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Comparison of nitrogen-doped graphene and carbon nanotubes as supporting material for iron and cobalt nanoparticle electrocatalysts toward oxygen reduction reaction in alkaline media for fuel cell applications

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ABSTRACT

In this work the electrocatalytic performance of nitrogen-doped graphene (NG)-based non-precious metal (NPM) catalysts for oxygen reduction reaction (ORR) have been compared with their counterparts while supported on multiwalled carbon nanotubes (MWCNTs). Fe and Co nanoparticles were precipitated on NG (M/NG, M = Fe, Co) and for comparison on MWCNTs (M/MWCNT, M = Fe, Co) using a modified polyol method. The electrocatalytic properties of all catalysts towards oxygen reduction reaction in 0.1 M KOH solution were investigated. In comparison with M/MWCNTs, M/NG catalysts exhibited higher ORR activity, which indicates a better electrocatalytic performance of nitrogen-doped graphene compared to those which were supported by MWCNTs. Chronoamperometric results also demonstrated that the Co/NG catalyst was more stable for ORR in alkaline solution rather than Co/MWCNT and commercial Pt/C.

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Introduction

Fuel cells have been considered clean energy-converting devices due to their high efficiency and eco-friendly functions. Oxygen reduction reaction (ORR) have crucial effect on fuel cells performance, as ORR determine the overall function of these energy storage and conversion systems. The alkaline fuel cells (AFCs) are preferred over polymer electrolyte

membrane (PEM) fuel cells because of less corrosive environment and having more facile kinetics for oxygen reduction reaction (ORR) [1,2]. However, the sluggish oxygen reduction reaction (ORR) usually requires to be catalyzed by Pt-based electrocatalysts, which exhibit excellent catalytic activity [3,4], but suffer from prohibitive cost, limited supply and poor stability [5,6]. Within the past few years, researchers have turned to non-precious metal containing catalysts (NPMCs)

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[7–9] and modification of carbon supporting materials in order to improve ORR activity and durability [10,11]. The Pt alternative candidates that have been highly regarded have been synthesized by heating precursors comprising nitrogen, carbon, and geologically abundant transition metals, such as iron and cobalt ($M = \text{Co}$ and/or Fe) in particular [12–14]. Among all the non-Pt catalysts, the graphene doped by hetero atoms [15–17] or modified by transition metal [18,19] with satisfying performance toward ORR have been demonstrated; however, the exact nature of active sites in these electrocatalysts is still under debate [20,21].

Among different carbon nanomaterials, graphene possesses intriguing properties, such as high specific surface area, superior electric conductivity and excellent mechanical elasticity as a supporting material [22,23]. Compared with carbon nanotubes, graphene has a unique basal plane structure, which makes it possible to load microspheres with a diameter size even bigger than several hundred nanometers. However, when the size of nanoparticles on carbon nanotubes is in the same range as, or larger than, the diameter of the CNTs, a good decoration is usually difficult to achieve. On the other hand, graphene materials can be produced at high levels and at affordable prices [11,24–26]. These properties make graphene a highly promising electrocatalyst support. Recent studies show that the incorporation of nitrogen atoms in carbon nanostructures enhances the interaction between metal nanoparticles and supporting materials [27], and creates more defect sites on graphene structures, which leads to more electro-active sites for ORR and active sites for metal nanoparticles deposition [28–30]. All of these items together show the advantages of nitrogen-doped graphene (NG), with its superior electrocatalytic performance, as a supporting material compared to carbon nanotubes.

Recently Du et al. [31] synthesized nitrogen-doped nanocomposites containing Fe, Co and Ni nanoparticles and have evaluated the ORR in alkaline media. It has been reported that Co/N/C and Fe/N/C were more active for ORR than Ni/N/C and Fe/N/C demonstrated more positive onset potential than that of the benchmark commercial Pt/C. Co/N/C showed a higher limiting current density (based on the geometric area of the electrode) relative to Fe/N/C. The different current of samples was ascribed to the difference in factors, such as particle size, surface area, and metal/nitrogen/oxygen content. Kong et al. [32] also compared the ORR performance of nitrogen-containing transition metal (Fe, Co) catalysts in alkaline and acidic media. It was reported that the origin of excellent ORR catalytic activity of mesoporous Fe (or Co)- N_x -C in both electrolytes was attributed to Fe (or Co)- N_x moieties embedded within the graphitic carbon frameworks.

In the past few years numerous works have also been conducted on the catalysts supported on carbon nanotubes by various researchers [33–35]. However, the comparison between non-precious metal catalysts supported on nitrogen-doped graphene and those supported on carbon nanotubes could be an interesting new area of research, which can be beneficial for the production of low cost and active catalysts. Furthermore, it would give scientists a better view on the carbon supporting materials. In the present work, a simple two-step method was used for the synthesis of transition metal catalysts (Fe, Co) supported on both NG and carbon

nanotubes, and the catalytic performance of synthesized catalysts was compared for ORR in alkaline media.

Experimental

Synthesis of N-doped graphene

In a simple solvothermal procedure, 1 g of pentachloropyridine ($\text{C}_5\text{Cl}_5\text{N}$ from Merck) was placed in a stainless steel autoclave reactor then 1 g of metallic potassium (K from Sigma Aldrich) was added to the autoclave. The autoclave was then heated to the target temperature (120 °C). After 10 h of reaction, the salty-dark precipitate product was filtered and washed with acetone, absolute ethanol and water in sequence and was then dried in a vacuum oven at 80 °C for 4 h [36].

Functionalization of MWCNT

MWCNTs (purity min. 95%; diameter 5–20 nm; length 1–10 mm) purchased from PlasmaChem GmbH. Before the precipitation of metal nanoparticles, MWCNTs were functionalized with $-\text{C}=\text{O}$, $-\text{COO}$ and $-\text{C}-\text{OH}$ groups by refluxing in a 65% nitric acid solution at about 110 °C for 6 h.

Synthesis of M/NG and M/MWCNTs ($M = \text{Fe}, \text{Co}$)

In the second step, transitional metals, iron and cobalt, nanoparticles were precipitated on synthesized NG sheets and in order to compare the activity and performance of supporting materials toward ORR, through a similar process, iron and cobalt nanoparticles were also deposited on functionalized carbon nanotubes as described below.

Briefly, 20 mg of NG (or MWCNTs) was first dispersed in a 1.5 mL mixture of ethylene glycol (EG) ($\text{C}_2\text{H}_6\text{O}_2$ from Merck) and deionized (DI) water (the volume ratio was EG:DI water 2:1) and sonicated for 1 h. Then, the calculated amount of two transitional metal salts, 57.87 mg of iron nitrate ($\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from Merck) and 39.5 mg of cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ from Merck) were separately dispersed in ethylene glycol (0.5 mL) and added to the NG (or MWCNTs) dispersion drop-wise. After stirring for 1 h, the mixture was adjusted to pH 7 by drop-wise addition of sodium hydroxide (NaOH from Merck; 2.5 M) and heat treated at 60 °C for 1 h to complete the reduction process of entire Fe and Co. Finally, the catalyst slurry was centrifuged and washed three to four times with deionized water and dried at 70 °C for 8 h in a vacuum oven. Iron and cobalt loading for all samples was around 40 wt. % with respect to support material by ICP measurements.

Physical characterizations

Scanning electron microscopy

Scanning electron microscopy images were obtained using a Hitachi S-4160 microscope operated at an accelerating voltage of 20 kV.

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