

Single-Atom Iron Catalyst on Hierarchical N-doped Carbon for Highly Efficient Oxygen Reduction in Zn-Air Battery

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1. Experimental section

1.1 Electrochemical measurements

All the electrochemical tests were performed on a CHI 760E electrochemical workstation (Shanghai Chenhua Instrument Factory, China) and coupled with a rotating-ring disc electrode (RRDE, Pine, AFMSRCE) in a three-electrode system. A glass carbon rotating disk electrode (RDE), a Hg/HgO electrode filled with 1 M KOH and Pt plate served as the working electrode (0.196 cm²), the reference electrode, and the counter electrode, respectively. All potentials in this work were referenced to the reversible hydrogen electrode (RHE). The homogeneous catalyst ink was prepared by dispersing 2.5 mg catalyst and 10 μ L Nafion (5%) into 0.5 mL aqueous isopropanol solution (V/V, 1:1) for 0.5 h sonication. Then 20 μ L of the catalyst ink was loaded onto the surface of RDE and dried at the room temperature. Before each measurement, the reference electrode was calibrated to the RHE in Ar saturated 0.1 M KOH electrolyte. Then, the pure O₂ was flowed into the cell for 30 minutes to achieve an O₂ saturated 0.1 M KOH electrolyte. Linear sweep voltammetry (LSV) tests were performed at rotating speeds from 400 to 2400 rpm at a sweep rate of 10 mV·s⁻¹ at room temperature. The cyclic voltammetry (CV) tests were conducted in Ar or oxygen saturated 0.1 M KOH at a scan rate of 20 mV·s⁻¹ at room temperature. In addition, the capacitive background of the carbon support was necessarily collected by testing the LSV at the same scan rate in an Ar saturated 0.1 M KOH electrolyte. The cyclic voltammetry (CV) measurement at different scan rates was performed to calculate the electrochemical double-layer capacitance (C_{dl}), $C_{dl} = j/v$, where j (mA·cm⁻²) is the average value of current density at 1.054 V vs RHE and v is the scan rate (mV·s⁻¹). The electrochemical surface area (ECSA) can be obtained from the equation: $ECSA = C_{dl} \text{ of catalyst } / C_s$. The specific capacitance (C_s) value $C_s = 40 \mu\text{F}\cdot\text{cm}^{-2}$ is adopted for the estimation of ECSA. The electron transfers number (n) and kinetic current density (J_k) were calculated from the Koutecky-Levich equation:

$$\frac{1}{J} = \frac{1}{J_L} + \frac{1}{J_k} = \frac{1}{B\omega^{0.5}} + \frac{1}{J_k} \quad (1)$$

$$B = 0.62nFC_0(D_0)^{2/3}\nu^{-1/6} \quad (2)$$

J is the measured current density and ω is the electrode rotating rate ($\text{rad}\cdot\text{s}^{-1}$). J_L and J_k are the diffusion- and kinetic-limiting current densities, respectively. n is the transferred electron number, F is the Faraday constant ($F = 96485 \text{ C}\cdot\text{mol}^{-1}$), C_0 is the O_2 concentration in the electrolyte ($C_0 = 1.2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$), D_0 is the diffusion coefficient of O_2 ($D_0 = 1.9 \times 10^{-5} \text{ cm}^2\cdot\text{s}^{-1}$), and ν is the kinetic viscosity ($\nu = 0.01 \text{ cm}^2\cdot\text{s}^{-1}$). The constant 0.62 is adopted when the rotation speed is expressed in $\text{rad}\cdot\text{s}^{-1}$.

The hydrogen peroxide (H_2O_2) yield and transfer number (n) were determined by the followed equations:

$$HO_2^- = 200 \frac{I_r/N}{I_d + I_r/N} \quad (3)$$

$$n = 4 \frac{I_d}{I_d + I_r/N} \quad (4)$$

where I_d and I_r are disk and ring currents, respectively. N is the ring current collection efficiency (37%).

