Supporting Information

Molten salts-assisted synthesis of special open-cell Fe, N co-doped porous carbon as an efficient electrocatalyst for zinc-air batteries

Xiaoying Gao[a], Xuan Xie[a], Kanjun Sun[b], Xiaofei Lei[a], Tianyu Hou[a], Hui Peng[a]*, and Guofu Ma[a]*

[a]Key Laboratory of Eco-functional Polymer Materials of the Ministry of Education, Key Laboratory of Polymer Materials of Gansu Province, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, China.

[b]College of Chemistry and Chemical Engineering, Lanzhou City University, Lanzhou 730070, China.

*Corresponding authors. E-mail addresses: penghui@nwnu.edu.cn (H. Peng), magf@nwnu.edu.cn (G. Ma)

S1. Materials characterizations

The morphology and microstructure of the as-prepared carbon materials were examined by field emission scanning electron microscopy (FE-SEM, Carl Zeiss-Ultra Plus, Germany) and transmission electron microscopy (TEM, FEI Tecnai G2 F20 S-Twin, USA). The crystallographic structure of the materials was determined by X-ray diffraction (XRD, D/Max-2400, Rigaku) equipped with CuKα radiation (k = 1.5418 Å). Raman spectra were collected on an in Via Raman spectrometer (Rainie Salt Public Co. Ltd., Britain) with a laser wavelength of 514 nm. X-ray photoelectron spectroscopy (XPS) measurement was performed on an Escalab 210 system (Germany) with Al Kα radiation source. The Brunauer-Emmett-Teller (BET) surface area of the samples was analyzed by nitrogen adsorption-desorption in a surface area and porosimetry analyzer (ASAP 2020, Micromeritics, U.S.A.).

S2. Electrochemical measurements

All ORR performance date using a rotating disk electrode (RDE, PINE Research Instrumentation) with an Autolab bipotentiostat (Model PGSTAT128N) workstation at ambient temperature. All test was carried out using a three-electrode system, a Pt wire as counter electrode, Ag/AgCl (3.0 M KCl) as reference electrode and glassy carbon (GC) disk electrode (5 mm in diameter) are used as the working electrodes. All potentials are converted to RHE, $E_{(RHE)} = E_{(Ag/AgCl)} + 0.059 \times pH + 0.197$.

The preparation of the working electrode is as follows: 5 mg catalysis was added to 1 ml Nafion/enthol and ultrasonic dispersion for 30 min. Measuring 8 μl drop onto the working electrode and waiting for natural dry (The catalyst loading is 0.2038 mg cm^{-2}). Before tests, 0.1 M KOH solution should be saturated with N_2/O_2.

Calculate kinetic current density (J_k) and electronic transfer number (n) according to the equation Koutecky–Levich given below:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{B\omega^{1/2}} \qquad (1)$$

$$B = 0.2nFD_0^{2/3}V^{-1/6}C_0 \qquad (2)$$

where J and J_k are the measured current density and the kinetic current density, respectively. ω is the electrode rotation speed, B could be determined from the slope of the K-L plots, n is the number of electrons transferred per oxygen molecule, F is the Faraday constant (96485 C mol^{-1}), D_0 is the diffusion coefficient of O_2 (1.9 × 10^{-5} cm^2 s^{-1}), V is the kinetic viscosity (0.01 cm^2 s^{-1}), and C_0 is the concentration of O_2 (1.2 × 10^{-6} mol cm^{-3}).

