



# Nitrogen and Sulfur Co-doped Graphene Supported Cobalt Sulfide Nanoparticles as an Efficient Air Cathode for Zinc-air Battery



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## ABSTRACT

Zinc-air battery is considered as one of the promising energy storage devices due to their low cost, eco-friendly and safe. Here, we present a simple approach to the preparation of cobalt sulfide nanoparticles supported on a nitrogen and sulfur co-doped graphene oxide surface. Cobalt sulfide nanoparticles dispersed on graphene oxide hybrid was successfully prepared by solid state thermolysis approach at 400 °C, using cobalt thiourea and graphene oxide. X-ray diffraction study revealed that hybrid electrode prepared at 400 °C results in pure CoS<sub>2</sub> phase. The hybrid CoS<sub>2</sub>(400)/N,S-GO electrode exhibits low overpotential gap about 0.78 V vs. Zn after 70 cycles with remarkable and robust charge and discharge profile. And also the CoS<sub>2</sub>(400)/N,S-GO showing deep discharge behavior with stability up to 7.5 h.

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## 1. INTRODUCTION

Our world is looking for the transition of fossil fuel based energy economy to the clean energy based economy. The inevitable worldwide need for sustainable energy harvesting, conversion and its storage. Batteries have long been considered as efficient way of convert and storing the electrical energy [1–7]. Zinc-air battery is low cost, eco-friendly and highly safe compared to the other kinds of batteries such as lead acid batteries, flow redox cell, sodium sulfur batteries and lithium-ion batteries. The advantages of zinc-air batteries like cost, safety and technology made it succeed over other metal-air batteries such as lithium-air batteries, aluminum-air batteries and magnesium-air batteries [8,9].

Zinc-air battery has a theoretical voltage of 1.65 V, but its practical working voltage is lower than 1.2 V. This is because of the deviation of charge and discharge potential from their standard value due to over-potentials of the oxygen positive electrode [1,10]. As a result, the practical zinc-air batteries usually have low round-trip efficiency [1,7]. One of the important challenges encountered by zinc-air battery is the sensitivity towards the feed gas stream. When we feed the air with appreciable amount of CO<sub>2</sub> into the zinc-air battery, it reacts with electrolyte and forming the carbonate [1,11,12]. This carbonate will clog the pores of the air

electrode and subsequently its affects and the performance and durability. So, the performance of the zinc-air battery in the open air atmosphere is very significant.

So far, various cobalt sulfide materials such as Co<sub>1-x</sub>S, Co<sub>3</sub>S<sub>4</sub> and Co<sub>9</sub>S<sub>8</sub> were synthesized and used as electrode materials for ORR [13,14] and lithium-ion batteries [15]. Cobalt sulfide nanoparticles supported on graphene have been used as ORR catalyst in alkaline medium [16,17]. Also sulfur and nitrogen-doped carbon and graphene exhibit reasonable ORR activity in alkaline medium [18,19]. The effect of temperature on the formation of different phases of cobalt sulfides in an open inert atmosphere has been reported [12]. Preparation of nanomaterials by solid-state thermolysis has been reported to be a good choice for solution free synthesis of metal-free and non-precious electro-catalysts [20–22].

Till now, cobalt sulfide (CoS<sub>2</sub>) nanoparticles supported on graphene was used as an electrocatalyst for fuel cells [23]. However, the use of such a material has not been explored for zinc-air batteries as well. Herein, we introduce a novel and facile synthesis of CoS<sub>2</sub> nanoparticles anchored on N,S-doped graphene oxide as an air-breathing electrode in alkaline medium. Cobalt sulfide nanoparticles anchored onto the graphene oxide support exhibits better charge-discharge profile due to the improved OER and ORR activities which is outperforming than the precious catalyst, Pt-Ru/C (40 wt%). We developed a scalable and reproducible method for the synthesis of cobalt sulfide anchored on nitrogen and sulfur co-doped graphene for durable air breathing zinc-air battery.

