MOFs derived catalysts for electrochemical oxygen reduction

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1. Materials and characterization techniques

1.1 Starting materials

Cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O, >99\%)$, cobalt acetate $(Co(OAc)_2 \cdot 4H_2O, >99.5\%)$ and zinc acetate $(Zn(OAc)_2 \cdot 2H_2O)$ were purchased from XILONG Chemical. Benzenedicarboxylate (H_2bdc) , 1,4-diazabicyclo[2.2.2]octane (dabco) and 2-Methylimidazole (MeIM, 99%) were purchased from J&K Chemicals. The carbon supported platinum catalysts (Pt/C, nominally 10 % on carbon black) and Nafion (5 wt% solution in ethanol and water) were purchased from Alfa Aesar and were used as received.

1.2 Structural characterization techniques

The structure and morphology of products are characterized by X-ray diffraction (XRD, Rigaku D/max 2000 diffractometer, Cu K α), and high-resolution transmission electron microscopy (HRTEM, JEM 2100, 200 kV). Thermogravimetric analysis (TGA) is carried out on a Q600 SDT thermoanalyzer (Thermal Analysis Corporation, USA). Raman spectra were collected using a HORIBA Jobin Yvon LabRam ARAMIS Raman spectrometer with excitation laser wavelength of 633nm. Nitrogen adsorption-desorption isotherms were measured on an Autosorb IQ gas sorption analyzer (Quantachrome) at 77 K. Before testing, samples were degassed at 200 °C for 2 h. The Brunauer–Emmett–Teller (BET) and the Quenched Solid density functional theory (QSDFT) methods were used to determine surface area and the pore size distribution, respectively. The X-ray photoelectron spectroscopy (XPS) analysis was performed on an AXIS-Ultra spectrometer (Kratos Analytical) using monochromatic Al K α radiation (225 W, 15 mA, 15 kV) and low energy electron flooding for charge compensation. The content of C, H and N was decided by an elemental analyzers of vario EL. ICP-OES (Inductively Coupled Plasma-Atomic Emission Spectrometer) was performed on a CCD-ICP-OES spectrometer PROFILE SPEC.

2. Electric conductivity measurement

About 0.1 g sample in finely grounded powder form is loaded into a resin cylinder mold with diameter of 13 mm and is pressed into a compact disc like pellet about 1 mm in thickness by two stainless steel rods with 50 bar pressure. The electric resistance of the sample together with the two stainless steel rods are measured in a two probe configuration with a Keithley 2000 Multimeter. The electric resistivity of the sample is corrected by subtracting the resistance of the remaining components in the measurement system.

3. Electrochemistry preparation and measurements

3.1 Electrode Preparation

To prepare the working electrode, 2 mg of samples are ultrasonically dispersed in a mixed solution of 100 μ L isopropanol and 100 μ L Nafion (0.5 wt% in ethanol and water) for about 1 h. Then 7 μ L suspension is dropped onto a glassy carbon rotating disk (RDE, 5 mm, Pine Research

Instrumentation, USA) or a rotating ring-disk electrode (RRDE, 5.61 mm of disk outer diameter, Pine Research Instrumentation, USA) surface and dried for at least 2 h at room temperature. The Pt/C catalyst loading is $0.36 \ \mu g \ Pt \ cm^{-2}$.

3.2 Electrochemistry measurements

All electrochemical measurements of the MOF-T samples, including cyclic voltammograms (CVs), linear scan polarization curves and chronoamperometry, are performed at room temperature in O_2 - or Ar-saturated 0.1 M KOH solutions or 0.5 M H₂SO₄ solutions. The performance of Pt/C in acidic electrolyte is measured in 0.1 M HClO₄ to avoid possible poisoning of Pt by the sulfur species. The electrolyte is purged with argon or oxygen for at least 30 min prior to each measurement. The data is recorded using a CHI 760D bipotentiostat (CHI Instruments, Inc., USA). The reference electrode is a saturated Ag/AgCl electrode in 0.1 M KOH solution and a saturated calomel electrode (SCE) in 0.5 M H₂SO₄ or 0.1 M HClO₄ solution. The counter electrode is a platinum foil. On the basis of RDE tests at different rotating rates, the overall electron transfer numbers per oxygen molecule involved in a typical ORR process can be calculated from the slopes of Koutecky-Levich plots using the following equation^{1, 2}:

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

Where j_k is the kinetic current in amperes at a constant potential, ω is the angular velocity of the disk ($\omega = 2\pi N$, N is the electrode rotating speed), and B is the Levich slope, could be determined from the slope of Koutecky-Levich plots (K-L plots) based on Levich equation as follows:

(2)

$$B = 0.62 n F A D_0^{2/3} v^{-1/6} c_0$$

Where n is the number of electrons transferred per oxygen molecule. F is the Faraday constant (F = 96485 C mol⁻¹). D_{O_2} is the diffusion coefficient of O_2 in electrolyte (1.9×10⁻⁵ cm² s⁻¹ in 0.1 M KOH, 1.93×10⁻⁵ cm² s⁻¹ in 0.5 M H₂SO₄). v is the kinetic viscosity (0.01 cm² s⁻¹ in 0.1 M KOH, 0.01009 cm² s⁻¹ in 0.5 M H₂SO₄). C_{O_2} is the bulk concentration of O_2 (1.2×10⁻³ mol cm⁻³ in 0.1 M KOH, 1.26×10⁻³ mol cm⁻³ in 0.5 M H₂SO₄). The constant 0.62 is adopted when the angular velocity of the disk is expressed in rad/s.², ³

The number of electron transferred and peroxide percentage during the ORR is calculated based on measurements on a rotating ring-disk electrode (RRDE, 5.61 mm of disk outer diameter, Pine Research Instrumentation, USA). The ring potential is set at 1.46 V vs RHE in 0.1 M KOH and 1.40 V vs RHE in 0.5 M H₂SO₄. Before experiments, the Pt ring was activated by potential cycling from 0 to 1.4 V (vs. RHE) at a scan rate of 50 mV s⁻¹ for at least 10 minutes. The number of electron transferred *n* and peroxide yield H₂O₂% in calculated using the following equations⁴.

$$n = \frac{4I_d}{I_d + \frac{I_r}{N}}$$
$$H_2O_2\% = \frac{200I_r}{NI_d + I_r}$$

Where N=0.37 is the collection efficiency, I_d and I_r is the disk current and the ring current, respectively.

4. Preparation and characterization of the MOF precursors

4.1 Preparation of ZIF-67 and ZIF-8

 $Co(Ac)_2 \cdot 4H_2O$ (10 mmol) and MeIM (20 mmol) are mixed by ball milling for 10 min. The mixture is divided equally into three 25 mL Teflon-lined autoclave. 10 mL ethanol is added to each autoclave. The autoclaves are sealed and heated in a programmable oven at 120 °C for 12 h. The purple products are separated by centrifugation, washed with ethanol for three times and dried at 80 °C. ZIF-8 is prepared in the same way, by using Zn(OAc)_2.2H_2O as the metal precursor instead of Co(OAc)_2.4H_2O.⁵

4.2 Preparation of Co₂(bdc)₂(dabco)

H₂bdc (0.84 mmol), 0.42 mmol of dabco, and 0.84 mmol of $Co(NO_3)_2 \cdot 6H_2O$ are dissolved in 10 mL DMF. Then the solution is sealed in a 25 mL Teflon-lined autoclave and kept at 110 °C for 24 h. The obtained purple crystalline powders are washed with DMF for three times and ethanol for at least one time, and dried at 60 °C.⁶

4.3 Characterization of the MOFs

The crystalline structures of obtained ZIF-67, Co₂(bdc)₂(dabco) and ZIF-8 are illustrated in Fig. S1. The obtained MOF structure is characterized by powder XRD (Fig. S2). The diffraction patterns are in good agreement with the simulated results using single crystal data.



Fig. S1 Crystal structures of ZIF-67, Co₂(bdc)₂(dabco) and ZIF-8. H atoms are omitted for clarity.



Fig. S2 Powder XRD patterns of the prepared MOF samples. The simulated patterns using single crystal data are also presented for comparison.

5. Structural characterization of the MOF-T samples

The content of C, H, and N in the carbonized products is analyzed by the combustion method. The metal content is estimated by TGA in air, assuming the residue is pure Co_3O_4 and ZnO phases (confirmed by XRD). The residue is dissolved in 3 M HNO₃ for ICP-AES measurement to further confirm the metal content. The analysis results are listed in Table 1 in the main text.





Fig. S4 Magnified TEM images of MOF-T. (a) Co₂(bdc)₂(dabco)-900, (b) ZIF-8-900.



Fig. S5 N₂ adsorption isotherms of the MOF-900 samples.



Fig. S6 Metal $2p_{3/2}$ (left) and the N 1s (right) XPS spectra of the MOF-T samples, (a-b) ZIF-67-900, (c-d) Co₂(bdc)₂(dabco)-900, (e-f) ZIF-8-900. The peaks at 778.3 and 780.4 eV in the Co $2p_{3/2}$ spectra are attributed to the metallic and divalent Co, respectively. The peaks at 1021.6 and 1022.8 eV in the Zn $2p_{3/2}$ spectra are attributed to the metallic and divalent Zn, respectively. The peaks at 398.4, 401 and 402.2 eV in the N 1s spectra are attributed to the pyridinic, pyrrolic and graphitic nitrogen, respectively.

6. Structural characterization of the ZIF-67-T samples



Fig. S7 TGA curves of ZIF-67 in the atmosphere of nitrogen. The curve indicates that the sample ZIF-67 has high thermal stability and decomposes at 400 °C.



Fig. S8 XRD patterns of ZIF-67-T. All the diffraction peaks are attributed to Co with fcc structures (JCPDS 15-0806).