S3. Preparation of Zn-air batteries

An Zn-air fuel cell was assembled according to the following process: First, 6 mol/L KOH was used as the electrolyte (250 mL). Then, a polished zinc foil with a thickness of about 0.2 mm and an area of 34×85 mm was used as the anode. Typically, the catalyst ink is applied to a gas diffusion layer made of nickel foam, a waterproof breathable membrane and carbon paper (effective area about 2 cm^2) to make an air cathode. The catalyst ink was prepared by mixing the electrocatalyst with a 5% Nafion solution and a water/ethanol solution (1:1 (v/v)). On average, 1 mg of catalyst can be mixed with 4 µL of Nafion solution. Small amounts of Nafion were used mainly to immobilize the electrocatalyst with negligible hydrophobicity. The loading of air electrode with electrocatalyst is 1 mg cm^{-2}. The discharge polarization curve was recorded by LSV at a scan rate of 5 mV s^{-1} on an Autolab electrochemical workstation. The specific capacity (mAh g^{-1}) of Fe_3-N-C-800 and Pt/C were calculated based on the following equations[2]:

$$\text{Specific capacity} = \frac{\text{discharge current} \times \text{working time}}{\text{mass of consumed zinc}} \qquad (5)$$

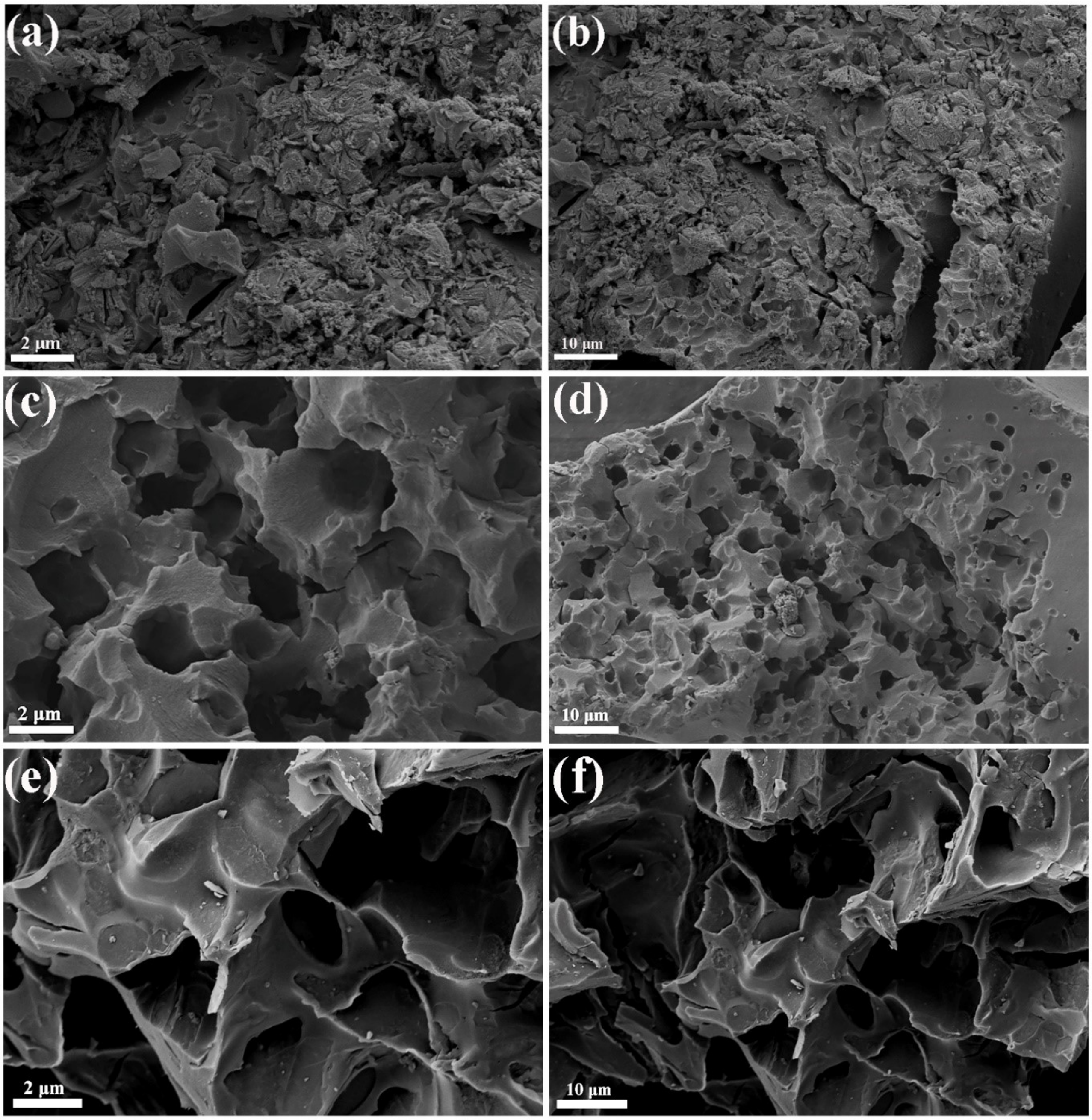

Fig. S1 SEM images of (a-b) N-C-800, (c-d) Fe_1-N-C-800 and (e-f) Fe_5-N-C-800.