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## 2. Experimental

### 2.1. Synthesis of Graphene oxide

Graphene oxide (GO) was synthesized from graphite powder by a modified Hummer method [24]. The graphite powder (Sigma Aldrich) about one gram was grounded with 50 g of sodium chloride (Daejung, Seoul, Korea) and washed with deionized (DI) water several times to remove sodium chloride. After drying, 4 mL of  $\text{H}_2\text{SO}_4$  (Sigma Aldrich, 99%) was added and then followed by 0.84 g of  $\text{K}_2\text{S}_2\text{O}_8$  (Kanto, Japan) and  $\text{P}_2\text{O}_5$  (Kanto, Japan) at 80 °C (375 rpm) were added and stirred for 4.5 h. Then at room temperature, 167 mL of DI water was added and the mixture was stirred overnight. And the mixture was filtered and washed using DI water and completely dried. The obtained powder was added to a two neck flask containing 40 mL of  $\text{H}_2\text{SO}_4$  and 5 g of  $\text{KMnO}_4$  (Aldrich) placed in an ice bath and stirred slowly until the contents were completely dissolved. Then, 84 mL of DI water was added into the mixture and stirred for 2 h at 35 °C. Finally, more DI water (167 mL) was added along with 10 mL of  $\text{H}_2\text{O}_2$  (Samchun, Korea), and the reaction was terminated via stirring for 30 min in an ice bath. The resulting mixture was centrifuged several times until the mixture reached pH 7 and then collected sample was dried in the vacuum oven to get a brown powder [25].

### 2.2. Synthesis of Cobalt thiourea complex

Cobalt nitrate ( $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.01 M, Sigma Aldrich) and thiourea (0.04 M, Sigma Aldrich) were dissolved in 25 mL of hot butanol (Sigma Aldrich). Then, the mixture was heated to reach boiling until all solids dissolved indicating the solution changing from red to blue. On cooling, a blue solid of  $\text{Co}(\text{TU})_4(\text{NO}_3)_2$  was separated out. This was suction filtered, washed with diethyl ether (Fluka analyst) to remove impurities and dried under vacuum at 30 °C and the obtained yield was 3.9 g.

### 2.3. Synthesis of $\text{CoS}_2$ /Graphene oxide

About 0.2 g of graphene oxide was sonicated in 7 mL of acetone until it completely dispersed. Then, 0.15 g of cobalt thiourea complex,  $\text{Co}(\text{TU})_4(\text{NO}_3)_2$  was added to the dispersion and stirred at 35 °C until the whole solvent was evaporated. Then, the dried solid at 55 °C until no moisture content was present. The solid was ground well and loaded into a Swagelok union cell. The cell was heated to 400 °C for 2 h at a heating rate of 5 °C/min. After cooling to room temperature, the Swagelok cell was carefully opened and the product was collected for further characterization. During the solid state thermolysis under autogenic pressure has been going on, the heteroatoms were doped in the graphene oxide surface and there was a simultaneous formation of  $\text{CoS}_2$  nanoparticles on graphene surface and producing  $\text{CoS}_2(400)/\text{N,S-GO}$  [17]. The same preparation procedure was also followed to prepare  $\text{CoS}_2(400)$  without graphene oxide, the cobalt thiourea complex was heated to 400 °C ( $\text{CoS}_2$ ). To prepare a control sample,  $\text{N,S-GO}$  without  $\text{CoS}_2$  particles, thiourea and graphene oxide were heated to 400 °C. We also compared the Zn-air battery performance of  $\text{CoS}_2(400)/\text{N,S-GO}$  with  $\text{CoS}_2(400)/\text{VX-72}$  carbon and  $\text{CoS}_2(400)/\text{CNT}$  samples to understand the effect of nitrogen and sulfur co-doped graphene oxide support. The  $\text{CoS}_2(400)/\text{VX-72}$  carbon and  $\text{CoS}_2(400)/\text{CNT}$  samples are prepared by mixing 50% CNT (Sigma Aldrich) and Vulcan carbon, VX-72 carbon (CABOT Co.) with 49% of as prepared  $\text{CoS}_2(400)$  sample, respectively.

