected. The color of the electrolyte changed from colorless to yellow and then dark brown. In second stage a visible corrosion and expansion of the graphite anode can be seen. In the third stage the expanded flakes peel off from the anodes and form the black slurry with the electrolyte.

2.2. Preparations of Pd/RGO, Co/RGO and $Pd_3Co/$ RGO

For the synthesis of graphene-supported PdCo (PdCo(3:1)/graphene) catalysts, 50 mg of graphene oxide was dispersed in 20ml of ethylene glycol solution as a reducing agent [17] and sonicated for 1 h. Subsequently, 1mL of palladium chloride solution (0.03M) and 1ml of $Co[NO_3]_2.6H_2O$ solution (0.01M) were added to the graphene oxide solution and sonicated for 2h. The pH of the solution was adjusted to 10 using sodium hydroxide. The resulting mixture was filtered, washed with distilled water and acetone, and then dried in an oven at 80–100ºC for 10h. For the synthesis of the graphene-supported Pd (Pd/RGO) and graphene-supported Co (Co/RGO) catalysts, the only difference was the omission of the $PdCl_2$ solution in the solution of graphene oxide or $Co [NO_3]_2.6H_2O$.

2.3. Passive direct methanol fuel cell tests

A home-made, air-breathing DMFC with stainless steel current collectors (316) was used to investigate the electrochemical performance of the synthesized reduced graphene oxide supported Pd and Pd_3Co electrocatalysts in comparison with commercial Pt/C. A pretreated Nafion 115 membrane with a thickness of 125 µm was used in this work. The pretreated membranes were kept in the DI water prior to the

fabrication of MEAs. Carbon paper was used as the backing support for the anode and cathode electrodes. Pt/C (10 wt.%) was used as the anode and Pd_3Co or Pd (20 wt.%) on RGO was employed as the cathode. In order to comparison with commercial DMFC 10 wt.% a Pt/C (Electrochem) was used as the anode and 20 wt.% Pt on Vulcan XC-72 was used as the cathode. MEA catalyst loadings for both the anode and cathode were 0.3 mg cm^{-2}. The active area of the MEAs was 4cm^2, and the methanol reservoir volume was 4 ml.

3. Results and discussion

3.1. Physical characterization of Co/G, Pd/G and Pd_3Co/G bimetallic electro catalysts

Typical SEM micrographs of the Co/RGO, Pd/RGO and Pd_3Co/RGO electrodes are shown in Fig.1. SEM analysis for the electrodes containing RGO revealed the presence of large, transparent graphene sheets with few layers. Metal naoparticles were too small to be detecting at the maximum resolution.
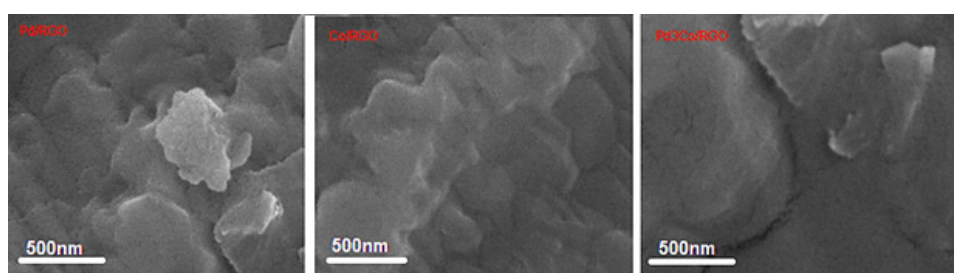
electrocatalysts. The first peak in all the XRD patterns is attributable to the graphene support. The other three peaks are characteristics of face-centered-cubic (fcc) crystalline Pd corresponding to the (1 1 1), (2 0 0) and (2 2 0) planes indicating that all the catalysts generally resemble a single-phase disordered structure (solid solution) matching that of JCPDS file 87-0638 [18].
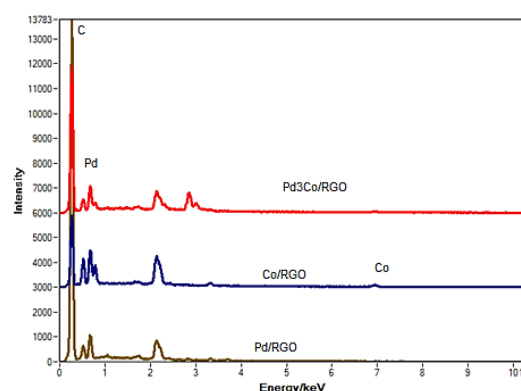

