Electronic Supporting Information

Hierarchically porous aggregates of Co-N-C nanoparticles for oxygen electrocatalysis

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1. Experimental Section

1.1 Preparation of Co-N-C materials

First, Co(NO₃)₂·6H₂O (1.164 g) and PSS (200 mg) were dissolved in methanol (50 mL) and stirred for about half an hour. Second, a solution of 2-methylimidazole (1.32 g, 50 mL methanol) was added to the Co solution. The resulting solution was aged for ~ 24 h. Finally, purple powers were obtained and defined as PSS-ZIF-67. The A-Co-N-C material was obtained by pyrolyzing precursor PSS-ZIF-67 at 900 °C for 3 h under Ar. For comparison, common ZIF-67 nanoparticles with the large and small size of PSS-ZIF-67 were prepared according to the method reported in the literature.¹ The resulting materials, named Co-N-C and S-Co-N-C, were obtained with the same pyrolysis procedure. The precursor PSS-ZIF-67 was washed with water and methanol and then pyrolyzed in the same way to obtain A-Co-N-C-2.

1.2 Material Characterizations

X-ray diffraction (XRD) patterns of materials were obtained by an X-ray diffractometer (D8 Advance, Bruker). Morphologies of materials were obtained by scanning electron microscopy (SEM, SU8020, Hitachi) and transmission electron microscopy (TEM, JEM-2100, JEOL). Brunauer-Emmett-Teller (BET) surface areas of materials were obtained by a specific surface area analyzer (ASAP 2020, Micromeritics). The weight by loss data of materials obtained thermoanalyzer were а system (Q1000DSC+LNCS+FACS Q600SDT, TA Instruments). X-ray photoelectron

spectroscopy (XPS) spectra of materials were obtained by an X-ray photoelectron spectrometer (AXIS ULTRA, Kratos Analytical Ltd.).

1.3 Electrochemical measurements

1.3.1 ORR

Electrochemical ORR performance was obtained with an electrochemical workstation (CHI 760E) and measured in O₂-saturated 0.1 M KOH. The rotating ring-disk electrode (RRDE; disk: 0.247 cm²; ring: 0.186 cm²) was selected as the working electrode. The RRDE was installed on a Pine Modulated Speed Rotator. Particularly, 20 μ L of catalysts ink (4 mg of catalysts in 640 μ L deionized water, 320 μ L isopropanol and 40 μ L Nafion solution (5 wt%, DuPont)) was coated onto a RRDE electrode (catalyst loading: ~ 0.3 mg cm⁻²). Cyclic voltammogram (CV) data were at 0.05 V s⁻¹. Linear sweep voltammogram (LSV) data were measured at 1600 rpm and 0.002 V s⁻¹. The number of transfer electron (*n*) was calculated with equation 1 based on LSV data measured at 1600 rpm with RRDE.

$$n = 4 \frac{i_d}{i_d + i_r / N}$$
(1)

Here, i_d is the current obtained on the disk, i_r is the current obtained on the ring, and N is the current collection efficiency of the ring electrode (~ 0.37). The production of hydrogen peroxide (%H₂O₂) can be calculated with equation 2.

$$^{\circ}H_2O_2 = 200 \frac{i_r / N}{i_d + i_r / N}$$
 (2).

Under the same instrument and working electrode conditions as for the ORR test, the collection coefficient (*N*) was tested in 1M KNO₃ and 2 mM K₃Fe(CN)₆ electrolyte. LSV data were measured at 1600 rpm and 0.005 V s⁻¹. The following reactions occur on the disk and ring respectively²:

Disk: $Fe(CN)_6^{3-} + e^- \rightarrow Fe(CN)_6^{4-}$

Ring: $Fe(CN)_6^{4-} \rightarrow Fe(CN)_6^{3-} + e^{-}$

The formula for calculating N is as follows:

$$N = \left| \frac{I_r}{I_d} \right|$$
(3)

According to test results of Fig. S1, it can be obtained that N = 0.37.

