



# Surface decorated cobalt sulfide as efficient catalyst for oxygen evolution reaction and its intrinsic activity



Jingde Li<sup>a,b,1</sup>, Guihua Liu<sup>b,1</sup>, Jing Fu<sup>b</sup>, Gaopeng Jiang<sup>b</sup>, Dan Luo<sup>b</sup>, Fathy M. Hassan<sup>b</sup>, Jing Zhang<sup>b</sup>, Ya-Ping Deng<sup>b</sup>, Pan Xu<sup>b</sup>, Luis Ricardez-Sandoval<sup>b</sup>, Zhongwei Chen<sup>b,\*</sup>

<sup>a</sup> School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin, 300130, China

<sup>b</sup> Department of Chemical Engineering, University of Waterloo, Waterloo, ON N2L 3G1, Canada

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## ABSTRACT

Here, we report an efficient surface decorated, e.g. oxidation and nitrogen doped, cobalt sulfide (O-N-Co<sub>9</sub>S<sub>8</sub>) oxygen electrocatalyst, which shows excellent activity especially for oxygen evolution reaction (OER), and good stability over 900 charge-discharge cycles at 10 mA cm<sup>-2</sup> in Zinc-air battery. Moreover, we found that O-N-Co<sub>9</sub>S<sub>8</sub> was completely converted into Co<sub>3</sub>O<sub>4</sub> after OER, showing oxide is actual active phase. Density functional theory calculations reveal the continuous exposure of oxidized surface Co sites during O-N-Co<sub>9</sub>S<sub>8</sub> → Co<sub>3</sub>O<sub>4</sub> is essential for its high OER activity. These Co sites promote the kinetics for OH\* transformation to O\* and also ensure fast O<sub>2</sub> desorption. Once Co<sub>3</sub>O<sub>4</sub> is generated, the high activity is contributed by its resulting characteristic surfaces. Thus, we propose and demonstrate that oxides *in-situ* generated during OER are more active than the directly calcined oxides. This work advances fundamental insight of metal chalcogenides “catalysts” and guides the design of active OER catalysts.

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## 1. Introduction

The development of efficient bi-functional electro-catalysts for both oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is of critical importance for rechargeable Zinc-air batteries. Precious metals such as Pt, Ir, Ru are the best performing catalysts for oxygen electro-catalysis in alkaline [1,2]. However, the scarcity and poor catalytic bi-functionality hinder their application in Zinc-air batteries. The most promising non-precious bi-functional catalysts are derived from carbon-transition metals (e.g. Co, Ni, Fe, Mo, etc.) hybrid materials [3]. The carbon, as a support, ensures the good conductivity of the catalysts, and when doped with N, S or transition metal elements, e.g. Fe, Co, it shows excellent ORR activity [4]. On the other hand, the transition metals, especially their oxides, hydroxides, phosphide, sulfide or nitride can exhibit good OER activities [5–8].

Recently, surface engineering, e.g. NH<sub>3</sub> etching, cation or anion substituting, heteroatom doping, of transition metal chalcogenides and nitrides can effectively improve their activities, especially towards OER [9–12]. Many studies have attributed the enhance-

ment of catalytic activities to synergistic effect or vacancy sites on these engineered transition metal surfaces [13–15]. However, other studies have reported that, during OER, there exist a progressive oxidation of the metal-based materials [16–20], and the oxidized metal surfaces might be responsible for the catalytic activity [21,22]. These reports raised a question that, in the absence of post-OER characterization of the as-prepared catalysts, the explanations on catalytic activity might be inadequate and sometime non-convincing [21]. On the other hand, these reports also imply that considering surface oxidation in the development of metal chalcogenides catalyst might be also beneficial for OER activity.

Based on the above, in the present study, we have engineered an efficient bi-functional catalyst with excellent OER activity that consists of mildly oxidized, N-doped imperfect Co<sub>9</sub>S<sub>8</sub> crystals supported on N-doped reduce graphite oxide (O-N-Co<sub>9</sub>S<sub>8</sub>@N-RGO). The origin of its high OER activity (over-potential of 350 mV at current density of 10 mA cm<sup>-2</sup> under 0.1 M KOH) was investigated by conducting experimental and theoretical research, including detailed experimental characterization of the as-prepared catalysts before and after OER reaction, and Density functional theory (DFT) calculation of the OER kinetics on catalyst surfaces. Note that most of the previous DFT studies on OER have been focusing on the thermodynamics of the reaction through Gibbs free energy-based anal-

\* Corresponding author.

