



# Gently reduced graphene oxide incorporated into cobalt oxalate rods as bifunctional oxygen electrocatalyst



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## ARTICLE INFO

### Article history:

Received 15 December 2013

Received in revised form 6 May 2014

Accepted 7 May 2014

Available online 20 May 2014

### Keywords:

Cobalt oxalate

bifunctional electrocatalyst

graphene

oxygen evolution reaction (OER)

oxygen reduction reaction (ORR)

## ABSTRACT

Water-oxygen electrochemistry is at the heart of key renewable energy technologies (fuel cells, electrolyzers, and metal-air batteries) due to the sluggish kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Although much effort has been devoted to the development of improved bifunctional electrocatalysts, an inexpensive, highly active oxygen electrocatalyst, however, remains to be a challenge. In this paper, we present a facile and robust method to create gently reduced graphene oxide incorporated into cobalt oxalate microstructures (CoC<sub>2</sub>O<sub>4</sub>/gRGO) and demonstrate its excellent and stable electrocatalytic activity in both OER and ORR, arising from the inherent properties of the components and their physicochemical interaction. Our synthesis technique also explores a single pot method to partially reduce graphene oxide and form CoC<sub>2</sub>O<sub>4</sub> structures while maintaining the solution processability of reduced graphene oxide. While the OER activity of CoC<sub>2</sub>O<sub>4</sub>/gRGO is exclusively due to CoC<sub>2</sub>O<sub>4</sub>, which transformed into OER-active Co species, the combination with gRGO significantly improves OER stability. On the other hand, CoC<sub>2</sub>O<sub>4</sub>/gRGO exhibits synergistic effect towards ORR, via a quasi-four-electron pathway, leading to a slightly higher ORR limiting current than Pt/C. Remarkably, gRGO offers dual functionality, contributing to ORR activity via the N-functional groups and also enhancing OER stability through the gRGO coating around CoC<sub>2</sub>O<sub>4</sub> structures. Our results suggest a new class of metal-carbon composite that has the potential to be alternative bifunctional catalysts for regenerative fuel cells and metal-air batteries.

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## 1. Introduction

Increased interest in renewable energy has led to intense efforts to understand the fundamental and applied aspects of old and novel energy conversion and storage technologies. Successful incorporation of renewable energy to society's energy mix requires efficient and green energy storage and reutilization technologies. Among renewable energy storage options, hydrogen has been considered as the most promising energy carrier because it does not produce carbon dioxide as combustion product. Because the energy from most renewable energy systems is easily converted to electricity, water electrolysis is practically the best method to obtain hydrogen. Fuel cells, such as the practically proven alkaline fuel cells (AFCs) [1] for example, can then produce electrical energy from hydrogen

using the reverse reaction of water electrolysis. In addition, metal-air batteries are also attractive technologies for portable energy storage in terms of their excellent specific energy densities.

Water-oxygen electrochemistry is at the heart of several renewable energy technologies, such as water electrolysis, fuel cells, and metal-air batteries, because of the sluggish kinetics in the electrocatalytic reduction and evolution of molecular oxygen that severely limits the efficiency of these devices [2]. Oxygen reduction reaction (ORR,  $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ ) is the ubiquitous cathode reaction in fuel cells, while oxygen evolution reaction (OER,  $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$ ) is the highly controlling anode reaction in electrolysis cells. A vast range of materials has been explored in order to find an active and stable oxygen electrocatalyst. Platinum (Pt), for instance, displays the best performance in ORR, while ruthenium (Ru) and iridium (Ir) oxides are best suited as OER electrocatalysts, in terms of their activity and stability, respectively [3,4].