1.3.2 OER

Electrochemical OER performance was obtained with an electrochemical analyzer (CHI 630E). The glassy carbon (GC, 0.07 cm²) electrode was selected as the working electrode. Particularly, 5 μ L of the above catalyst ink was coated onto the GC electrode. LSV data were measured in 1.0 M KOH at 0.01 V s⁻¹ with *iR* compensation (100%). The overpotential (η , V) at 10 mA cm⁻² can be calculated with equation 4.

$$\eta = E_{Ag/AgCl} + (0.197 + 0.059 \times pH) - 1.23 \ (4)$$

Tafel slopes were calculated based on LSV data measured at 0.002 V s⁻¹. To compare the electrochemical surface area of catalysts, CV data were measured at 0.02, 0.04, 0.06, and 0.08 V s⁻¹ without *iR* compensation. Electrochemical impedance spectroscopy (EIS) results were obtained at 1.60 V (vs. RHE) from 0.1 to 1 mHz. To confirm the production of O₂ during the electrocatalytic process, LSV data of A-Co-N- C were measured with RRDE at 1600 rpm. Herein, the potential of the ring electrode was set at 0.4 V (vs. RHE). To obtain the Faraday efficiency (FE) of O_2 production, the controlled potential electrolysis of A-Co-N-C was carried out with the RRDE at 1600 rpm. Herein, potentials of ring and disk electrode were set at 0.4 V and 1.6 V (vs RHE), respectively. The FE can be calculated with equation 5.³

$$FE = 2\frac{i_r}{i_d / N}$$
(5)

The electrochemical double-layer capacitance (C_{dl}) was obtained by measuring CV curves in the non-Faraday region at different scan rates. C_{dl} was calculated by the following formula:

$$j = C_{dl} \times v \quad (6)$$

The ECSA value was calculated using the following formula⁴:

$$ECSA = \frac{C_{dl}}{C_s}$$
(7)

The $C_{\rm s}$ is the specific capacity, which is a parameter for Co-based materials.

1.3.3 Zn-air battery

The performance of a Zn-air battery constructed with catalysts was evaluated with an electrochemical workstation (CHI 660E). A Zn-air battery includes three parts: the anode, electrolyte, and cathode. The anode is a new polished Zn plate. The electrolyte is a mixed solution of KOH (6.0 M) and ZnCl₂ (0.2 M). The cathode was obtained by coating catalysts (0.50 mg cm⁻²) on a carbon cloth/gas diffusion layer hybrid electrode.



Fig. S1 Determination of the collection coefficient (N) of the RRDE by $[Fe(CN)_6]^{4-}$

oxidation.



Fig. S2 TGA of (a) PSS-ZIF-67 and (b) ZIF-67.

An obvious peak of derivative mass was observed at 500 °C for PSS-ZIF-67 compared with ZIF-67. The introduction of PSS makes the decomposition temperature earlier.



Fig. S3 XRD patterns of ZIF-67, PSS-ZIF-67, and calculated ZIF-67.



Fig. S4 N_2 adsorption and desorption curves of PSS-ZIF-67.



Fig. S5 Pore size distribution of PSS-ZIF-67.



Fig. S6 The CV curve of A-Co-N-C was measured in O_2 -saturated 0.1 M KOH.



Fig. S7 The CV curve of Co-N-C was measured in O_2 -saturated 0.1 M KOH.



Fig. S8 SEM image of ZIF-67 with small size (~ 100 nm).



Fig. S9 SEM image of S-Co-N-C obtained by calcining ZIF-67 with small size (~ 100

nm).



Fig. S10 LSV data of S-Co-N-C.



Fig. S11 LSV data of A-Co-N-C-2.



Fig. S12 Controlled potential electrolysis tests of A-Co-N-C and Pt/C measured at

0.66 V (vs RHE).



Fig. S13 Tafel plots of A-Co-N-C and Co-N-C for OER.



Fig. S14 CV data of A-Co-N-C (a) and Co-N-C (b) at scan rates of 0.02, 0.04, 0.06

and 0.08 V s⁻¹ for OER.



Fig. S15 I-t curves of A-Co-N-C measured with the RRDE in 0.1 M KOH.



Fig. S16 Charge–discharge voltages at j = 10 mA cm⁻².



Fig. S17 SEM image of A-Co-N-C after several hours stability test.



Fig. S18 Full survey XPS spectrum (a), XPS spectra of Co 2p (b), N 1s (c) and S 2p (d) for A-Co-N-C after several hours stability test. The SO₄²⁻ become the dominate phase of S 2p due to the electrolysis.

Table S1 Comparison of EIS for A-Co-N-C and Co-N-C.