The turnover frequency (TOF) of the catalysts were calculated based on the surface mole of the iron single atoms. The value of TOF was determined by the equation:

$$TOF = \frac{J_k \times S}{4N \times F} \quad (5)$$

where J_k indicated the kinetic current density at 0.9 V, S represented the specific area of RDE (0.196 cm^2), 4 is the number of electrons transferred during O_2 reduction, N was the mole number of the iron single atom sites on the electrode obtained from the metal concentrations, F was the Faraday constant ($96485 \text{ C}\cdot\text{mol}^{-1}$).

The mass activity of the catalysts was calculated by the following equation:

$$MA = \frac{J_k \times S}{m \times C} \quad (6)$$

where J_k indicated the kinetic current density at 0.9 V, S represented the specific area of RDE (0.196 cm^2), m was the mass of the catalysts loading on RDE, C indicated the metal concentration based on the results of ICP.

1.2 Zn-air battery tests

To construct the liquid ZABs, a polished zinc foil and carbon paper loaded with catalysts were worked as the anode and air cathode, respectively. The electrolyte was a 6 M KOH solution with 0.2 M $\text{Zn}(\text{COOH})_2$. The air cathode was prepared by dropping Fe-SA@NC/ RuO_2 (mass ratio, 1:1) or Pt/C- RuO_2 (mass ratio, 1:1) on the carbon paper to achieve a catalyst loading of $1 \text{ mg}\cdot\text{cm}^{-2}$ for rechargeable air electrode.

The solid-state ZABs were fabricated by a zinc foil as anode, Fe-SA@NC loaded carbon paper as air cathode, respectively. The Zn foil was polished by abrasive paper and washed with ethanol. The solid electrolyte was composed of polyvinyl alcohol (PVA), KOH and $\text{Zn}(\text{COOH})_2$. The mass loading of catalyst is $2 \text{ mg}\cdot\text{cm}^{-2}$ for flexible solid rechargeable air electrode. The solid electrolyte was prepared as the following steps: PVA powder was added into 50 mL H_2O at $90 \text{ }^\circ\text{C}$ and stirred for 30 minutes. When the solution turned into transparent gel, the mixture of 6 M KOH and 0.2 M $\text{Zn}(\text{COOH})_2$ was added drop by drop. After being stirred for 30 minutes, the gel was evenly placed at the evaporating dish and refrigerated in the refrigerator for 24 h. Then the gel was taken out and thawed at room temperature.

2. Supplementary data

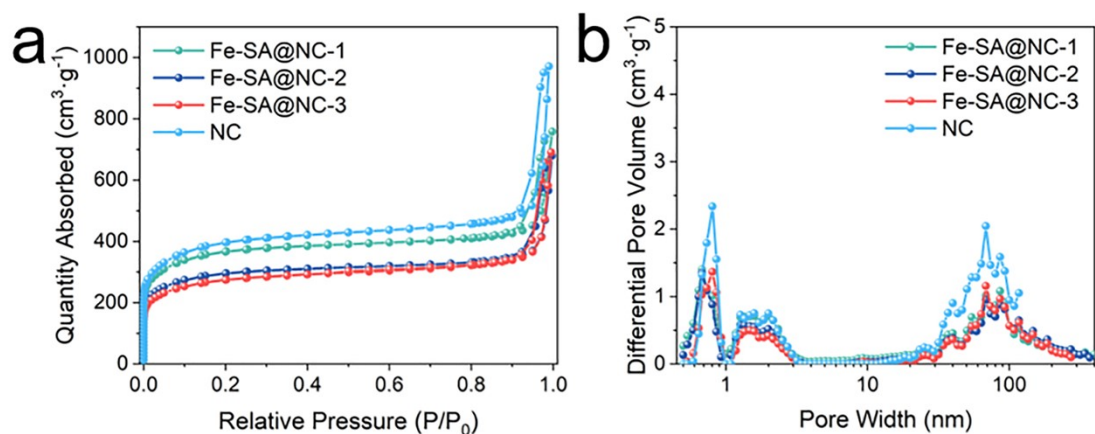


Fig. S1. (a) N_2 adsorption-desorption isotherms, (b) Pore-size distribution curves of the catalysts.

