



Advances in Material & Processing Technologies Conference

Effect of Synthesis Methods on Methanol Oxidation Reaction on Reduced Graphene Oxide Supported Palladium Electrocatalysts

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Abstract

Direct methanol fuel cells (DMFCs) have been found to be an efficient power source for portable electronic products that uses methanol as fuel. The intermediate species, carbon monoxide (CO) that forms owing to the incomplete oxidation of methanol poison the catalysts and thus leads to low stability and methanol oxidation reaction (MOR). Palladium (Pd) emerges as a potential electrocatalyst with better tolerance to CO-poisoning and is cheaper than the currently used platinum (Pt) electrocatalyst. Synthesis method has been reported to have prominent effect on the catalytic performance. In this study, Pd nanocatalysts were loaded on reduced graphene oxide (rGO) by two methods, the microwave and hydrothermal synthesis methods, designated as Pd/rGO_M and Pd/rGO_H. X-ray powder diffraction (XRD), field emission scanning electron microscopy (FESEM) coupled with energy dispersive X-ray spectroscopy (EDX) and Raman spectroscopy were used to investigate the structure and morphology of rGO supported Pd electrocatalysts (Pd/rGO). The methanol oxidation activity and stability were evaluated by cyclic voltammetry (CV) and chronoamperometry (CA). Electrocatalysts synthesized by both methods showed uniform loading on the surface of graphene. Pd/rGO_M showed higher methanol oxidation activity, larger electrochemically active surface area (ECSA) and better stability over the Pd/rGO_H which could be due to the much smaller particle size of the former electrocatalyst.

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Peer-review under responsibility of the organizing committee of the Urban Transitions Conference

Keywords: Graphene; palladium nanocatalysts; electrocatalysts; methanol oxidation reaction; microwave synthesis; hydrothermal synthesis.

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1. Introduction

Fossil fuels have been important resources to generate energy for worldwide usage. Nonetheless, its scarce reserve and negative impacts on the environment such as air pollution and global warming have sparked interests of scientists and engineers to explore alternative energy supply [1]. Fuel cells are one of the most popular renewable energy devices which directly convert chemical energy into electric energy. Among the various types of fuel cells, DMFCs attain great attention owing to its cheap liquid fuel, reduced emission of pollutants, high efficiency, low operating temperature, high theoretical energy density and relatively quick start-up [2].

Pt has been widely used as electrocatalysts for both anodes and cathodes in DMFCs. Unfortunately, its limited reserve, low resistance to methanol oxidation and high cost that account for half of the cost DMFCs have hindered it from being commercialized [3, 4]. On the contrary, Pd is found as a suitable substitute. Compared to Pt, Pd is cheaper, 50 times more abundant on earth, has higher tolerance to CO intermediate poisoning and better stability during methanol oxidation reaction [5, 6]. Despite the above mentioned superiorities, Pd electrocatalysts share a similar problem with Pt and many other free standing electrocatalysts, aggregation, which greatly reduces their specific surface area and thus inferior performance.

Loading catalysts onto catalyst supports has been proved effective to avoid aggregation and maximize the surface area for electron transfer as well as mass transportation to and from electrocatalysts [7, 8]. Since the successful synthesis of single-layered graphene via “Scotch-tape” method in 2004, it grabs great attention of scientific communities [9]. Its unique structures, atomically thin and sp^2 hybridized two-dimensional honeycomb lattice, endow it excellent electrical conductivity (10^5 - 10^6 Sm^{-1}), extremely large specific surface area (~ 2630 m^2g^{-1}) and high thermal conductivity (5300 W/mK) [10, 11]. Among various synthesis approaches of graphene supported Pd, hydrothermal method renowned for the relatively low temperature, fast reaction kinetics and scalable process has been widely applied [8]. Microwave synthesis is another method characterized by homogeneous and rapid heating. With microwave heating, the reduction time was successfully shortened to about a few minutes [12, 13]. Nonetheless, there is so far no report on the difference in morphology and MOR of Pd/rGO electrocatalysts synthesized using these two methods. In this study, Pd precursors and GO were co-reduced by either microwave or hydrothermal method to get Pd/rGO. The surface morphology, crystallinity and defect levels were examined by FESEM, XRD and Raman measurements. The electrochemical performance and ECSA were evaluated using CV and CA.

2. Experimental

2.1 Preparation of Pd/rGO

Graphite flake was oxidized to graphite oxide by improved Hummer’s method published elsewhere with some modification but the main features are briefly illustrated here [14]. The concentrated sulfuric acid (H_2SO_4) was mixed with concentrated phosphoric acid (H_3PO_4) at a ratio of 360:40 mL followed by the addition of 3g of graphite flake (50 mesh). Then, 18 g of potassium permanganate (KMnO_4) was added into the above mixture and stirred. After 3 days of stirring, by immersing in ice bath, 500 mL of deionized (DI) water was added to the above mixture and 17 mL of hydrogen peroxide (H_2O_2) was added dropwise to reduce excess KMnO_4 , so the oxidation process stopped. The mixture was then sequentially washed by 1M of fuming hydrochloric acid (HCl, 37%) for 3 times at 6,000 rpm for 30 minutes and by DI water for 7 times at 10,000 rpm for 1 hour by using centrifuge. Next, the synthesized graphite oxide was dried overnight at 60°C in oven.

The dried graphite oxide (40mg) was dispersed in 20 mL of DI water and ultrasonicated for 2 hours to obtain graphene oxide. To synthesize Pd/rGO, 40 mg of PdCl_2 was added and sonicated for 30 minutes. Then, the above mixture was stirred for 1 hour at room temperature. Meanwhile, 40 mL of ethylene glycol (EG) was added drop by drop. The pH of the mixture was then adjusted to 9 by 1M of sodium hydroxide (NaOH). Subsequently, the mixture was microwave reduced by household microwave oven at 700 W for 100s or hydrothermally reduced in a polytetrafluoroethylene lined stainless steel autoclave for 2 hours at 210°C , designated as Pd/rGO_M and Pd/rGO_H, respectively. Finally, the resulting black solid powders were washed by DI water via centrifugation at 10,000 rpm for 30 minutes and dried overnight in an oven at 60°C .

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