Although both reactions are present separately in most electrochemical technologies, they can concurrently occur in a unit of electrochemical cells so that the mode of operation is switched

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from fuel cell to electrolysis, which is the case in unitized regenerative fuel cells (URFCs) and rechargeable metal-air batteries [5–9]. Integrating the operation modes into a single cell module is definitely beneficial to save space. The best catalysts discovered so far (Pt, RuO<sub>2</sub>, and IrO<sub>2</sub>), however, are selective only to one specific reaction. Thus, bifunctional oxygen electrocatalysts are conventionally prepared as alloys of precious metals. These precious metal alloys, however, are extremely expensive and the combination is usually detrimental to their respective catalytic performances in ORR and OER. Hence, there is a necessity to find alternative bifunctional electrocatalysts, preferably without using precious metals [10–13].

Cobalt (Co) and its oxides, for example, are widely studied for their excellent OER activity and have been shown also to exhibit bifunctional electrocatalytic property in several instances [3,14–16]. On the other hand, nitrogen-doped (N-doped) graphene has drawn significant attention as a cost-effective catalyst for ORR [17,18]. Recently, Dai's group reported that Co oxide (Co<sub>3</sub>O<sub>4</sub>) nanocrystals on N-doped graphene displayed bifunctional oxygen electrocatalytic ORR activity arising from the synergistic interaction between the metal oxide and graphene [19]. They synthesized the hybrid material by low temperature heating of graphene oxide (GO) and Co precursor for ten hours, followed by simultaneously reducing GO and growing Co<sub>3</sub>O<sub>4</sub> nanocrystals in a pressurized hydrothermal reactor for three hours. Despite these innovative results, however, the search for cheaper bifunctional catalysts that are easily prepared would contribute significantly to making URFCs and metal-air batteries more economically viable.

In this paper, we synthesized a highly active and stable bifunctional electrocatalyst using a facile and energy efficient room temperature process. A low-cost alternative, Co oxalate (CoC<sub>2</sub>O<sub>4</sub>) is rapidly formed from the reaction between the Co precursor and oxalic acid [20]. The fast kinetics, however, can be disadvantageous in preparing a uniform catalyst layer on the electrode. Hence, introducing a 2-D structure, such as that of reduced graphene oxide (RGO) that is highly dispersible in aqueous solution, can enhance the homogeneity, solution processability, and stability of the oxalate structures. We further demonstrated the activity and stability of CoC<sub>2</sub>O<sub>4</sub>/gRGO as a bifunctional oxygen electrocatalyst and discussed the origin of the performance enhancement in both reactions.

## 2. Experimental

### 2.1. Synthesis of graphene oxide (GO)

GO was synthesized following the chemically-modified Hummer's method. Graphite powder (4 g) was pre-oxidized by concentrated H<sub>2</sub>SO<sub>4</sub> (10 mL), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (2 g), and P<sub>2</sub>O<sub>5</sub> (2 g), with vigorous stirring. The pre-oxidized graphite was further oxidized using H<sub>2</sub>SO<sub>4</sub> (90 mL) and KMnO<sub>4</sub> (12 g), while the reaction temperature was maintained below 20 °C and slowly increased to 80 °C, before kept constant at 37 °C for 2 h. Consequently, the oxidized sample was diluted with DI water (184 mL) and 30 wt. % H<sub>2</sub>O<sub>2</sub> solution (560 mL) was added to the solution, followed by continuous stirring for 15 min. Next, we filtered the sample using a Whatman No. 2 filter paper, and then the graphite oxide was collected from the suspension. To produce the GO solution, the collected graphite oxide was oven-dried at 50 °C. Then, we diluted the dried graphite oxide by DI water (1:200, g/g) and put in the sonication bath for 1 h before centrifugation (4000 rpm, 30 min, 25 °C). The obtained GO solution was dialyzed to remove the residual acid, and metal and polyatomic ions. The dialyzed GO solution was then filtered by a cellulose nitrate membrane to collect GO slurry, which was oven-dried at 60 °C to produce GO flakes.