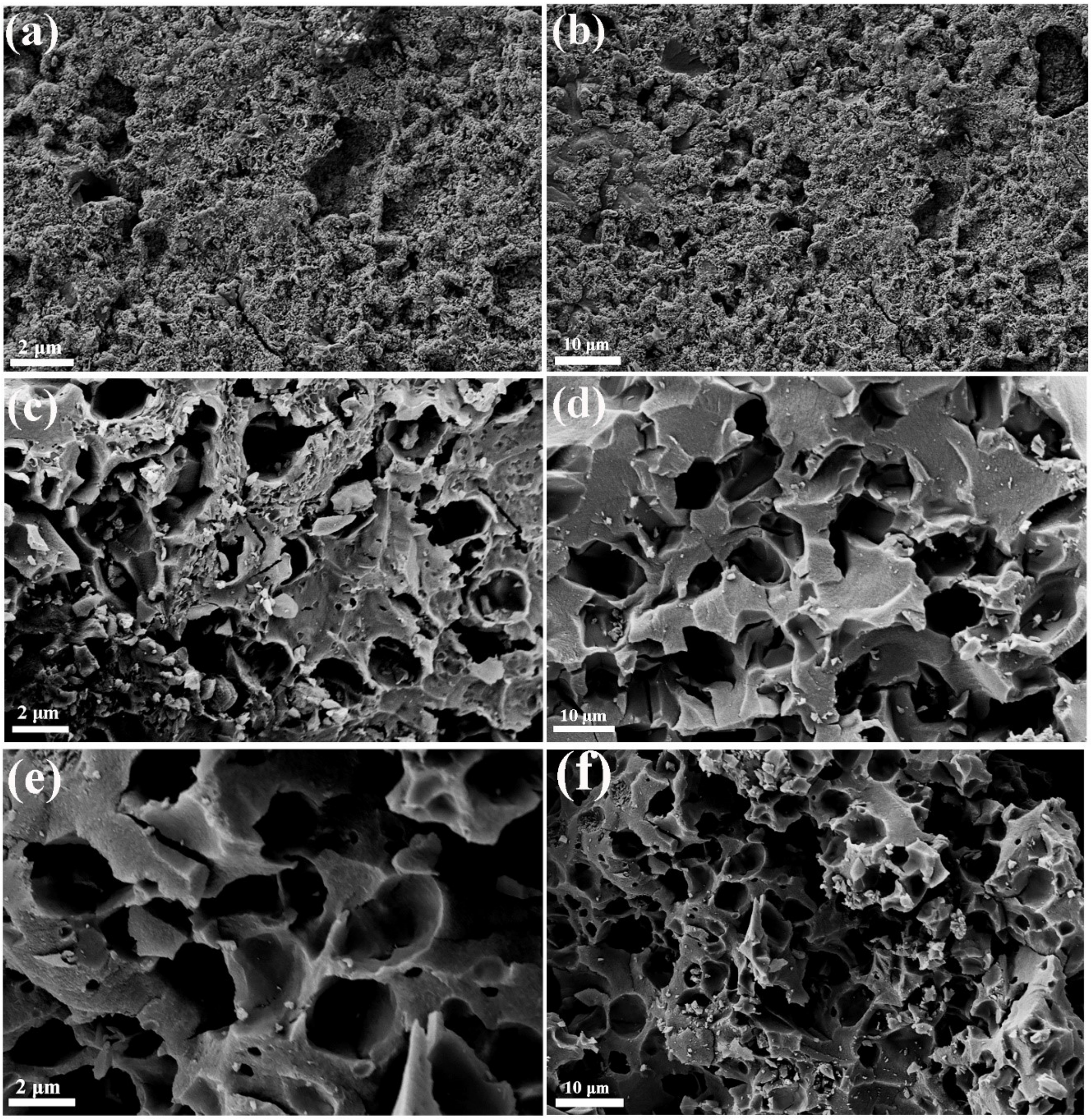

Fig. S2 SEM images of (a-b) Fe_3-N-C-700, (c-d) Fe_3-N-C-800, and (e-f) Fe_3-N-C-900.

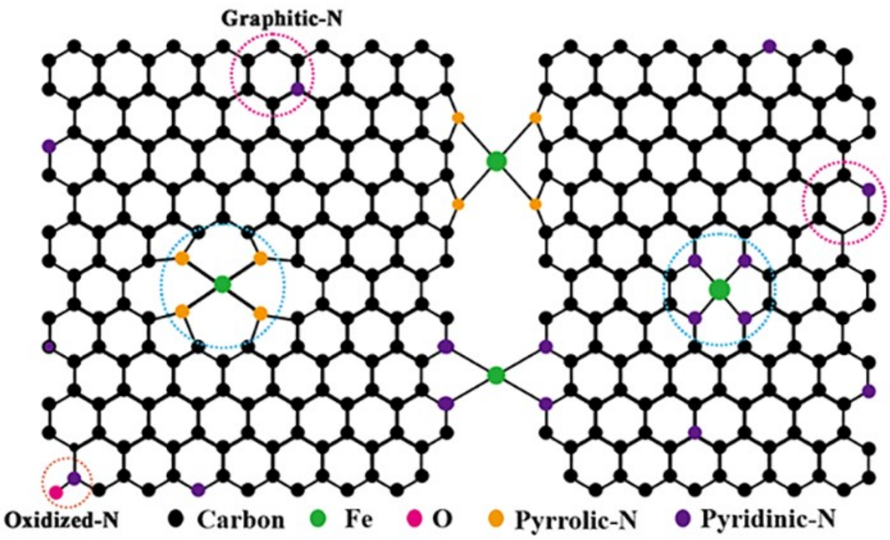

Fig. S3 Putative Fe-N_x ORR active site and molecular model structures.