Fig.2 EDX spectra for three typical catalysts.

In the Pd/RGO catalyst these three diffraction peaks for the Pd_3Co/RGO bimetallic electrocatalysts are shifted slightly to higher 2Θ values with respect to the

Fig.1. SEM micrograph of the surface of the Pd_3Co/RGO, Pd/RGO and Co/RGO

The practical compositions of the graphene oxide (GO) supported Pd_3Co electro catalysts were estimated by ICP analysis and EDX analysis. The EDX pattern of Pd_3Co/RGO,Pd/RGO and Co/RGO is displayed in Fig. 2. The ICP and EDX compositions of the prepared electro catalysts (atomic ratio) are remarkably close to the original stoichiometric values, indicating that Pd and Co could be co-reduced and that Co may be alloyed with Pd in this synthesis method. Fig. 3 shows the XRD patterns of the Pd_3Co/G bimetallic

corresponding peaks. Such angle shifts reveal an alloy formation between Pd and Co and specify a lattice contraction which is caused by the incorporation of Co into the Pd fcc structure. Similar data has been reported by Gharibi et al. [19]. Moreover, the lattice parameter was estimated to be 3.8635 Å for Pd_3Co. This value is lower than that of the Pd/G catalyst (a = 3.8792 Å). The decrease of the lattice parameters and the diffraction characteristics of the fcc Pd structure demonstrate the formation of Pd_3Co alloys, reflecting
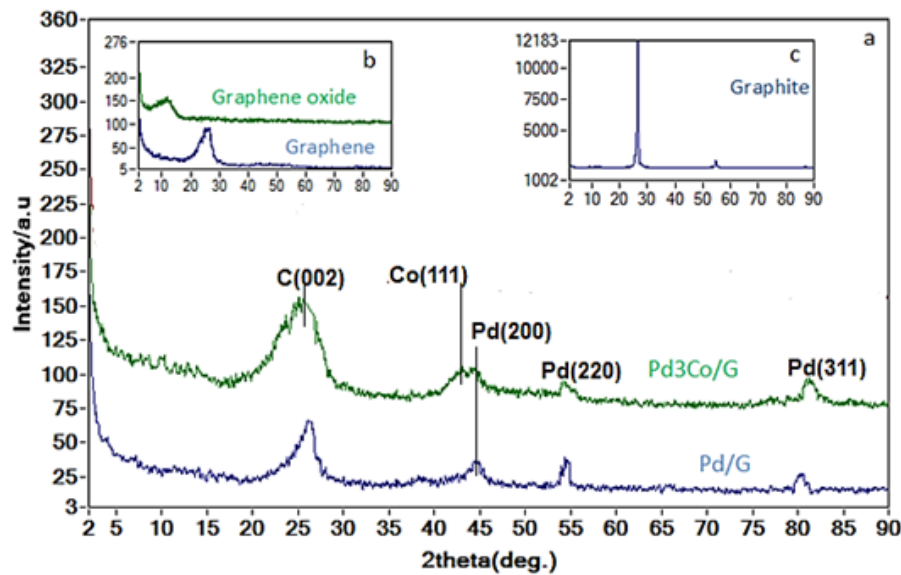
Fig.3. XRD patterns of the Pd₃Co/RGO, Pd/RGO and Co/RGO electrocatalysts. Each spectrum was arbitrarily shifted along the y-axis to facilitate comparison.

the lattice contraction for partial replacement of Pd by other elements [20-21].

