## **Supporting Information**

# In-Situ Gel Pyrolysis-Derived Efficient Self-Supporting Foldable Electrodes for Zinc-Air

## Batteries

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#### 1. Material preparation

#### Chemicals

 $Zn(NO_3)_2$  6H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, N,N-Dimethylformamide (DMF), Triethylamine, Potassium hydroxide (KOH), Ethanol (C<sub>2</sub>H<sub>5</sub>OH), and Methanol (CH<sub>3</sub>OH) were purchased from Sinopharm Chemical Reagent Co., Ltd. China., Pt catalyst (20 wt %, Pt/C) was purchased from Johnson Matthey. Terephthalic acid (1,4-BDC), Ruthenium oxide (RuO<sub>2</sub>), Nafion solution (5 wt%) were obtained from Sigma-Aldrich. All the chemicals were AR grade and used without any special treatment.

### **Preparation of ZIF Gel**

Dissolve 1.7489 g of zinc nitrate and 2.619 g of cobalt nitrate in 6 mL of DMF, then sonicate for 0.5 h to obtain a homogeneous solution. Dissolve 1.9704 g of dimethylimidazole in 6 mL of DMF and sonicate for 0.5 hours to obtain a homogeneous solution. Mix the two solutions, then add triethylamine (with a concentration of 2 M) and stand it for another 0.5 h to get the ZnCo-ZIF gel. For comparison, Zn-ZIF gel was prepared without adding cobalt nitrate.

#### Preparation of Co-NCNTs@CC and NC@CC

The ZnCo-ZIF gel was scraped onto a piece of carbon cloth, with a gel thickness of 200  $\mu$ m, and then placed in a tube furnace. It was heated to 900 °C at a rate of 2 °C/min under an argon atmosphere, held at that temperature for 3 h, and then cooled to room temperature to obtain the Co-NCNTs@CC. The synthesis of NC@CC follows a similar process, except that NC@CC is directly synthesized by pyrolyzing the Zn-ZIF gel.

#### 2. Material characterizations

The crystalline structure of the generated samples was analyzed using X-ray diffraction (D8 ADVANCE, Germany) with Cu K $\alpha$  radiation ( $\lambda = 0.15406$  nm), and the chemical states of the produced products were examined by X-ray photoelectron spectroscopy (XPS, PHI 5000C, Perkin Elmer). The morphological pictures of the goods were acquired using scanning electron microscopy (FESEM; Sigma 500, ZEISS, Germany) equipped with an X-ray energy dispersive spectrometer (EDS). Comprehensive microstructural analysis was conducted utilizing a Hitachi H-8100 transmission electron microscope (TEM), along with selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). Additionally, high-angle annular dark field-scanning TEM (HAADF-STEM) was performed at 200 kV on a JEM-ARM200F, which is equipped with double spherical aberration correctors.

#### **Electrochemical measurements**

To manufacture the rotating disk electrode (RDE) working electrode, catalyst ink was formulated by combining 5 mg of catalyst powder, 950  $\mu$ L of ethanol, and 50  $\mu$ L of 5% Nafion, followed by ultrasonication for 2 hours. Following the homogenization of the solution via sonication, 8  $\mu$ L of the ink was drop-cast onto a 5 mm diameter glassy carbon electrode (GCE) and then evaporated at ambient temperature to create a thin catalyst layer. The catalyst loading was determined to be 0.2 mg cm<sup>-2</sup>.

All electrochemical experiments were performed in a conventional three-electrode electrochemical cell at ambient temperature (25°C). Ag/AgCl served as the reference electrode, Pt wire functioned as the counter electrode, and all potentials in this study were adjusted to the reversible hydrogen electrode (RHE) using the equation ( $E_{RHE} = E_{Ag/AgCl} + 0.198 + 0.059$ pH), while a catalyst-coated GCE disk was employed as the working electrode. The electrocatalytic activity of catalyst samples for the ORR on GCE disks was investigated using the RDE approach with the Autolab PGSTAT302 N workstation (Metrohm, Switzerland) and IPS Rotating Unit (IPS Elektroniklabor GmbH & Co. KG, Germany). ORR polarization curves were acquired by linear sweep voltammetry (LSV), scanning from 0.2 V to -1.0 V vs Ag/AgCl at a rate of 5 mV s<sup>-1</sup> in O<sub>2</sub>-saturated 0.1 M KOH electrolyte using a rotating disk electrode (RDE) at various rotational speeds (400-3600 rpm).. Electron transfer number (n) was calculated from the slopes of the Kouteckye-Levich plots according to:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{B\omega^{1/2}}$$
(1)