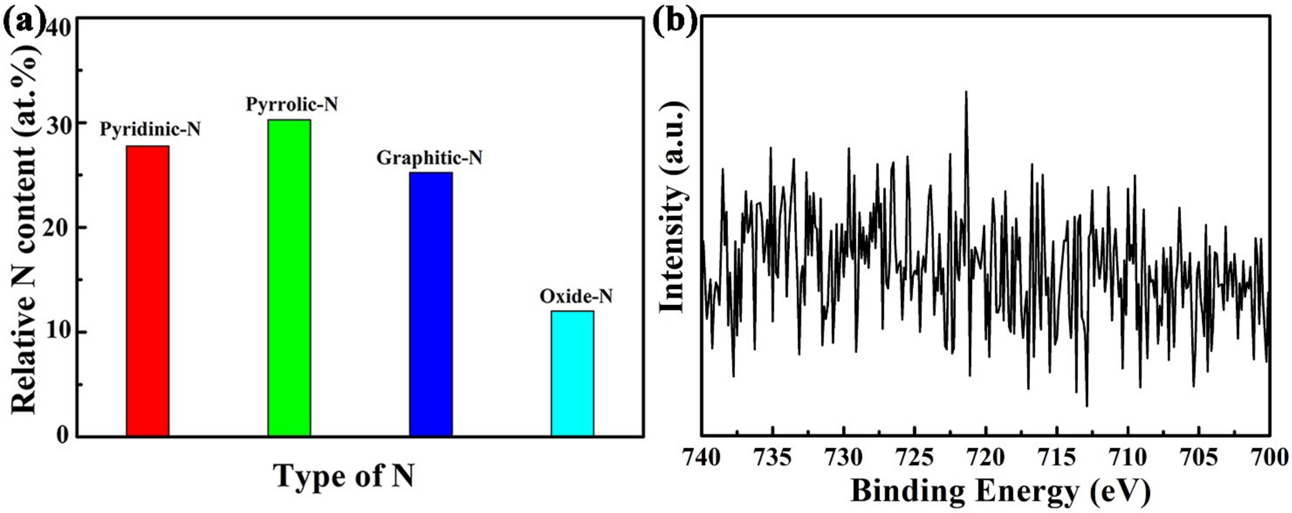

Fig. S4 (a) Fitted data of different N species in Fe_3-N-C-800. (b) High-resolution Fe 2p spectrum of Fe_3-N-C-800.

