Synthesis of silver/nitrogen-doped reduced graphene oxide through a one-step thermal solid-state reaction for oxygen reduction in an alkaline medium

Li Ting Soo [a], Kee Shyuan Loh [a, *], Abu Bakar Mohamad [a, b], Wan Ramli Wan Daud [a, b], Wai Yin Wong [a, c]

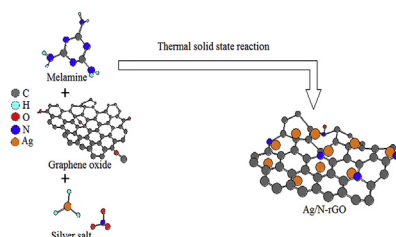[a] Fuel Cell Institute, Universiti Kebangsaan Malaysia, 43600 Bangi UKM, Selangor, Malaysia
[b] Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 Bangi UKM, Selangor, Malaysia
[c] School of Engineering, Taylor's University Lakeside Campus, No. 1, Jalan Taylor's, 46500 Subang Jaya, Selangor, Malaysia

HIGHLIGHTS

- Facile synthesis of Ag/N-rGO catalyst via a solid-state thermal method.
- The ORR performance of Ag/N-rGO catalyst was evaluated by CV and RRDE.
- The synergism effect of the Ag/N-rGO catalyst towards ORR was discussed.
- N-rGO support provides active sites for metal deposition and ORR.

GRAPHICAL ABSTRACT

ABSTRACT

One of the obstacles to the commercialisation of fuel cells is the high cost of noble metals, such as platinum, that are used as electrocatalysts. Silver-incorporated nitrogen-doped reduced graphene oxide (Ag/N-rGO) has been synthesised through the simple annealing of metal salts with graphene oxide and melamine. The presence of silver and nitrogen atoms in Ag/N-rGO was confirmed by X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS) analysis. Both the XPS and EDS results showed a higher Ag loading on the N-rGO surface compared with the rGO surface. Transmission electron microscopy (TEM) images revealed a wide size distribution of Ag particles loaded on the N-rGO surface. Electrochemical results indicate that N-rGO is a better support for Ag than rGO. Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) results indicate that Ag/N-rGO is a potential ORR catalyst candidate in alkaline as it exhibited an onset potential of -0.15 V vs. Ag/AgCl and a limiting diffusion current density of -4.38 mA cm^{-2} with four electron pathways. In addition, Ag/N-rGO also showed better methanol tolerance than Pt/C.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

A fuel cell is a clean and high-efficiency device that directly converts chemical reactions to electricity, resulting in low emission of pollutants and low environmental impact. The oxygen reduction reaction (ORR) at the cathode is kinetically sluggish, and the rate of

the reaction is six-fold slower than that of the oxidation of hydrogen (HOR) at the anode [1]. Platinum-based catalysts are commonly used in fuel cells to accelerate the rate of reaction at both the anode and cathode. However, the high cost and scarcity of Pt has prohibited the large-scale application of fuel cells. Consequently, non-Pt catalysts have been extensively investigated to replace Pt-based catalyst and thus reduce the material cost of fuel cells. For alkaline fuel cells, alternative catalysts much cheaper than Pt are available. Several groups have reported that high ORR performance was observed in alkaline electrolyte using non-Pt metal catalysts, such as ferrous- [2], cobalt- [3—5], manganese oxide- [6], nickel- [7], and silver-based [8,9] catalysts. In addition, various metal-free electrocatalysts for ORR in alkaline electrolyte, such as nitrogen-doped carbon materials [10—12], have also been extensively investigated in the past few years.

A variety of methods have been reported to produce this type of non-Pt catalyst: (1) heat treatment of a mixture consisting of metal salts and a nitrogen containing salt or polymer in an inert atmosphere [5,13]; (2) heat treatment of metal salts in an ammonia or acetonitrile atmosphere [14]; (3) wet chemical reduction of the metal supported on the carbon support via a reducing agent, such as sodium borohydride, hydrazine, etc. [15]; and (4) electrodeposition of metal on the carbon support from an electrolytic bath consisting of metal salts by cyclic voltammetry (CV) [16].

Permeation of the methanol fuel from the anode compartment to the cathode compartment (methanol crossover) is one of the technical challenges in a direct methanol fuel cell (DMFC) system. Simultaneous methanol oxidation and oxygen reduction reactions take place on the cathode due to the unresolved methanol crossover issue. This leads to the rise of mixed potentials in the cathode and consequently contributes to the performance loss in the fuel cell system. Therefore, it is important to investigate the selectivity of an electrocatalyst towards ORR in the presence of methanol. Several groups have reported enhanced activity of Pd—Ag-based catalysts [17] and heteroatom-doped carbon materials [18,19] towards selective ORR compared with Pt/C in the presence of methanol in the alkaline solution.