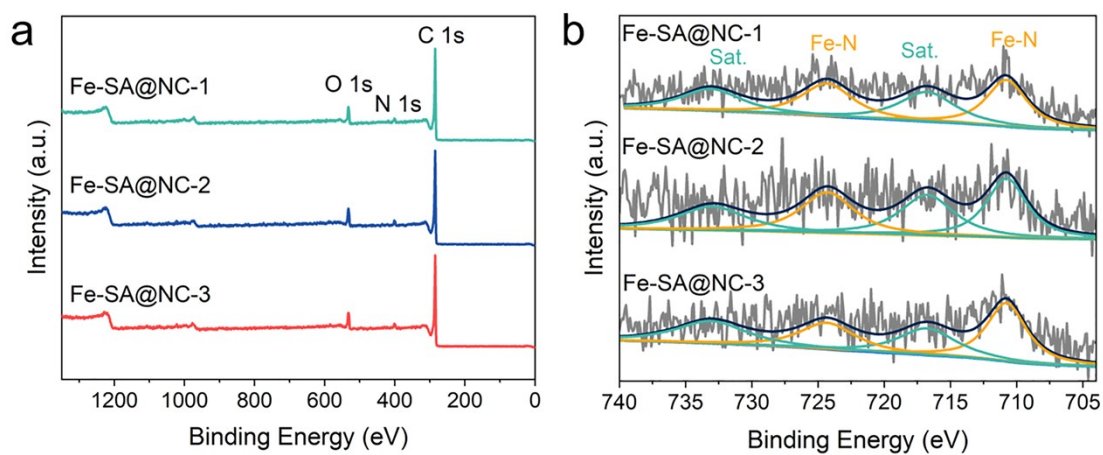


Fig. S2. (a) XPS survey of the Fe-SA@NC catalysts, (b) High-resolution of Fe 2p spectra of the catalysts.

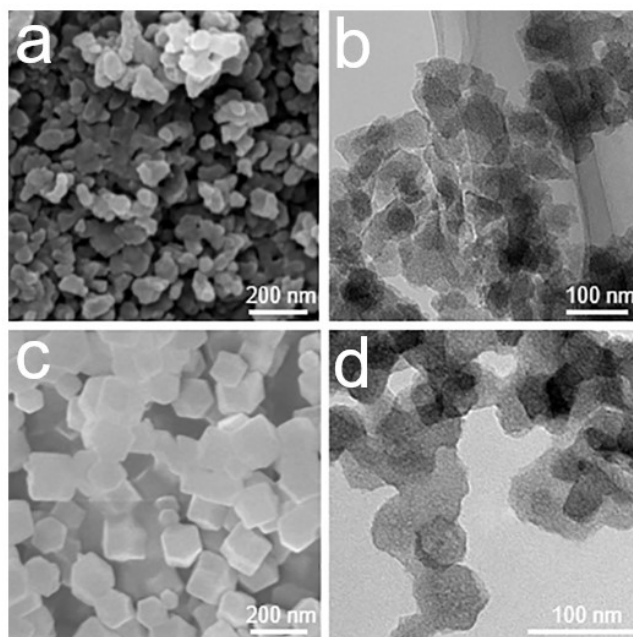


Fig. S3. (a) SEM and (b) TEM images of NC, (c) SEM and (d) TEM images of ZIF-8.

