# **Electronic Supplementary Information (ESI)**

## Fe-Co Heteronuclear Atom Pairs as Catalytic Sites for Efficient

## **Oxygen Electroreduction**

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#### Characterizations

Scanning electron microscopy (SEM) observations were carried out on a Hitachi S-4800 microscope with an acceleration voltage of 530 KV. Transmission electron microscopy (TEM), high resolution transmission electron microscopy (HR-TEM) were carried out on the Tecnai G2 F-20 microscope with an acceleration voltage of 200 KV. The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was carried out on a JEOL JEM-2100F with an acceleration voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was conducted on a PHI-1600 X-ray photoelectron spectrometer using AI Ka radiation, and C 1s peak (284.8 eV) of contamination carbon was adopted to calibrate binding energy.

The X-ray absorption structure spectroscopy (XAS) measurement was carried out at Beijing Synchrotron Radiation Facility with a 1W2B beamline, using an incident beam monochromatized by Si (111) double crystal monochromators.

X-ray diffraction (XRD) patterns were collected on a D8-Focus X-ray diffractometer system with Cu Ka radiation ( $\lambda$ = 1.5419 Å) with a scanning rate of 5 min<sup>-1</sup>. Fourier transform infrared (FT-IR) spectrum was recorded on a Bruker FTIR spectrophotometer. Nitrogen physisorption experiments were conducted on a Micomeritics ASAP 2460 volumetric absorption analyzer at -196 °C. The melting point of the catalyst is measured using MP50 Melting point system.

#### **Electrochemical measurements**

All electrochemical measurements were carried out on the IVIUMSTAT workstation (Ivium Technologies BV, Netherlands) under the three-electrode system at room temperature. The catalyst was supported on a glassy carbon electrode (GCE) with a diameter of 5 mm (Pine Research Instrumentation Inc.) was used as a working electrode, whereas graphite rod and Hg/HgO electrode were used as counter and reference electrodes, respectively.

The homogeneous catalyst ink was prepared by mixing 5 mg of catalyst, 725  $\mu$ L of isopropanol, 245  $\mu$ L deionized water and 30  $\mu$ L of Nafion solution (5 wt.%) with 0.5 h of sonication to obtain a uniform suspension. Then, a thin film catalyst layer (0.255 mg cm<sup>-2</sup> catalyst) was obtained by depositing 10  $\mu$ L of catalyst ink onto the rotating disk electrode (RDE, 0.196 cm<sup>-2</sup>).

Cyclic voltammetry (CV) tests were performed in an O<sub>2</sub>-saturated 0.1 M KOH with a scan rate of 50 mV/s. A three-electrode system was used to conduct the electrochemical measurements on an electrochemical workstation. The linear sweep voltammetry (LSV) polarization curves were performed at 0.3 and 1.1 V (vs RHE) in O<sub>2</sub>-saturated 0.1 M KOH solution at the scan rate of 5 mV·s<sup>-1</sup> with different rotating speeds of 400, 625, 900 and 1600 rpm. The electron transfer number (n) was obtained by RRDE measurements.

$$n = \frac{4 \times I_d}{\left(\frac{I_r}{N} + I_d\right)}$$

The peroxide yields  $(H_2O_2\%)$  in alkaline conditions wre calculated by the equation:

$$H_2 O_2 = \frac{200 \times I_r}{\left(I_r + N \times I_d\right)}$$

Where  $I_d$  is the disk current,  $I_r$  is the ring current, and N (0.37) is the collection coefficient. The accelerated durability test was conducted from 0.6 V to 1.0 V at a scan rate of 50 mV/s.

