Journal of Power Sources 198 (2012) 122–126

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

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

Short communication

Catalytic activity of graphene–cobalt hydroxide composite for oxygen reduction reaction in alkaline media

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ARTICLE INFO

Article history:
Received 21 August 2011
Received in revised form 2 October 2011
Accepted 3 October 2011
Available online 8 October 2011

Keywords:
Oxygen reduction reaction
Graphene
Cobalt hydroxide
Rotating ring-disk electrode
Disproportionation

ABSTRACT

The electrocatalysis of graphene–cobalt hydroxide ($Co(OH)_2$) composite towards oxygen reduction reaction (ORR) in 0.1 M KOH is studied with $Co(OH)_2$/graphene-modified glassy carbon (GC) electrode using cyclic and rotating ring-disk electrode voltammetry. The electrode is prepared by casting of graphene suspension on GC electrode and subsequent electrodeposition of $Co(OH)_2$ from $Co(NO_3)_2$ solution. A characteristic interlaced nanowalls morphology is observed for $Co(OH)_2$ with scanning electron microscopy. Raman spectra demonstrate the microstructure of graphene changes during electrochemical treatment in nitrate solutions, which has a great impact on its catalysis towards ORR. At GC electrode, two reduction processes both attributed to 2-electron reduction are recorded for ORR. The presence of $Co(OH)_2$ on GC electrode results in larger peak current without obvious potential shift due to its good catalytic activity towards the disproportionation of intermediates. Graphene not only increases the peak current and shifts the peak potential in the positive direction, but also leads to further reduction of HO_2^- at the second step. After electrochemical treatment in nitrate solutions, graphene is activated to catalyze the disproportionation of HO_2^- effectively, and its cooperation with $Co(OH)_2$ enables reduction of O_2 to OH^- at lower overpotential. Graphene–$Co(OH)_2$ composite is a potential electrode material for air cathodes in alkaline electrolyte electrochemical systems.

1. Introduction

Interest in alkaline fuel cells has been resurging in recent years, due to the alleviation of carbon dioxide poisoning problem with the development of anion exchange membrane [1]. As a low-temperature energy conversion technology, the sluggish oxygen reduction reaction (ORR) at the cathode decreases energy efficiency and power density. Thus, catalysts with high activity towards ORR are highly desirable. Pt and Pt-based alloys are still the most widely used catalysts for ORR in acid fuel cells for their excellent catalytic activity and stability, but the less corrosive alkaline electrolyte allows the use of non-Pt metals. Until now, many promising non-Pt catalysts have been reported, such as silver [2], manganese oxide and their combination with metal macrocyclic complex or carbon nanotube (CNT) [3–5], nonprecious-metal chalcogenides [6,7], Fe- or Co-based catalysts [8], and nitrogen-doped CNT [9,10].

Graphene, a novel carbon nanomaterial with unique physical and chemical properties, has a good potential in electrochemical application. It has been reported that graphene can be used in electrochemical sensors [11,12], capacitors [13,14], lithium batteries [15,16], solar cells [17], and catalysts for fuel oxidation [18,19]. There are also many reports on its utilization in ORR, either as catalyst support material or as catalyst itself. When used as support material, the supported catalysts are usually precious metals, like Pt, Au, Pd, and their alloys [20–23]. The presence of graphene results in better dispersion of active catalysts and thus improves the catalytic activity and durability [22]. Unlike precious metal catalysts, few studies are concerned about the combination of graphene with non-precious ORR catalysts. When used as catalyst itself, nitrogen-doped graphene is focused due to the fact that the introduction of nitrogen heteroatom creates active site for reduction of O_2 [24–26]. However, the synthesis of nitrogen-doped graphene usually involves chemical vapor deposition [27], nitrogen plasma treatment [28], arc discharge in the presence of protective gases and nitrogen source vapor [29], or high temperature treatment in ammonia [30]. These methods increase the cost and complicate the operation in comparison with chemical reduction of graphite oxide (GO).