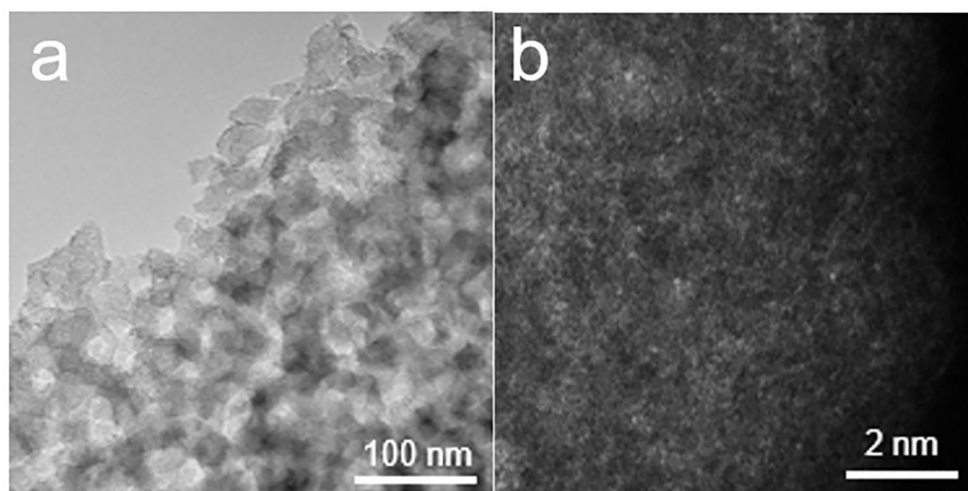


Fig. S4. (a) TEM image, (b) AC HAADF-STEM image of Fe-SA@NC-2.

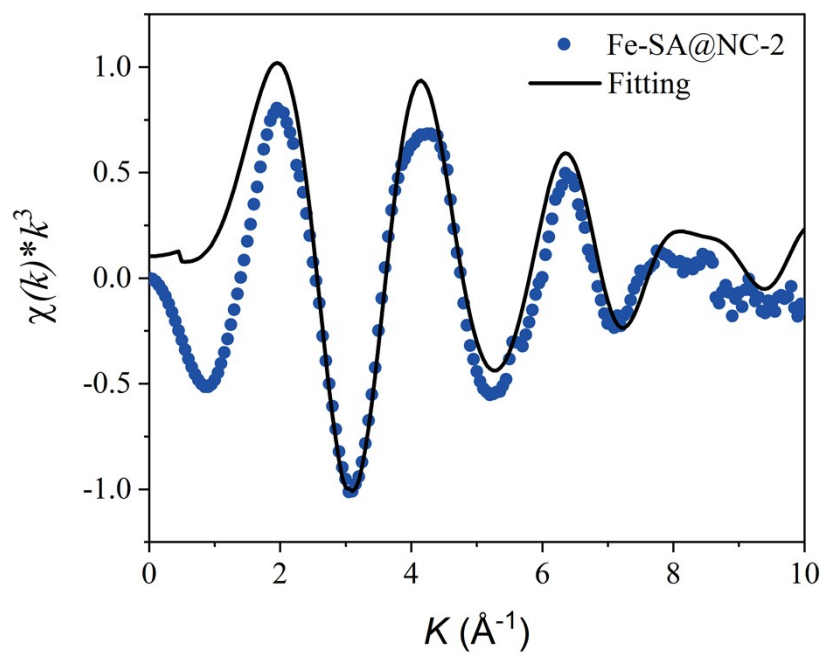


Fig. S5. Fe k-edge EXAFS and the fitting for Fe-SA@NC-2, shown in k^3 weighted K-space.