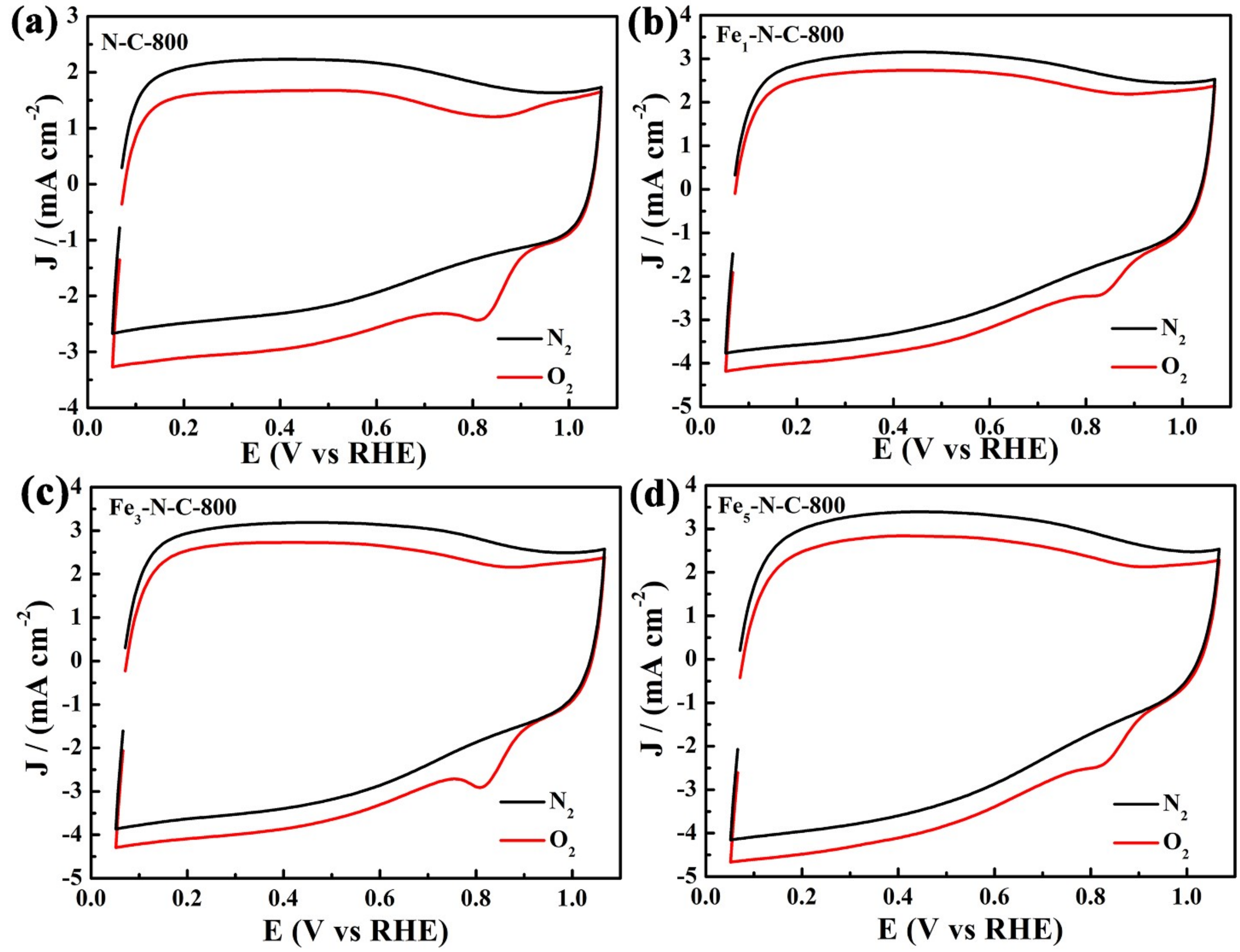

Figure S5. CV curves of catalysts at N_2 saturation (solid line) and O_2 saturation (dashed line) with 0.1 M KOH (scan rate: 50 mV s^{-1}): (a) N-C-800, (b) Fe_1-N-C-800, (c) Fe_3-N-C-800, (d) Fe_5-N-C-800.