Fig. S9 TEM images of ZIF-67-T. (a-b) ZIF-67-600, (c-d) ZIF-67-700, (e-f) ZIF-67-800. Aggregation of the Co particles at higher pyrolysis temperature leads to formation of nanoscale voids enclosed by graphitic layers.



Fig. S10 High-resolution XPS spectra of the ZIF-67-T and ZIF-67-AL samples: the Co $2p_{3/2}$ spectra (a) and the N 1s spectra (b). The peaks at 778.3 and 780.4 eV in the Co $2p_{3/2}$ spectra are attributed to the metallic and divalent Co, respectively. The peaks at 398.4, 401 and 402.2 eV in the N 1s spectra are attributed to the pyridinic, pyrrolic and graphitic nitrogen, respectively. The pyrrolic N/pyridinic N ratio increases with pyrolysis temperature.



Fig. S11 Raman spectra of the ZIF-67-T samples. The spectra are deconvoluted into four components following the approach by Sharifi et al⁷: the I band at 1180 cm⁻¹, the D band at 1330 cm⁻¹, the D" band at 1470 cm⁻¹ and the G band at 1590 cm⁻¹.

Table S1 Electric resistivity of the ZIF-67-T samples

Sample	ZIF-67-600	ZIF-67-700	ZIF-67-800	ZIF-67-900	Acetylene black	
Resistivity(Ω cm)	56	28	12	5	3	

7. Electrochemistry characterization of the ZIF-67-T samples



Fig. S12 Cyclic voltammograms of ZIF-67-900 in Ar- and O₂-saturated 0.1 M aqueous KOH electrolyte solution (a) and 0.5 M aqueous H_2SO_4 electrolyte solution (b) at a scan rate of 50 mV s⁻¹. The reduction peak around 0.4 V in (a) is attributed to the reduction of Co(II) to Co (0).



Fig. S13 Rotating ring disk voltammograms of ZIF-67-900 and ZIF-67-900-AL in O₂-saturated 0.1 M aqueous KOH and 0.5 M aqueous H_2SO_4 at a scan rate of 10 mV s⁻¹ at rotation rate of 1600 rpm. The ring potential was set at 1.46 V (vs RHE) in 0.1 M KOH and 1.40 V (vs RHE) in 0.5 M H_2SO_4 .



Fig. S14 Electron transfer number and peroxide percentage of Pt/C, ZIF-67-900 and ZIF-67-900-AL based on the RRDE data at 0.7 V and 0.5 V in alkaline and acidic electrolytes, respectively.



Fig. S15 Rotating disk voltammograms of ZIF-67-900 and ZIF-67-900-AL in O₂-saturated 0.1 M aqueous KOH at a scan rate of 10 mV s⁻¹ at different rotation rates (a-b); (c) and (d) Koutecky-Levich plots from Figure S15a and from Figure S15b at different electrode potentials.



Fig. S16 Rotating disk voltammograms of ZIF-67-900 and ZIF-67-900-AL in O₂-saturated 0.5 M aqueous H_2SO_4 at a scan rate of 10 mV s⁻¹ at different rotation rates (a-b); (c) and (d) Koutecky-Levich plots from Figure S16a and from Figure S16b at different electrode potentials.



Table S2 Electron transfer number *n* calculated from the K-L plots and RRDE tests.

Fig. S17 Chrono-amperometric responses in O_2 - saturated 0.1 M KOH at the potential of 0.56 V vs RHE (a) and 0.5 M H₂SO₄ (0.1 M HClO₄ for Pt/C) at the potential of 0.50 V vs RHE (b). Methanol is introduced at the time indicated by the arrow, giving a final concentration of 3 M. The rotating rate of the RDE is 1600 rpm.

Materials	Condition	Onset potential (V vs RHE)	Ref
Co3O4 Nanocrystals on Graphene	Alkaline	0.88	8
Triangular Trinuclear Co-N4 Complexes	Alkaline	0.82	9
Cobalt Oxide Nanocrystals and Carbon Nanotubes	Alkaline	0.93	10
Co-containing N-doped carbon	Alkaline	0.85	11
Cobalt and nitrogen-cofunctionalized graphene	Alkaline	0.86	12
Graphene-based non-noble-metal Co/N/C catalyst	Alkaline	0.85	13
ZIF-67-900	Alkaline	0.91*	this work
ZIF-67-900-AL	Alkaline	0.93*	this work
Pt/C	Alkaline	0.92*	this work
$Fe/Co-N_x$ doped porous carbon	Acidic	0.89	14
Electrocatalysts derived from Polyaniline, and Cobalt	Acidic	0.80	15
Electrocatalysts derived from Cobalt	Acidic	0.83	4

Table S3 A comparison with the state of the art noble metal free ORR catalysts based on Co and N-containing carbons reported recently and our work.

Imidazolate Framework			
ZIF-67-900	Acidic	0.85*	this work
ZIF-67-900-AL	Acidic	0.85*	this work
Pt/C	Acidic	0.88^{*}	this work

*Onset potential is obtained by the intersection of the tangents at the halfwave potential and the baseline.

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