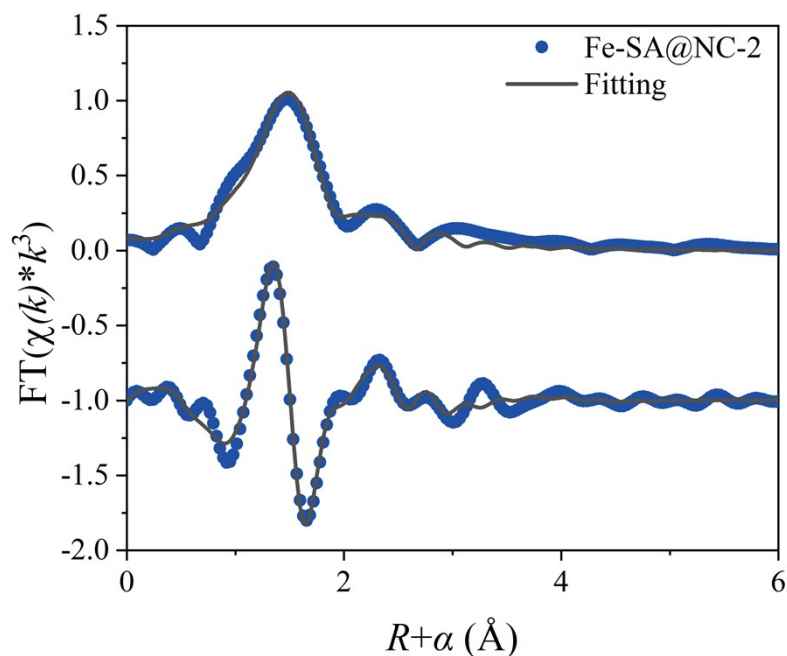


Fig. S6. Fe K-edge EXAFS and the fitting for Fe-SA@NC-2, shown in R-space. (FT magnitude and imaginary component) The data are k^3 weighted and not phase-corrected.

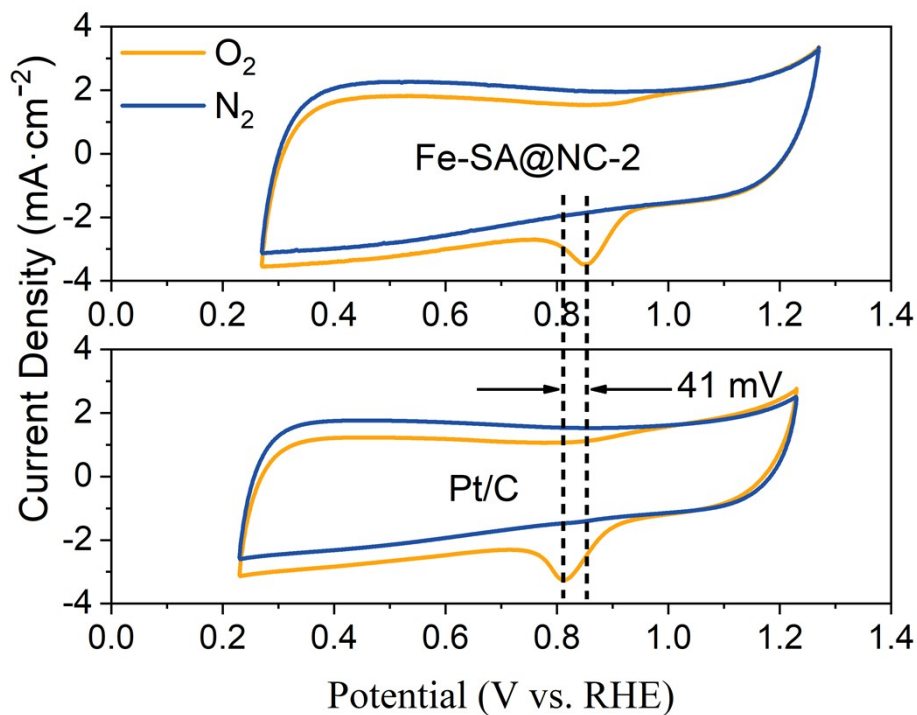


Fig. S7. CV plots of Fe-SA@NC-2 under Ar- and O₂-saturated 0.1 M KOH medium.