#### Zinc-air battery and Hydrogen Fuel Cell Tests.

The performance of Zn-air battery was measured in home-made electrochemical cells. The zinc-air battery was composed of a polished zinc foil as anode,  $1 \times 1 \text{ cm}^2$  carbon paper loaded with catalysts as cathode and 6.0 M KOH solution served as the electrolyte. The catalyst loading of the 20 wt.% Pt/C or FeCo-N-C was 1 mg cm<sup>-2</sup>. For the fuel cell test, the cathode and anode inks were obtained by dispersing FeCo-N-C and commercial Pt/C catalysts (TKK, 50%) in a combination of FAA-3-solut-10 ionomer (5 wt %) and isopropanol/water (3:1 v/v, 5 mL). The inks were then sonicated, stirred, and separately spray coated onto the twosides of an anion-exchanged membrane (AEM, FAA-50, FuMATech). The mass loadings for the cathode and anode are 4.0 mg<sub>catalyst</sub> cm<sup>-2</sup> and 0.1 mg<sub>Pt</sub> cm<sup>-2</sup>, respectively. The fuel cell performance was examined at 80 °C by supplying fully humidified (100% RH) H<sub>2</sub> (0.5 L min<sup>-1</sup>) and O<sub>2</sub> (1.0 L min<sup>-1</sup>) to the anode and cathode, respectively.

### .In Situ SR-FTIR Measurements.

In situ SR-FTIR measurements were performed by using a INVENIO S spectrometer equipped with a DRIFTS accessory. An MCT detector, a KBr beam splitter, and an external microscope (Bruker Hyperion 3000) were used in combination with a custom-fabricated electrochemical cell. The working electrode was a Au-plated silicon wafer loaded with catalyst.



Figure S1. Photographs of FeCo-N-C catalyst.



Figure S2. SEM images of carbon black ECP-600JD.



Figure S3 EDS elemental mapping images for Fe-N-C.



Figure S4 (a) TEM image and (b) SAED pattern for Fe-N-C.



Figure S5 EDS elemental mapping images for Co-N-C.



Figure S6 (a) TEM image and (b) SAED pattern for Co-N-C.



Figure S7 (a)TEM image and (a) SAED pattern for Fe@Fe-N-C catalyst without preheating treatment.



Figure S8. Melting point tester test result of Fe-phen. The sample began to melt at 88.8 °C.



Figure S9. TGA curve of Fe-phen@C tested in  $N_2$  ambient.



Figure S10 (a) Aberration-corrected HAADF-STEM image of Fe-Co-N-C are highlighted by red circles (The red circles 4, 5, 6 and 7 are partially enlarged on the right). (c) Intensity profiles of the four sites in b.



Figure S11. Pore distribution curve of FeCo-N-C.



Figure S12. Wavelet transform plots for (a) Fe of FePC and (b) Co of CoPC .

Note: For Wavelet Transform analysis, the  $\chi(k)$  exported from Athena was imported into the Hama Fortran code. The parameters were listed as follow: R range, 0 - 4 Å, k range, 0 - 16Å<sup>-1</sup> for samples; k weight, 2; and Morlet function with  $\kappa$ =10,  $\sigma$ =1 was used as the mother wavelet to provide the overall distribution.



Fig S13 Comparison between the experimental K-edge XANES spectra of FeCo-N-C and the theoretical spectra calculated based on  $FeCoN_6$  structure<sup>1</sup>. Blue and pink represent Fe and Co, respectively, while blue and gray spheres represent N and C. The Fe and Co K-edge theoretical XANES calculations were carried out with the FDMNES code in the framework of real-space full multiple-scattering (FMS) scheme using Muffin-tin approximation for the potential<sup>2–4</sup>. The energy-dependent exchange-correlation potential was calculated in the real Hedin–Lundqvist scheme, and then the spectra convoluted using a Lorentzian function with an energy-dependent width to account for the broadening due both to the core–hole width and to the final state width.



Figure S14. (a) Polarization curves of FeCo-N-C at different rotating speeds from 400 to 1600 rpm and (b) corresponding Koutecky-Levich plot.