Catalysts	$R2/\Omega$
A-Co-N-C	43.88
Co-N-C	172.6

The R_2 of A–Co–N–C is 43.88 Ω , which is much smaller than that of Co–N–C (172.6

Ω).

		ORR	OER	
Catalysts	Synthesis methods	$E_{1/2}$	overpotential	References
		(mV)	$(mV)(j_{10})$	
A-Co-N-C	pyrolysis with PSS	875	334	This work
SSM/Co ₄ N/CoNC	in situ grown	833	270	5
Onion-like carbon/Co-N- C	pyrolysis with P123	855	344	4
N/P-C-CoP-850	gelatinized guar gum 825		306	6
CoNC-NB ₂	self-catalyzed chemical vapor deposition	880	350	7
Co/Co-N-C	electrochemical deposition and pyrolyzation strategy	690	400	8
MoC/Co-N-C-600	pyrolysis with MoC	865	370	9
	low-energy pulsed-laser irradiation			
Co ₃ O _{4-X} doped graphene	technique and a hydrothermal	829	327	10
	method			
Mn/Co-N-C-0.02-800	pyrolysis	800	430	11
NiS ₂ @Co-N-C/CNF	high-temperature carbonization and hydrothermal method	800	300	12
FeCo/Co-N-C	one-step annealing method	860	380	13
Pt _{SA} -PtCo NCs/N-CNTs-	melamine-orientation-induced and	860	252	14
900	pyrolysis	800		
Co/Co-N-C	Sandwich-like confinement pyrolysis route	850	-	15
G-CoNOC	-CoNOC Graphene quantum dots (GQDs)		-	16
chemical vapor deposition		850	_	17

Table S2 Comparison of the synthesis methods, ORR and OER performance of A-

Co-N-C and other similar materials.

process

Co@NG-800	hydrometallurgical method	850	-	18
Co-N-C/CNTsHS	spray-drying	870	-	19
Co-N ₃ -C	pyrolysis of CNT-inserted ZIFs	891	-	20
Co-NCS-2	ultrasonication-assisted strategy	900	-	21
Co-SAs/N-C/rGO	spatial-isolation strategy	840	-	22
Ru/Co-N-C-800	pyrolyzing and acid etching	-	276	23

Catalysts	Electrolytes	∆(charge– discharge)E (mV)	Durability (h)	Peak power density (mW cm ⁻²)	References
A-Co-N-C	6 M KOH, 0.2 M Zn(Ac) ₂	0.85	25	240	This work
NiCo-N-C	6 M KOH, 0.2 M Zn(Ac) ₂	0.8	140	163	24
Co porphyrin@ZIF-67	6 M KOH, 0.2 M Zn(Ac) ₂	0.85	112	220	25
Co/Co-N-C	6 M KOH, 0.1 M Zn(Ac) ₂	0.82	330	132	26
Onion-like carbon/Co-N-C	6 M KOH, 0.1 M ZnCl ₂	0.8	105	238	27
$Co-N_{4-x}-C_x$	6 M KOH	0.8	60	184	28
Zn,Co-N _x -C-S _y	KOH/ZnAc (0.1:0.02 M) solid polymer electrolyte	-	-	150	29
PdMo	6 M KOH,	0.7	116	154	30
bimetallene/C	0.2 M Zn(Ac) ₂	0.7	-		
NiCo ₂ O ₄ /N-	6 M KOH,	0.8	15	103	31
graphene CoFe ₂₀ @carbon cages	0.1 M ZnCl ₂ 6 M KOH, 0.2 M Zn(Ac) ₂	1	130	190	32
Co@N-C	6 M KOH, 0.2 M Zn(Ac) ₂	0.53	120	105	33

Table S3 Comparison of peak power densities of Zn-air batteries constructed with A-Co-N-C and other reported catalysts.

Co@Co-N-C	6 M KOH	-	-	155	34
(Co,Fe) ₃ N	6 M KOH,	0.85	300	234	25
	0.2 M Zn(Ac) ₂	0.85			55
CoFe-N-C	6 M KOH,	0.8	267	203	36
	0.2 M Zn(Ac) ₂	0.0			50
Co/CoO@Co-N-C	6 M KOH,	0.86	11	157	37
	0.2 M Zn(Ac) ₂	0.00			51

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