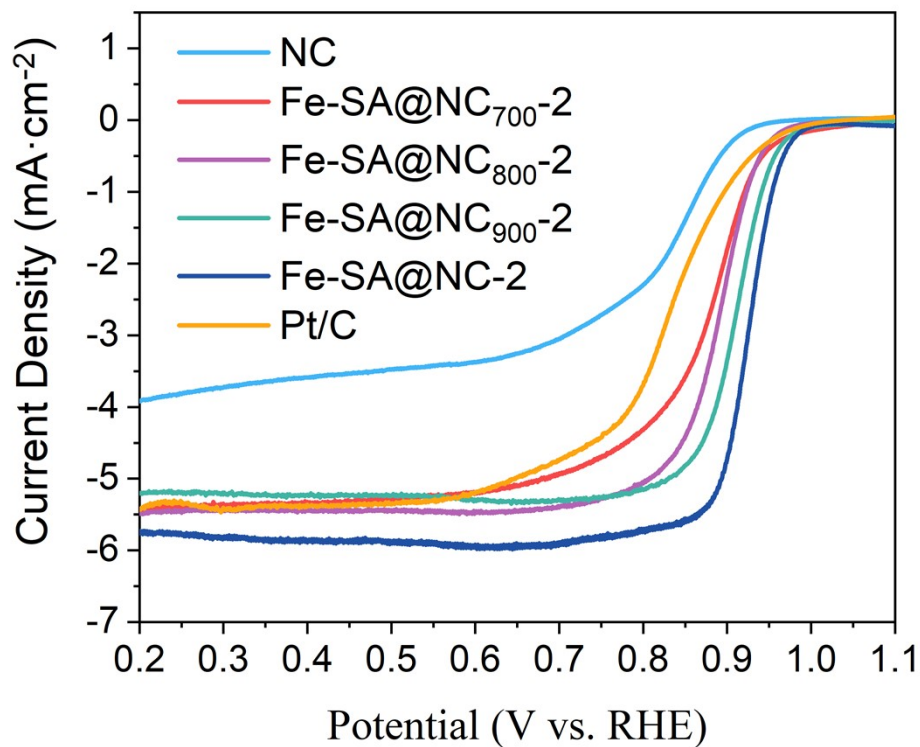


Fig. S8. LSV curves of Fe-SA@NC_T-2 catalysts at a rotation rate of 1600 rpm under 10 mV·s⁻¹ (the NC for Fe-SA@NC-2 was 1000 °C as mentioned above).

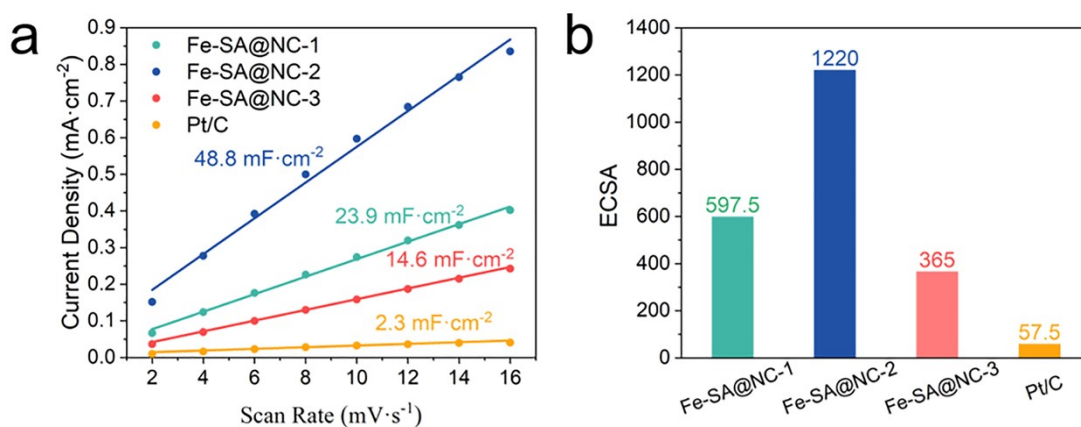


Fig. S9. (a) The double-layer capacitance (C_{dl}), (b) electrochemical surface area (ECSA) of the catalysts.

Table S1. The BET surface area, Langmuir surface area, pore volume and pore size of the catalysts.

Sample	BET Surface Area ($\text{m}^2\cdot\text{g}^{-1}$)	Langmuir Surface Area ($\text{m}^2\cdot\text{g}^{-1}$)	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)	Average pore size (nm)
Fe-SA@NC-1	1348	1457	0.55	1.18
Fe-SA@NC-2	1090	1178	0.45	1.16
Fe-SA@NC-3	1006	987	0.41	1.17
NC	1445	1562	0.60	1.19

Table S2. Elemental analysis of Fe-SA@NC catalysts.