In this paper, we have developed a non-noble metal catalyst through thermal annealing of silver nitrate supported on nitrogen-doped graphene under an N_2 atmosphere. Silver metal is less expensive and more abundant than noble metals, such as Pt and Pd. The market price of Ag is 1/60th the price of Pt. Moreover, recent studies have demonstrated that thermal annealing is a cost-effective method for large-scale production of graphene-based catalysts [19—21].

2. Experimental

2.1. Materials

Graphite flakes, sulfuric acid (95.0—98.0%), melamine, urea, potassium permanganate, and sodium nitrate were commercially obtained from Sigma-Aldrich. Hydrochloric acid (fuming; 37%) was supplied by Merck corporation from 64271 Darmstadt, Germany, and hydrogen peroxide was obtained from System (40150 Shah Alam, Selangor, Malaysia). All of the materials were of analytical grade and were used without further purification. Deionized water was obtained from the lab and was used throughout the experiment.

2.2. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was prepared according to Hummer's method, with modification [22]. Briefly, 3.0 g of graphite flakes, 1.5 g of sodium nitrate and 100 ml of 95.0—98.0% concentrated

H_2SO_4 were added into an 800-ml beaker in an ice bath with the temperature maintained below 5 °C. Subsequently, 12.0 g of potassium permanganate was slowly added to the mixture over 1 h at the same temperature. The mixture was then allowed to stir for one night. Next, 150 ml of deionized water was slowly added to the dark brown slurry, whereby white smoke was forcefully released. The slurry was allowed to stir for another 24 h. Fifteen millilitres of 30 wt% H_2O_2 was added to the slurry. A spontaneous change in colour from brown to yellow was observed, indicating the successful oxidation of graphite oxide. The yellow slurry was then washed with 5% HCl 5 times to remove the excess metal ions. Finally, it was washed with excess deionized water ~15 times. The brown dispersion was then dried in the oven at 70 °C for further testing.

2.3. Synthesis of silver-decorated nitrogen-doped reduced graphene oxide (Ag/N-rGO)

An aqueous GO suspension (3 mg/ml) was prepared by dissolving 0.3 g of GO in 100 ml of deionized water with 1 h of sonification. Seventy milligrams of silver nitrate was dissolved in 50 ml of 95% ethanol, which was then added to the GO suspension for another 30 min of sonification. The mixture was allowed to dry in the oven at 90 °C for 24 h to evaporate the solvent. The obtained solid mixture and melamine powder were ground evenly in a mortar. The powder mixture was loaded on a quartz boat before insertion into a quartz tube placed inside a horizontal furnace for thermal annealing. The thermal annealing process was performed at 900 °C under N_2 flow for 1 h with a heating rate of 10 °C/min. A high annealing temperature of 900 °C was used in this work because synthesis of the Ag-based catalyst through the thermal annealing process at more than 800 °C had not yet been reported.

2.4. Physical characterisation

Ag/N-rGO was characterised by transmission electron microscopy (TEM) using an HT7700 microscope and field emission scanning electron microscopy (FESEM) with a SUPRA 55 VP model to study its surface morphology. For TEM characterisation, the catalyst was suspended in isopropyl alcohol, and a drop of the suspension was placed on a copper grid, followed by solvent evaporation in a vacuum at room temperature (~25 °C). An X-ray diffractometer (XRD) model Bruker D8 Quest SC-XRD was used to analyse the crystallinity of the samples. The diffraction angle 2θ from 10° to 80° was used. X-ray photoelectron spectroscopy (XPS) was performed on an Axis ultra DLD X-ray photoelectron spectrometer using Al-Kα sources to analyse the surface composition of the catalyst. Raman spectra were recorded on a WITec Alpha 300R spectrometer with an excitation wavelength of 514 nm to determine the chemical structure of the samples by measuring molecular vibrations.

2.5. Electrochemical characterisation

CV and rotating ring-disk electrode (RRDE) (Gamry Instruments, Inc) measurements were conducted using a potentiostat (Autolab PGSTAT 128N) to study the catalytic activity of the as-prepared catalysts for oxygen reduction in a KOH electrolyte. Three electrode systems that included platinum wire, Ag/AgCl and glassy carbon were used as counter, reference and working electrodes. One milligram of catalyst was dissolved in a 1-ml mixture of deionized water and Nafion solution (9:1 v/v) and homogenised for 3 min. Twenty micro litres of the catalyst ink was then drop-casted on the glassy carbon electrode with a 5-mm diameter and then dried overnight before the measurement was performed. The