The crystallite sizes were estimated from the (2 2 0) diffraction plane according to Scherer's equation, yielding values of 6 and 4 nm for the Pd₃Co/RGO and Pd/RGO catalysts, respectively. Surface area of the catalysts was calculated using the equation Asp = 6000/pd where p (p Pd = 2.0 g cm⁻³ pCo = 8.9 g cm⁻³).

contraction upon alloying.

3.2. Electrochemical characteristics

The electrochemical behavior of different electrodes was investigated by cyclic voltammetry (CV) at 50 mV/s and H_2SO_4 0.5M (Fig. 4). At low potentials, between 0.1 to and -0.35 V, the typical peaks are
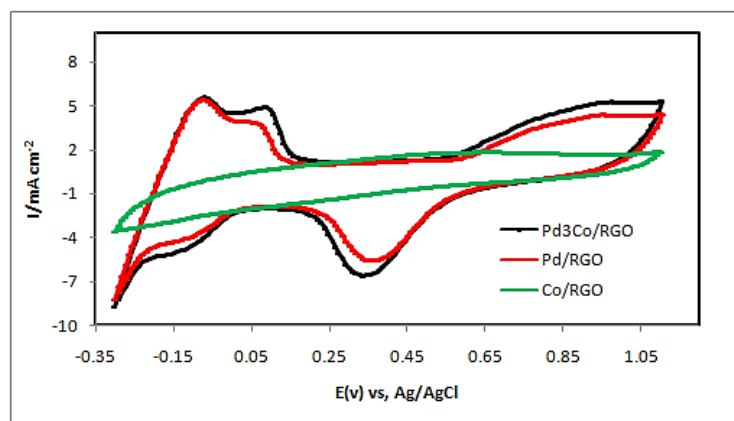

Fig.4. Cyclic voltammograms of Pd₃Co/RGO, Pd/RGO and Co/RGO electrocatalysts in 0.5 M H_2SO_4 at 50 mV/s and room temperature

The lattice parameters and Pd–Pd interatomic distances obtained for Pd₃Co/C bimetallic electrocatalysts are smaller than that of Pd/C, indicative of a lattice

attributed to hydrogen adsorption/desorption on Pd nanoparticles. At high potentials, from a potential greater than 0.65 V, a broad oxidation peak could be

attributed to the transformation of the palladium metal present in the surface film into palladium (II) oxide (PdO). The corresponding peak between 0.55 and 0.2 V in the reverse scan is ascribed to the reduction of Pd (II) oxide into elemental Pd. It should be noted that Pd is inherently a hydrogen-storage metal and certainly absorbs a certain amount of hydrogen into the interior of the lattice space, resulting in the fact that it is impossible to quantitatively differentiate between under potential deposited hydrogen ((HUPD) and absorbed hydrogen ((Habs) [3]. So, the electrochemical active surface area (EASA) of the Pd-based catalyst is measured by the Pd oxide reduction analysis [3, 11]. The EASA of the Pd/RGO and Pd_3Co/RGO electrodes were calculated to 40 and 53 m2/g, respectively.

Fig. 5 shows the polarization and power density curves of the MEAs based on Pd_3Co/RGO, Pd/RGO and Pt/ C electrocatalysts as a cathode in passive DMFC under identical testing conditions filled with 1.0 M methanol

supported Pd_3Co electro-catalyst as a cathode electrode has high catalytic activity for ORR in comparison with data reported by Gharibi et al. on other supports [22].