E-mail address: [zhwchen@uwaterloo.ca](mailto:zhwchen@uwaterloo.ca) (Z. Chen).

<sup>1</sup> These authors contributed equally to this work.

ysis [23–27]. Although successful in predicting catalysts' OER activity, a DFT analysis of OER kinetic would be more suitable for the identification of active catalytic sites: it determines the reaction pathway and associated energetics on surface sites, which is a direct determination of catalyst activity. In addition, although the oxidation O-N-Co<sub>9</sub>S<sub>8</sub> crystal during OER is expected, some questions still remain. For example, will high OER activity be maintained (good stability performance) after catalysts oxidation, and why? Addressing these questions will provide an in-depth knowledge on the intrinsic OER activity and “stability” of metal chalcogenides and will potentially guide the design of efficient OER catalysts.

## 2. Experimental section

### 2.1. Preparation of O-N-Co<sub>9</sub>S<sub>8</sub>@N-RGO composite

Reduce graphene oxide (RGO) is obtained by thermal-shock heat treating graphene oxide (GO) in Ar at 900 °C for 1 min, in which the GO was synthesized from graphite powder using modified Hummers method [28,29]. Then, 30 mg of RGO was dispersed in 150 mL of water by ultrasonication for 1 h. Cobalt nitrate hexahydrate [Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 655 mg] and sodium dodecyl sulfate [SDS, 865 mg] were added to the RGO dispersion. Ammonia solution (28–30%, 10 mL) was drop-wisely added to the solution with a rate of 5 mL min<sup>-1</sup> under stirring at room temperature. The above suspension was then put into oil bath at 90 °C with stirring for 6 h under ambient atmosphere. After that, the solution was naturally cooled down to room temperature. The suspended black product was collected by centrifugation and washed with DDI water and ethanol, and then freeze-dried. The as-obtained powder product, referred to as Co-S-O-N-RGO precursor, was thermal-shock treated under NH<sub>3</sub> atmosphere at 700 °C in tube furnace for 5 mins, and then cooled down to room temperature in Ar. The resulting product is O-N-Co<sub>9</sub>S<sub>8</sub>@N-RGO composite.

### 2.2. Characterization

X-ray diffraction (XRD) was carried out on a Rigaku D/Max 2550 X-ray diffractometer with Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The morphology of the as-prepared composite was investigated using field emission scanning electron microscopy (FE-SEM) (Zeiss Ultra Plus, United Kingdom), and high-resolution transmission electron microscopy (HRTEM) instrument (FEI/Philips CM 300, United States). X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-Alpha XPS spectrometer) was used to investigate the chemical composition of the as-prepared composites. Note that, the post-OER characterizations (e.g. XRD, XPS) were performed using the catalysts sprayed on carbon paper. Thus, their XRD figures show some patterns of the carbon background.

### 2.3. Electrochemical activity evaluation

The half-cell electrochemical evaluation of the ORR-OER activity of the as-prepared composites were conducted via rotating disk electrode (RDE) voltammetry using a three-electrode system and potentiostat (CH Instruments 760D). Ink solution was prepared by mixing the composites and carbon black (Vulcan Carbon XC-72) in a 2:1 mass ratio in 1-propanol solution with a total mass concentration of 4 mg mL<sup>-1</sup>. The working electrode was prepared by coating the ink onto a polished glassy carbon disk electrode with an active material loading of 0.40 mg cm<sup>-2</sup>. A graphite rod and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All potentials were referenced to a reversible hydrogen electrode (RHE) by adding a value

of  $(0.245 + 0.059 \times \text{pH}) \text{ V}$ . The electrolyte is 0.1 M KOH. Cyclic voltammetry (CV) analysis was performed at the scan rate of 50 mV s<sup>-1</sup>. The ORR and OER activities were measured in the O<sub>2</sub> and N<sub>2</sub> saturated electrolyte, respectively, through LSV at the scan rate of 10 mV s<sup>-1</sup>. The OER and ORR activity of as-developed catalysts and commercial Pt/C or Ir/C catalysts were normalized by the geometry area of RDE electrode. The potentials in OER and ORR were corrected for iR losses and background current, respectively. The latter is the current obtained when N<sub>2</sub> is purged into the electrolyte in ORR test.