### 2.4. Material characterizations

The X-ray diffraction (XRD) measurements were carried out using an X-ray diffractometer (Rigaku, MiniFlex 600). The morphological structure of the samples was examined by means of field-emission scanning electron microscopy (FE-SEM, Hitachi, S-4800 II, 3 kV). Thermo gravimetric analysis (TGA) was carried out using Thermoplus Evo-Rigaku (TG 5180) at a heating rate of 10 °C per minute under air. A primary and secondary battery performance of the zinc-air battery was carried out using the split test cell (EQ-STC-MTI-Korea). The electrodes were fabricated with 9.4 mg of active material, 1 mL of isopropyl alcohol and 67  $\mu\text{L}$  of 5 wt% Nafion ionomer solution coated on the gas diffusion layer (thickness 0.27 mm). Air cathodes of geometrical area 2.54  $\text{cm}^2$  were coated with 4.5 mg catalyst achieving a loading of 1.71  $\text{mg cm}^{-2}$ . A polished zinc plate was negative electrode (anode), a Whatman glass microfiber filter membrane was used as a separator, and 6 M KOH was used as the electrolyte. The charge-discharge studies were carried out using a Battery analyzer (BAT8-3); battery cells consumed under air ambient condition. The 40% Pt-Ru (1:1) with atomic ratio was purchased from the Premetek Co.  $\text{RuO}_2$  and  $\text{IrO}_2$  (Alfa Asesar) were used to compare the oxygen electrode activity. The charge-discharge studies of these materials were compared with our  $\text{CoS}_2(400)/\text{N,S-GO}$  under similar experimental conditions.

### 2.5. Electrode preparation and electrochemical measurements

The oxygen electrode behavior (ORR and OER) of the catalysts were evaluated using cyclic voltammetry (CV) and a rotating disc electrode (RDE) in an  $\text{O}_2$ -saturated KOH (0.1, 1 and 6 M) electrolyte at a scan rate of 10  $\text{mV s}^{-1}$  using a computer controlled potentiostat (Bio-Logic) with a typical three-electrode system. Five milligrams of catalyst was dispersed in the mixture of isopropanol, DI water and Nafion in the ratio 160  $\mu\text{L}$ , 30  $\mu\text{L}$  and 10  $\mu\text{L}$ , respectively was added, and the contents were dispersed by ultra-sonication for approximately 30 min to obtain a homogeneous suspension. The catalyst ink (1.5  $\mu\text{l}$ ) was dropped onto the surface of a glassy carbon disk (working electrode, 0.07  $\text{cm}^2$ ) and dried at room temperature. The working electrode was immersed in a glass cell containing aqueous KOH electrolyte. A platinum coil and saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. All potentials reported in this work were converted from the SCE to the RHE scale using  $E(\text{RHE}) = E(\text{SCE}) + 0.998 \text{ V}$  in 0.1 M KOH. The ORR activity was measured in an  $\text{O}_2$  saturated electrolyte (before using an Ar saturated electrolyte for background correction under the same conditions) with a potential range from 0.2 to 1.00 V vs. RHE at various electrode rotations. For the OER measurement, the potential range was 0.95 to 1.7 V vs. RHE with a rotation speed of 1600 rpm. The OER stability test was carried by continuous cycles in a potential window of 0.95 to 1.7 V at a scan rate of 50  $\text{mV s}^{-1}$ . The electrode stability was carried out for both ORR and OER activity to understand the durability of bifunctionality. The ORR durability test was studied by experimentally repeated potentiodynamic cycling for 2500 cycles with a potential range of 0.2 to 1.0 vs. RHE at a scan rate of 50  $\text{mV s}^{-1}$  in an  $\text{O}_2$  saturated 0.1 M KOH electrolyte.

## 3. RESULTS AND DISCUSSION

### 3.1. Structural characterization

Fig. 1 shows the crystalline phase of the  $\text{CoS}_2$  with space group  $\text{Fm-3m}$  (ICSD PDF no. 01-083-0573); these observations were well match for the  $\text{CoS}_2(400)/\text{N,S-GO}$  and  $\text{CoS}_2(400)$ . In this XRD pattern, a broad peak at 23 ( $2\theta$ ) was observed, which is responsible

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