4. Conclusions

A facile and efficient synthesis process to obtain Pd_3Co/RGO nanostructures was presented. Graphene oxide-supported Pd–Co nanoparticles with a mean diameter of 6 nm were produced using a simple one-step controllable chemical reduction method without allowing total graphene oxide to be reduced to graphene. Following characterization, using XRD, SEM, the Pd–Co nanoparticles were shown mainly to be present in the form of a Pd–Co alloy and RGO. Finally, it can be concluded the MEA based on Pd_3Co/RGO catalyst is a perfect candidate as a cathode in DMFC which is highly desirable for small-scale DMFC portable devices and micro electromechanical
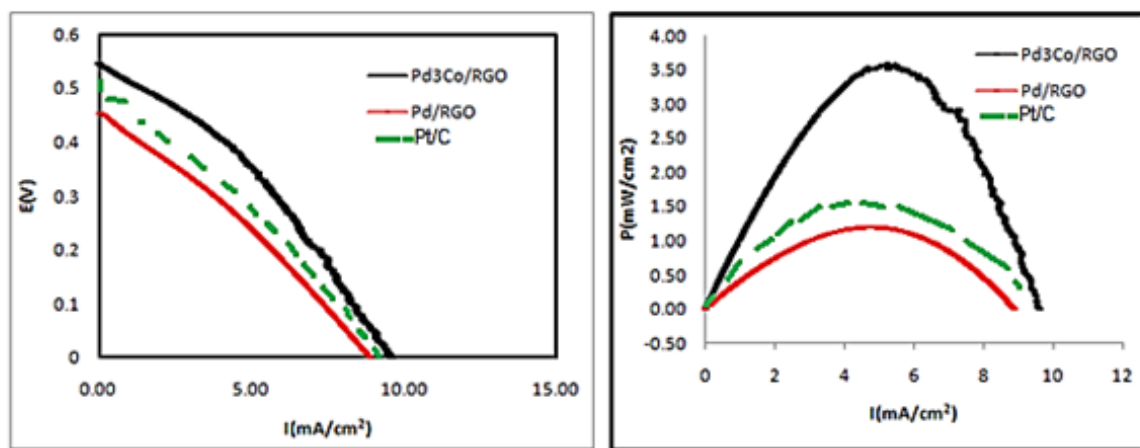

Fig.5. Performance of the MEAs based on Pd₃Co/RGO, Pd/RGO and Pt/C in passive DMFC. The concentration of Methanol 1.0 M, at anode side   and cathode catalyst loading: 3.0 mg cm⁻².

solution. The difference in performance is more pronounced in the low current density region, where the activation over-potential of the MEA based Pd_3Co/RGO is approximately higher than MEA based on Pd/RGO and commercial Pt/C. The better performance of the MEA based on Pd_3Co/RGO suggests that using the reduced graphene oxide

systems.

5. References

[1] Bianchini C, Shen PK. Palladium-Based Electrocatalysts for Alcohol Oxidation in Half Cells

and in Direct Alcohol Fuel Cells. Chem Rev. 2009;109(9):4183-206.

[2] Liu H, Song C, Zhang L, Zhang J, Wang H, Wilkinson DP. A review of anode catalysis in the direct methanol fuel cell. Journal of Power Sources. 2006;155(2):95-110.

[3] Kakaei K, Gharibi H. Palladium nanoparticle catalysts synthesis on graphene in sodium dodecyl sulfate for oxygen reduction reaction. Energy. 2014;65:166-71.

[4] Song S, Tsiakaras P. Recent progress in direct ethanol proton exchange membrane fuel cells (DE-PEMFCs). Appl Catal B Environ. 2006;63(3–4):187-93.

[5] Kakaei K, Zhiani M. A new method for manufacturing graphene and electrochemical characteristic of graphene-supported Pt nanoparticles in methanol oxidation. Journal of Power Sources. 2013;225:356-63.

[6] Kakaei K. One-pot electrochemical synthesis of graphene by the exfoliation of graphite powder in sodium dodecyl sulfate and its decoration with platinum nanoparticles for methanol oxidation. Carbon. 2013;51:195-201.