Figure S15. ORR polarization curves of (a) FeCo-N-C and (b) 20% Pt/C before and after 5000 CV cycles (inset: onset potential and half-wave potential evolution of FeCo-N-C and 20% Pt/C before and after 5000 CV cycles).



Figure S16. Current–time (i–t) chronoamperometric response of FeCo-N-C at 0.8 V (vs. RHE) in 0.1 M KOH solution.



Figure S17. HRTEM image of FeCo-N-C after ORR measurement.



Figure S18. XRD image of FeCo-N-C after ORR measurement.



Figure S19. Raman image of FeCo-N-C after ORR measurement.



Figure S20. LSV curves and corresponding electrochemical performance of catalysts prepared with different types of carbon black as substrate under alkaline conditions.

Note: The experiment found that the catalytic activity of catalysts prepared using different types of carbon black as substrate loading varies greatly, which may be due to the significant influence of the morphology of carbon black on the adsorption of catalyst precursors; Among them, the Fe-N-C catalyst prepared on the basis of Ketjen black ECP-600JD exhibited the highest catalytic activity.



Figure S21. LSV curves and corresponding electrochemical performance of catalysts prepared with different amounts of carbon black added under alkaline conditions. (The specific amount of addition is shown in the Table S3).

Note: Under alkaline conditions, as the amount of carbon black added increases, the activity of the catalyst first increases and then decreases; When the amount of carbon black added is 1200 mg/mmol Fe<sup>2+</sup>, the catalyst activity was the highest.



Figure S22. LSV curves and corresponding electrochemical performance of catalysts prepared with different iron sources under alkaline conditions.

Note: Due to the inability to remove anions from iron metal salts during the reaction process, different types of iron metal salts have an impact on the final catalyst activity; When several common ferrous metal salts are used as iron sources, the catalyst prepared by FeCl<sub>2</sub> exhibited the highest activity.



Figure S23 LSV curves and corresponding electrochemical performance of catalysts prepared with different loading methods under alkaline conditions.

Note: Due to the rapid reaction between Fe<sup>2+</sup> and phen, this process mainly considers the loading process of Fe (phen) on carbon black after the reaction ; Comparing the catalysts prepared by three methods, the catalyst prepared using "Ultrasound + rotary steaming" had the highest activity.



Figure S24. LSV curves and corresponding electrochemical performance of catalysts prepared with different preheating treatments under alkaline conditions.

Note: Preheating the material can partially melt the precursor Fe(phen) of the catalyst, leading to a preliminary connection with carbon black; Comparing several pre-treatment temperatures and catalysts prepared without pre-treatment, it was found that the catalytic activity of the materials increased after pre-treatment, and the samples prepared at 150 °C had the highest activity among different pre-treatment temperatures.



Figure S25. LSV curves and corresponding electrochemical performance of catalysts prepared with different calcined treatments under alkaline conditions.

Note: After pre-treatment, the material still needs to be further calcined to convert the Fe(phen) precursor into the required  $Fe-N_x$  site and make the combination more firm ; Comparing catalysts prepared at different calcination temperatures, it was found that with the increase of calcination temperature, the activity of the prepared catalyst first increased and then decreased, and the sample prepared at 800 °C had the highest activity.



Figure S26. LSV curves and corresponding electrochemical performance of catalysts prepared with different ratio of Fe : phen under alkaline conditions.

Note: As one of the reactants, the coordination between phen and  $Fe^{2+}$  directly affects the formation of catalytic sites; Comparing several catalysts prepared with different ratios, it was found that as the amount of phen gradually decreased, the activity of the prepared catalyst first increased and then decreased. The sample prepared at a Fe: phen ratio of 1:3 had the highest activity.



Figure S27. LSV curves and corresponding electrochemical performance of catalysts prepared with different Co ion addition amount under alkaline conditions.