In our previous work, we have studied the catalytic activity of graphene synthesized via hydrazine reduction of GO and cobalt hydroxide ($Co(OH)_2$) prepared by galvanostatic electrodeposition towards ORR [31,32]. Both materials show good catalytic activity, in which graphene decreases the reaction overpotential and $Co(OH)_2$ catalyzes the disproportionation of intermediates. Inspired by this,

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doi:10.1016/j.jpowsour.2011.10.007

we attempted to prepare a composite of graphene and $Co(OH)_2$ as ORR catalyst in this study and reduction of O_2 to OH^- did occur at low overpotential in 0.1 M KOH. Furthermore, it was found that graphene could be activated during the potentiostatic electrodeposition of $Co(OH)_2$, and the activated graphene can catalyze the disproportionation of peroxide (HO_2^-), which has not been reported before. To our best knowledge, this is the first report on the catalysis of graphene–$Co(OH)_2$ composite towards ORR.

2. Experimental

2.1. Chemicals and materials

For synthesis of graphene, natural graphite powder (99.99%) was purchased from Beijing Chemical Company (China) and reagents including H_2SO_4 (98%), $NaNO_3$, $KMnO_4$, H_2O_2 (30%), $N_2H_4{\cdot}H_2O$ (85%), and $NH_3{\cdot}H_2O$ (28%) with analytical grade were provided by Sinopharm Chemical Reagent Co. Ltd. (China). $Co(NO_3)_2$ and KOH were utilized to prepare solutions for electrodeposition of $Co(OH)_2$ and electrochemical measurements. Ultra-high purity N_2 and O_2 (Heli Gas Co. Ltd., China) were used for the deaeration of solutions and the preparation of O_2-saturated solutions, respectively. All aqueous solutions were prepared with Milli-Q water (Millipore, USA).

2.2. Synthesis of graphene

Graphene was synthesized via chemical reduction of GO. GO was made by a modified Hummers method [33], which consists of pre-oxidation of natural graphite with concentrated H_2SO_4 and $KMnO_4$, re-oxidation with H_2O_2, and exfoliation by sonication. Then, the chemical reduction of GO was carried out according to the method reported by Li et al. [34]. In brief, 10 mL of GO dispersion with a concentration of 0.5 mg mL^{-1} was mixed with 70 μL $NH_3{\cdot}H_2O$ (28%) and 4 μL $N_2H_4{\cdot}H_2O$ (85%) in a 20 mL glassy vial. After being stirred for 5 min, the vial was put in a water bath (95 °C) for 1 h to obtain graphene dispersion.

2.3. Preparation of modified glassy carbon (GC) electrodes

A rotating ring-disk electrode (RRDE, Pine Research Instrument Inc., USA) with a GC disk (5.61 mm diameter) and a Pt ring (7.92 mm outer diameter and 6.25 mm inner diameter) was used in this study. Prior to the surface modification, the disk electrode was polished with 1.0 and 0.05 μm alumina slurries, and then cleaned by sonication for 15 min. A graphene modified GC (graphene/GC) electrode was prepared by casting the graphene suspension on the disk electrode surface and drying in N_2 atmosphere at ambient temperature. The loading of graphene on the surface of GC electrode was ca. 0.04 mg cm^{-2}. $Co(OH)_2$ was electrodeposited on the graphene/GC or bare GC electrode by applying a potential of −1.1 V vs. Ag/AgCl (KCl-sat.) for 30 s in 10 mM $Co(NO_3)_2$ solution. The deposition of $Co(OH)_2$ can be expressed by the following reactions:

$$NO_3^- + 7H_2O + 8e^- \rightarrow NH_4^+ + 10OH^- \quad (I)$$

$$Co^{2+} + 2OH^- \rightarrow Co(OH)_2 \quad (II)$$

Cathodic reduction of NO_3^- results in the electrogeneration of OH^- (reaction (I)), which causes a steep increase in the pH close to the electrode surface, and then $Co(OH)_2$ precipitation takes places (reaction (II)). To investigate whether the catalytic activity of graphene was affected by electrodeposition process, we also treated the graphene/GC electrode in 20 mM $NaNO_3$ solution in the same manner.