[7] Kakaei K, hasanpour k. Synthesis of graphene oxide nanosheets by electrochemical exfoliation of graphite in cetyltrimethylammonium bromide and its application for oxygen reduction. J Mater Chem A. 2014.

[8] Baldauf M, Preidel W. Status of the development of a direct methanol fuel cell. J Power Sources. 1999;84(2):161-6.

[9] Dinh HN, Ren X, Garzon FH, Piotr Z, Gottesfeld S. Electrocatalysis in direct methanol fuel cells: in-situ probing of PtRu anode catalyst surfaces. J Electroanal Chem. 2000;491(1–2):222-33.

[10] Xu C, Shen Pk, Liu Y. Ethanol electrooxidation on Pt/C and Pd/C catalysts promoted with oxide. J Power Sources. 2007;164(2):527-31.

[11] Kakaei K, Dorraji M. One-pot synthesis of Palladium

Silver nanoparticles decorated reduced graphene oxide and their application for ethanol oxidation in alkaline media. Electrochim Acta. 2014;143:207-15.

[12] Ahmed MS, Jeon S. Highly Active Graphene-Supported NixPd100–x Binary Alloyed Catalysts for Electro-Oxidation of Ethanol in an Alkaline Media. ACS Catal. 2014;4(6):1830-7.

[13] Awasthi R, Singh RN. Graphene-supported Pd–Ru nanoparticles with superior methanol electrooxidation activity. Carbon. 2013;51:282-9.

[14] Zhang F, Wen M, Cheng M, Liu D, Zhu A, Tian Y. Pt–NiCo Nanostructures with Facilitated Electrocatalytic Activities for Sensitive Determination of Intracellular Thiols with Long-Term Stability. Chem Eur J. 2010;16(36):11115-20.

[15] Gharibi H, Golmohammadi F, Kheirmand M. Palladium/Cobalt Coated on Multi-Walled Carbon Nanotubes as an Electro-catalyst for Oxygen Reduction Reaction in Passive Direct Methanol Fuel Cells. Fuel Cells. 2013;13(6):987-1004.

[16] Kakaei K. Decoration of graphene oxide with Platinum Tin nanoparticles for ethanol oxidation. Electrochim Acta. 2015;165:330-7.

[17] Zhang L, Lee K, Zhang J. Effect of synthetic reducing agents on morphology and ORR activity of carbon-supported nano-Pd–Co alloy electrocatalysts. Electrochim Acta. 2007;52(28):7964-71.

[18] Navaladian S, Viswanathan B, Varadarajan TK, Viswanath RP. A Rapid Synthesis of Oriented Palladium Nanoparticles by UV Irradiation. Nanoscale Res Lett. 2009;4(2):181-6.

[19] Gharibi H, Golmohammadi F, Kheirmand M. Palladium/Cobalt Coated on Multi-Walled Carbon Nanotubes as an Electro-catalyst for Oxygen Reduction Reaction in Passive Direct Methanol Fuel Cells. Fuel Cells. 2013;13(6):987-1004.

[20] Zheng J-N, He L-L, Chen F-Y, Wang A-J, Xue M-W, Feng J-J. A facile general strategy for synthesis of palladium-based bimetallic alloyed nanodendrites with enhanced electrocatalytic performance for methanol and ethylene glycol oxidation. J Mater Chem A. 2014;2(32):12899-906.

[21] Li N, Tang S, Meng X. Reduced Graphene Oxide Supported Bimetallic Cobalt–Palladium Nanoparticles with High Catalytic Activity towards Formic Acid Electro-oxidation. J Mater Sci Technology. 2015;31(1):30-6.

[22] Gharibi H, Golmohammadi F, Kheirmand M. Fabrication of MEA based on optimum amount of Co in PdxCo/C alloy nanoparticles as a new cathode for oxygen reduction reaction in passive direct methanol fuel cells. Electrochim Acta. 2013;89:212-21.