### 2.2. Synthesis of CoC<sub>2</sub>O<sub>4</sub>/gRGO

To fabricate the CoC<sub>2</sub>O<sub>4</sub>/gRGO catalyst, dried GO flakes were dissolved in DI water to obtain 0.5 mg mL<sup>-1</sup> of concentration. The gRGO was prepared by a GO reduction process using 25 wt. % NH<sub>3</sub> solution (1:0.01 v/v ratio, GO solution: NH<sub>3</sub> solution) and a heat-treatment up to 100 °C for 30 min. The reduction of GO was observed through the visible color change from dark brown to black. Meanwhile, CoC<sub>2</sub>O<sub>4</sub> was formed in gRGO by dissolving 0.5 mmol oxalic acid powder (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) into 15 mL of the gRGO solution, followed by sonication. Subsequently, cobalt nitrate hexahydrate, Co(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O, was added into the solution as a Co precursor and immediately sonicated using a rod-homogenizer for 1 min before immersing it in the sonication bath for 30 min.

### 2.3. Characterization

The morphology and structure of CoC<sub>2</sub>O<sub>4</sub>/gRGO composition were observed on the smooth surface of a silicon wafer substrate under field emission scanning electron microscopy (FE-SEM, Hitachi S-4700). The interface between the CoC<sub>2</sub>O<sub>4</sub> rod-structures and graphene sheets was investigated by transmission electron microscope (TEM, Phillips TECNAI F20) at an operating voltage of 200 kV. The crystal structures of CoC<sub>2</sub>O<sub>4</sub>/gRGO were confirmed using an automated X-ray diffraction equipment (XRD, Rigaku D/MaXIII, Japan). To confirm the formation of CoC<sub>2</sub>O<sub>4</sub>, the oxidation state of Co was determined from the catalyst powder sample using the Co K-edge X-ray absorption near edge spectra (XANES) at the 7D beamline of Pohang Accelerator Laboratory with 30% detuned X-ray beam intensity. The surface functional groups of graphene were also characterized by X-ray photoelectron spectroscopy (XPS, MultiLab 2000). Thermogravimetric analysis (TGA, Shimadzu TGA-50) was carried out to investigate Co content in the electrocatalyst, with continuous N<sub>2</sub>-flow at a ramping rate of 5 °C min<sup>-1</sup>. Fourier transform infrared spectrometer (FT-IR, Jasco FT/IR-6100) was utilized to characterize the presence of different functional groups.

### 2.4. Electrochemical measurements

Electrochemical experiments for testing electrocatalytic activity were carried out using a three-electrode set-up by performing linear sweep voltammetry (LSV) using a potentiostat/galvanostat device (Autolab, PGSTAT301 N) at a scan rate of 100 mV s<sup>-1</sup>. Working electrodes were prepared by drop coating 20 μL aliquot of catalyst ink with 0.5 mg mL<sup>-1</sup> concentration on 5 mm glassy carbon (GC) and drying for 15 min. The loading amounts of all the catalysts were fixed at 50 μg cm<sup>-2</sup>. Pt mesh and Hg/HgO electrode in 1 M NaOH were used as counter and reference electrodes, respectively. To assess ORR activity, rotating disk electrode (RDE) was used for LSV experiments under O<sub>2</sub>-saturated 0.1 M KOH electrolyte within the window potential range of -0.8 V to 0.2 V. Likewise, in OER, LSV was performed under N<sub>2</sub>-saturated 0.1 M KOH solution in the window range of 0 to 1.0 V. The stability of catalyst was tested by chronoamperometry (CA), at a fixed potential of -0.4 V in O<sub>2</sub>-saturated solution for ORR, while a constant potential of 0.9 V was applied in the N<sub>2</sub>-saturated solution in OER for 30 min.

## 3. Results and discussion

### 3.1. Synthesis and characterization

The process to synthesize Co oxalate structures on gently reduced graphene oxide (CoC<sub>2</sub>O<sub>4</sub>/gRGO) is illustrated in Fig. 1. The brown aqueous solution of GO was partially reduced using 25 wt. % ammonia (NH<sub>3</sub>) at 100 °C to obtain a black dispersion of gRGO

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