Note: Under alkaline conditions, it was found that the introduction of  $Co^{2+}$  ions can indeed increase the activity of the catalyst ; As the amount of  $Co^{2+}$  ions added gradually decreases, the activity of the prepared catalyst first increases and then decreases. When  $Fe^{2+}:Co^{2+}$  is 4:1, the catalyst activity was highest.



Figure S28. ZABs open circuit voltage diagram based on FeCo-N-C catalyst.



Figure S29. Polarization and power density curves of Fe-N-C and Co-N-C in ZABs.



Figure S30. LED test of (a) FeCo-N-C and (b) Pt/C based ZABs.



Figure S31. Device diagram of the AEMFC.



Figure S32. In suit ATR-SEIRAS operation system.

Sample	Scattering pair	CN	R(Å)	σ²(10 <sup>-3</sup> Ų)	ΔE <sub>o</sub> (eV)	R factor
FeCo-N-C	Fe-N1	1.9	1.97	4.6		
	Fe-N2	1.0	2.07	4.0	-4.3	0.0155
	Fe-Co	1.1	2.58	6.6		

Table S1. Structural parameters extracted from the Fe K-edge EXAFS fitting of FeCo-N-C.

Table S2. Structural parameters extracted from the Co K-edge EXAFS fitting of FeCo-N-C ( $S_0^2$ =0.73).

Sample	Scattering pair	CN	R(Å)	σ²(10 <sup>-3</sup> Ų)	ΔE₀(eV)	R factor
FeCo-N-C	Co-N1	2.0	1.96	0.0080		
	Co-N2	1.0	2.08	0.0186	-2.5	0.0158
	Co-Fe	1.0	2.80	0.0066		

<sup>*a*</sup>*CN*: coordination numbers; <sup>*b*</sup>*R*: bond distance; <sup>*c*</sup> $\sigma^2$ : Debye-Waller factors; <sup>*d*</sup> $\Delta E_0$ : the inner potential correction. *R* factor: goodness of fit.

The obtained XAFS data was processed in Athena (version 0.9.26) for background, pre-edge line and postedge line calibrations. Then Fourier transformed fitting was carried out in Artemis (version 0.9.26). The k<sup>2</sup> weighting, k-range of 3 ~ 12 Å<sup>-1</sup> and R range of 1 - 3 Å were used for the fitting of Co foil; The k<sup>2</sup> weighting, k-range of 3 ~ 8 Å<sup>-1</sup> and R range of 1 - 3 Å were used for the fitting of Sample. The four parameters, coordination number, bond length, Debye-Waller factor and E<sub>0</sub> shift (CN, R,  $\Delta$ E<sub>0</sub>) were fitted without anyone was fixed, the  $\sigma^2$  was set.

Carbon black addition amount (mg)/mmol Fe <sup>2+</sup>	Carbon black addition amount	Fe <sup>2+</sup>	phen
800	200 mg	50 mg(0.25 mmol)	135 mg(0.75 mmol)
1000	—	40 mg(0.2 mmol)	108 mg(0.6 mmol)
1200	—	32.6 mg(0.166 mmol)	89.6 mg(0.498 mmol)
1400	_	28 mg(0.143 mmol)	78 mg(0.429 mmol)

Table S4. Electrochemical composition of different catalysts.

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	Fe-N-C	Co-N-C	FeCo-N-C
Fe (wt%)	3.77	—	3.42
Co (wt%)	_	4.17	1.17

Element	(kev)	Mass%	Counts	Sigma	Atoms%
С	0.277	92.77	48479.77	0.32	97.07
Ν	0.392	1.99	1537.13	0.06	1.78
Fe	0.705	2.62	977.94	0.16	0.59
Со	0.776	2.62	910.45	0.14	0.56
Total	~	100.00	~	~	100.00

Table S5. Thin Film Standardless Quantitative Analysis of FeCo-N-C in Fig. 1d.

Table S6. Thin Film Standardless Quantitative Analysis of Fe-N-C in Fig S3.