### 2.4. Rechargeable Zinc-air battery test

The full-cell Zinc-air battery tests were performed using homemade plastic prototypes. Polished Zinc-plate was used as the Zinc electrode. The O-N-Co<sub>9</sub>S<sub>8</sub>@N-RGO air electrode was prepared by spraying catalyst ink onto the front side of a carbon paper gas diffusion layer (GDL; SGL Carbon 39 BC; Ion Power Inc.) with an active catalyst loading of 0.67 mg cm<sup>-2</sup>. The catalyst ink is prepared from 2.67 mg O-N-Co<sub>9</sub>S<sub>8</sub>@N-RGO composite, 1.33 mg Vulcan XC-72 carbon black, 13.33 mg 15 wt% Nafion (LIQUion solution, Ion Power Inc.) and 5.0 mL 1-propanol. Stainless steel meshes was used as the current collector for the air cathode, in which it was placed in contact with the backside of the carbon paper. The current collector for the Zinc anode is copper foil. The electrolyte is a solution of 6 M KOH and 0.2 M Zn(CH<sub>3</sub>COO)<sub>2</sub>.

## 3. DFT calculations

The periodic DFT calculations were performed using the VASP package [30,31]. The Perdew-Burke-Ernzerhof (PBE) functional was used for the exchange and correlation energy terms [32]. A Dudarev “+U” term acting on the Co 3d states (referred as GGA + U) was applied. The U value was set to 2 eV [33,34]. A plane-wave cutoff of 400 eV was used. Using the calculated lattice constant (9.73 Å) for cubic Co<sub>9</sub>S<sub>8</sub>, (2 × 1) and (1 × 1) supercell were constructed for Co<sub>9</sub>S<sub>8</sub> (1 1 1) and (3 1 1) surfaces, respectively. The Co<sub>9</sub>S<sub>8</sub> (1 1 1) slab have six atomic layers and there are seven atomic layers in the Co<sub>9</sub>S<sub>8</sub> (3 1 1) slab. The lattice parameters of cubic Co<sub>3</sub>O<sub>4</sub> is calculated to be 8.05 Å. The Co<sub>3</sub>O<sub>4</sub> (1 1 1) and (4 0 0) surface are represented by a 2 × 1 unit cell, whereas the Co<sub>3</sub>O<sub>4</sub> (3 1 1) and (4 2 2) surface are modeled by 1 × 1 unit cell. All the slabs have a vacuum height of 15 Å. The O-N-Co<sub>9</sub>S<sub>8</sub> (1 1 1) and O-N-Co<sub>9</sub>S<sub>8</sub> (3 1 1) surfaces were developed by tuning (removing and substituting) the corresponding Co<sub>9</sub>S<sub>8</sub> (1 1 1) and (3 1 1) slabs, respectively, into the same Co, S, O, N compositions as those observed from XPS analysis (Table S2). Under the specific composition, local stable slab configurations were determined by optimizing extensive slabs with different O, N and S distributions. When the resulting local stable O-N-Co<sub>9</sub>S<sub>8</sub> (1 1 1) and O-N-Co<sub>9</sub>S<sub>8</sub> (3 1 1) slabs were used to study the OER kinetics, the bottom three atomic layers were fixed, whereas the remaining layers and the adsorbates were allowed to relax. Same atom constrain setting was applied to the Co<sub>9</sub>S<sub>8</sub> (1 1 1), (3 1 1) and Co<sub>3</sub>O<sub>4</sub> slabs. The k-space was sampled using a 2 × 2 × 1 Monkhorst–Pack grid. Structures are fully relaxed until the forces acting on the atoms are smaller than 0.03 eV/Å. The reaction transition states are determined using the climbing image nudged elastic band method (CI-NEB) [35] and confirmed by vibration analysis with only one negative frequency.

## 4. Results and discussion

The O-N-Co<sub>9</sub>S<sub>8</sub>@N-RGO composite was developed by “thermal shock” heat treatment of the Co, S, N and RGO-containing precursor

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