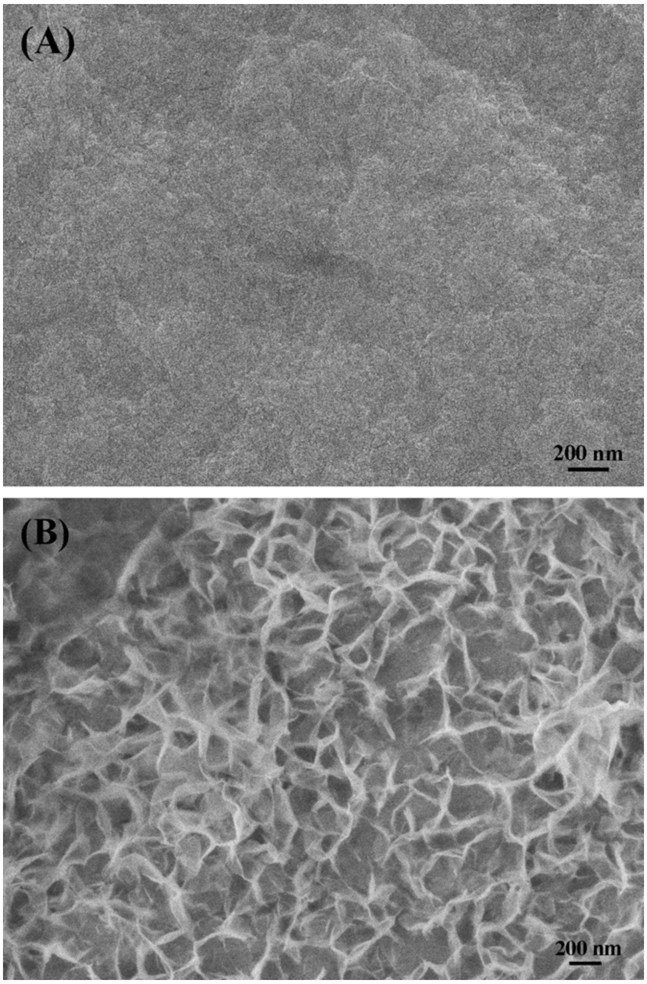

Fig. 1. SEM images of graphene/GC (A) and $Co(OH)_2$/graphene/GC (B) electrodes.

2.4. Electrochemical, scanning electron microscopic, and Raman spectroscopic measurements

Cyclic and RRDE voltammetric electrochemical measurements were performed on a computer-controlled electrochemical analyzer (CHI 760C, CH Instruments, Inc., USA) with a three-electrode electrochemical cell. A Pt wire and a Ag/AgCl (KCl-sat.) electrode were used as the counter electrode and reference electrode, respectively. The working electrodes consisted of GC, graphene/GC, $Co(OH)_2$/GC, $Co(OH)_2$/graphene/GC, and $NaNO_3$-treated graphene/GC disk electrodes and Pt ring electrode. In RRDE measurement, Pt ring electrode was kept at +0.5 V to determine HO_2^- produced at the disk electrode. All potentials are reported vs. the Ag/AgCl (KCl-sat.) electrode. A JOEL JSM-6700F scanning electron microscope (SEM) was employed for morphology observation and Raman Spectra were obtained using a Jobin-Yvon LabRam-Infinity system. All experiments were carried out at room temperature (25 °C).

3. Results and discussion

3.1. SEM images and Raman spectra of modified GC electrodes

SEM images of graphene/GC and $Co(OH)_2$/graphene/GC electrodes are shown in Fig. 1. The graphene film made of many stacked graphene layers exhibits a rough structure, which is an ideal support for depositing nanomaterials. For $Co(OH)_2$ electrodeposited on the surface of graphene film, a characteristic interlaced nanowalls