Sample	C (%) ^a	H (%) ^a	N (%) ^a	Fe (%) ^b
Fe-SA@NC-1	68.85	1.61	3.34	0.66
Fe-SA@NC-2	63.47	1.54	3.30	1.00
Fe-SA@NC-3	65.86	1.58	3.46	1.31

^a measured by CHNS/O Elemental Analyzer, ^b measured by ICP-OES.

Table S3. XPS elemental analysis of Fe-SA@NC catalysts.

Sample	Fe (atom%)	N (atom %)	C (atom %)
Fe-SA@NC-1	0.57	4.05	95.37
Fe-SA@NC-2	0.68	4.74	94.58
Fe-SA@NC-3	0.75	4.67	94.58

Table S4. Content of different N species of Fe-SA@NC catalysts analyzed by XPS.

Sample	Pyridinic-N (%)	Fe-N (%)	Pyrrolic-N (%)	Graphitic-N (%)	Oxidized-N (%)
Fe-SA@NC-1	22	22.8	27.2	10	18
Fe-SA@NC-2	33.4	21.4	25	11.2	9
Fe-SA@NC-3	31.5	25	23.4	10.8	9.3

Table S5. Structural parameters of samples obtained by fitting the EXAFS data.

Sample	Path	N	R(Å)	σ^2 ($\times 10^{-3} \text{Å}^2$)	ΔE_0 (eV)	S_0^2	R-factor (%)
Fe-SA@NC-2	Fe-N	4.3±0.1	2.02±0.009	0.01	0.95±0.75	1.00	0.015

Table S6. Comparison of ORR performance of Fe-SA@NC-2 electrocatalyst with recent studies on alkaline ORR electrocatalyst (0.1 M KOH).

Catalyst	Half potential ($E_{1/2}$, V vs.RHE)	J_k ($\text{mA}\cdot\text{cm}^{-2}$)	TOF (s^{-1})	MA ($\text{A}\cdot\text{mg}^{-1}$)	Tafel ($\text{mV}\cdot\text{dec}^{-1}$)	Ref.
Fe-SA@NC-1	0.920	16.45 @0.90 V	12.92	4.98	47.6	This work
Fe-SA@NC-2	0.932	28.38 @0.90 V	14.71	5.68	44.3	This work
Fe-SA@NC-3	0.925	14.38 @0.90 V	5.69	2.19	46.1	This work
Fe-N-C SAC-950	0.895	3.34 @0.90 V	4.85	1.87	64	1
C-FeZ8@PDA-950	0.910	16.8 @0.85 V	10.75	4.15	71	2
Fe-SAs/NSC-vd	0.920	32.7 @0.87 V	18.59	56.2	75.2	3
Fe/N/C-MW	0.900	4.61 @0.85 V	0.76	0.294	45	4
Fe-NC	0.890	4.87 @0.80 V	3.41	1.31	65	5
Fe-N ₄ @NC-PCSSs	0.938	23.15 @0.90 V	8.46	3.26	49.5	6
FeN _x /NC-S	0.880	10.2 @0.90 V	1.19	0.46	61.3	7
Fe-SNC	0.920	40.80 @0.80 V	25.2	0.04	31	8
P-O/FeNC-SAC	0.912	7.54 @0.90 V	1.21	2.38	68.7	9
Fe-ISAS/CN	0.881	6.92 @0.85 V	3.25	1.25	72	10
Fe-N-C-900	0.900	19.69 @0.85 V	3.29	1.27	83.6	11
FeN ₄ -O-NCR	0.942	39.56 @0.90 V	38.39	14.81	54.3	12
meso-Fe-N-C	0.846	4.69 @0.85 V	1.04	0.40	-	13
Fe SA/NPCs	0.830	35.42 @0.85 V	16.91	6.52	65.3	14
Fe _{SA} -N-C	0.900	37.19 @0.85 V	9.94	3.84	-	15
SA-Fe-NHPC	0.930	57.2 @0.85 V	59.28	22.88	-	16

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