Where  $j_k$  is the kinetic current density at a constant potential,  $j_d$  is the measured current density,  $\omega$  is the electrode rotating speed in rpm, and the theoretical value of the Levich slope (B) is evaluated from the following equation:

$$B = 0.2nFC_{0_2}(D_{0_2})^{2/3} v^{-1/6}$$
(2)

Where n is the overall number of transferred electrons in the ORR process, F is the Faradaic constant (96485 C mol<sup>-1</sup>),  $C_{O2}$  is the oxygen concentration in 0.1 M KOH ( $1.2 \times 10^{-6}$  mol cm<sup>-3</sup>),  $D_{O2}$  is the diffusion coefficient of  $O_2$  in 0.1 M KOH ( $1.73 \times 10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>), and v is the kinematic viscosity of 0.1 M KOH (0.01 cm<sup>2</sup> s<sup>-1</sup>).

#### **Oxygen evolution reaction (OER) tests**

The testing settings for OER were analogous to those for ORR. The LSV polarization curves for all catalysts were conducted from 0.1 to 0 V (vs. Hg/HgO) in a 1 M KOH solution at a scan rate of

5 mV s<sup>-1</sup> without iR compensation. All potentials in this study were converted to the reversible hydrogen electrode (RHE) scale using the equation ( $E_{RHE} = E_{Hg/HgO} + 0.098 + 0.059$ pH). Electrochemical impedance spectroscopy (EIS) measurements were conducted using an electrochemical workstation (Autolab, PGSTAT302 N) with an applied AC amplitude of 5 mV and a frequency range of 0.1 to 1000 kHz.

#### Liquid rechargeable Zn-air battery tests

The performance of the zinc-air battery was evaluated using a home-built system. A polished zinc sheet served as the anode, while the prepared catalyst was used as the air cathode. The electrolyte consisted of a 6 M KOH solution with 0.2 M zinc acetate. The catalyst layer was applied by coating catalyst ink onto the carbon cloth, with a loading of 1 mg cm<sup>-2</sup>. Polarization curves for the zinc-air battery were measured using an electrochemical workstation at ambient temperature. Galvanostatic discharge-charge cycling (10 minutes per cycle, reaching a current density of 10 mA cm<sup>-2</sup>) was conducted on a blue power testing system from Wuhan. For comparison, Pt/C-RuO<sub>2</sub> (with a mass ratio of Pt/C: RuO<sub>2</sub> = 1:1) with the same loading mass was also applied to carbon cloth, and the Pt/C-RuO<sub>2</sub>-based zinc-air battery was tested under the same conditions. The specific capacity was calculated using the following equation: specific capacity = (current × service hours) / weight of consumed zinc.

#### Flexible solid-state Zn-air battery zinc-air battery tests

A polished zinc foil (0.05 mm thickness) was used as the anode. The gel polymer electrolyte was prepared as follows: 5 g of polyvinyl alcohol (PVA) powder was added to 50 mL of 0.1 M KOH solution containing 0.2 M zinc acetate and heated to 90°C while stirring until the solution became homogeneous. The resulting solution was then poured onto a glass plate to form a thin electrolyte film. The film was stored in a freezer at -3°C and allowed to thaw at room temperature for 12 hours before use. The battery was assembled by placing a thin layer of the catalyst on one side and zinc foil on the other side of the PVA gel. A piece of pressed Ni foam was used as the current collector. The assembly process did not require an inert atmosphere or glove box.

# 3. Supporting Figures



Fig. S1 SEM images of NC@CC and Co-NCNTs@CC.



Fig. S2 XPS full spectrum of Co-NCNTs@CC.



Fig. S3 CV plots of Co-NCNTs@CC in nitrogen (a) and oxygen (b).



Fig. S4 LSV curves of Co-NCNTs@CC at different rotation speeds (a); K-L plots (b).



Fig. S5 The photos of MOF-gel.



Fig. S6 The photo of Co-NCNTs@CC flexible air electrode.



Fig. S7 The fabrication diagram of the flexible solid-state Zn-air battery.