Element	(kev)	Mass%	Counts	Sigma	Atoms%
С	0.277	95.34	9627.91	0.75	96.23
Ν	0.392	4.25	635.38	0.19	3.68
Fe	0.705	0.41	29.43	0.24	0.09
Total	~	100.00	~	~	100.00

Table S7. Thin Film Standardless Quantitative Analysis of Co-N-C in Fig S5. Element (kev) Mass% Counts Sigma Atoms% С 0.277 95.70 18129.17 0.54 97.22 0.392 2.84 979.14 0.11 2.48 Ν 0.776 1.46 183.19 0.18 0.3 Со ~ ~ ~ Total 100.00 100.00

Catalyst	E <sub>onset</sub> (mV)	E <sub>1/2</sub> (mV)	Reference	Catalyst loading (mg cm <sup>-2</sup> )
FeCo-N-C	1.08	0.892	This Work	0.255
Fe <sub>1</sub> Co <sub>3</sub> -NC-1100	1.05	0.877	5	0.736
FeCo-N-HCN	0.98	0.86	6	0.1
FeCo-DACs/NC	0.98	0.87	7	0.26
CoFe@HNSs	1	0.89	8	0.28
CoFe@NC/C	0.92	0.75	9	~
FeCo-NC-850	0.997	0.864	10	0.28
CoFe/N-GCT	0.91	0.79	11	~
FeCo@MNC	0.98	0.86	12	0.36
D-FeCo@NHC	0.971	0.874	13	~
Fe,Co/DSA-NSC	1.03	0.879	14	0.25
FeCoNC-800	0.93	0.88	15	0.5
CoNP@FeNC	0.98	0.85	16	0.153

Table S8. Comparison of ORR performance of FeCo-N-C with other reported M-N-C catalysts.

Catalyst	lonomer	Membrane	Maximum power density (mW cm <sup>-2</sup> )	Operating condition	Reference
FeCo-N-C	Fumion FAA-3- solut-10	Fumasep FAA- 50	444.7	80 °C, 100% RH	This Work
Fe-N-Gra	HMT-PMBI	HMT-PMBI	243	60 °C, 200 kPa	17
Fe-NMG	AS-4	Tokuyama A201	218	70 °C, 100% RH, 140 kPa	18
Fe-N-comp-2	AS-4	Tokuyama A201	120	50 °C, 80% RH, 20 kPa	19
g-CN-CNF-700	AS-4	Tokuyama A201	171	50 ℃, 100% RH, 150 kPa	20
Fe-N/C	VTLC	VTLC-PET	380	80 °C, 100% RH	21
Fe <sub>x</sub> Co <sub>y</sub> -N-C	AS-4	Tokuyama	117	60 °C, 100% RH	22
p-KB/FePC	HMT-PMBI	HMT-PMBI	182	60 °C, 100% RH, 200 kPa	23
FePc-KCB	~	<b>FePc-KCB</b>	108	50 °C, 100% RH	24
NiCu/KB	AS-4	Tokuyama A201	350	80 °C, 140 kPa	25
NFC@Fe/Fe₃C -9	FAA-3- SOLUT-10	Fumapem FAA3	273	60 °C, 100% RH, 250 kPa	26
Fe/Co/IL- CNF800b	HMT-PMBI	HMT-PMBI	195	60 °C, 80% RH, 200 kPa	27
Fe-N <sub>x</sub> -C	AS-4	Tokuyama A201	255	50 °C, 28 psi	28
Fe/IL-PAN- A1000	HMT-PMBI	HMT-PMBI	289	60 °C, 100% RH, 200 kPa	29
o-MFe-10: 20 :5	AS-4	Tokuyama A201	407.5	80 °C, 100% RH, 150 kPa	30

Table S9. Comparison of  $H_2/O_2$  AEMFC performance of FeCo-N-C with other reported Pt-free catalysts.

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