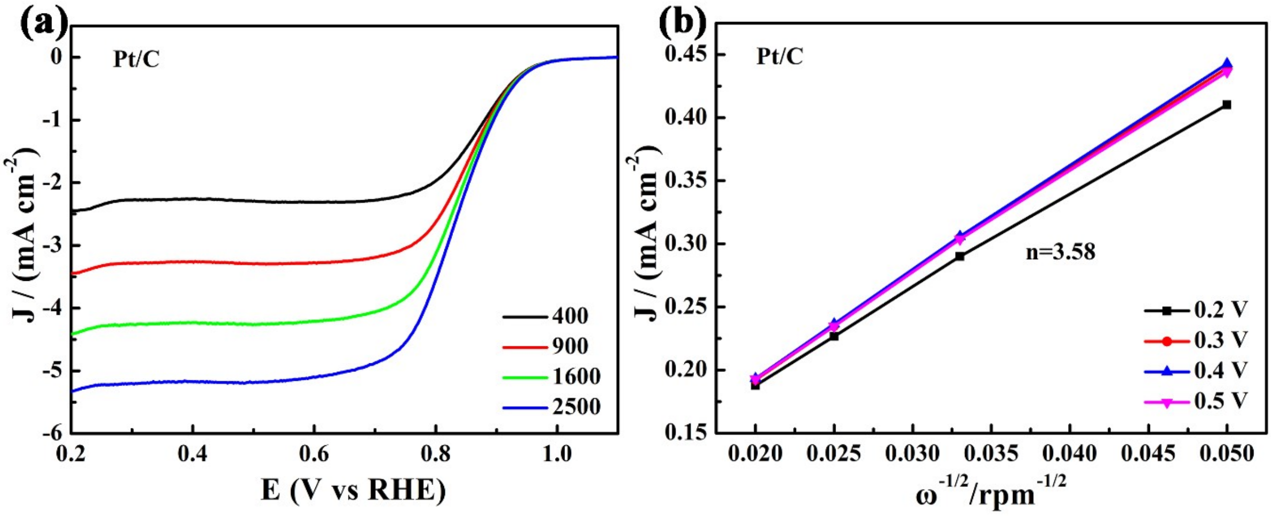

Fig. S6 (a) LSV curves of the 20% Pt/C in O_2-saturated 0.1 M KOH solution with various rotation rates. (b) The K-L plots of 20% Pt/C at different potential

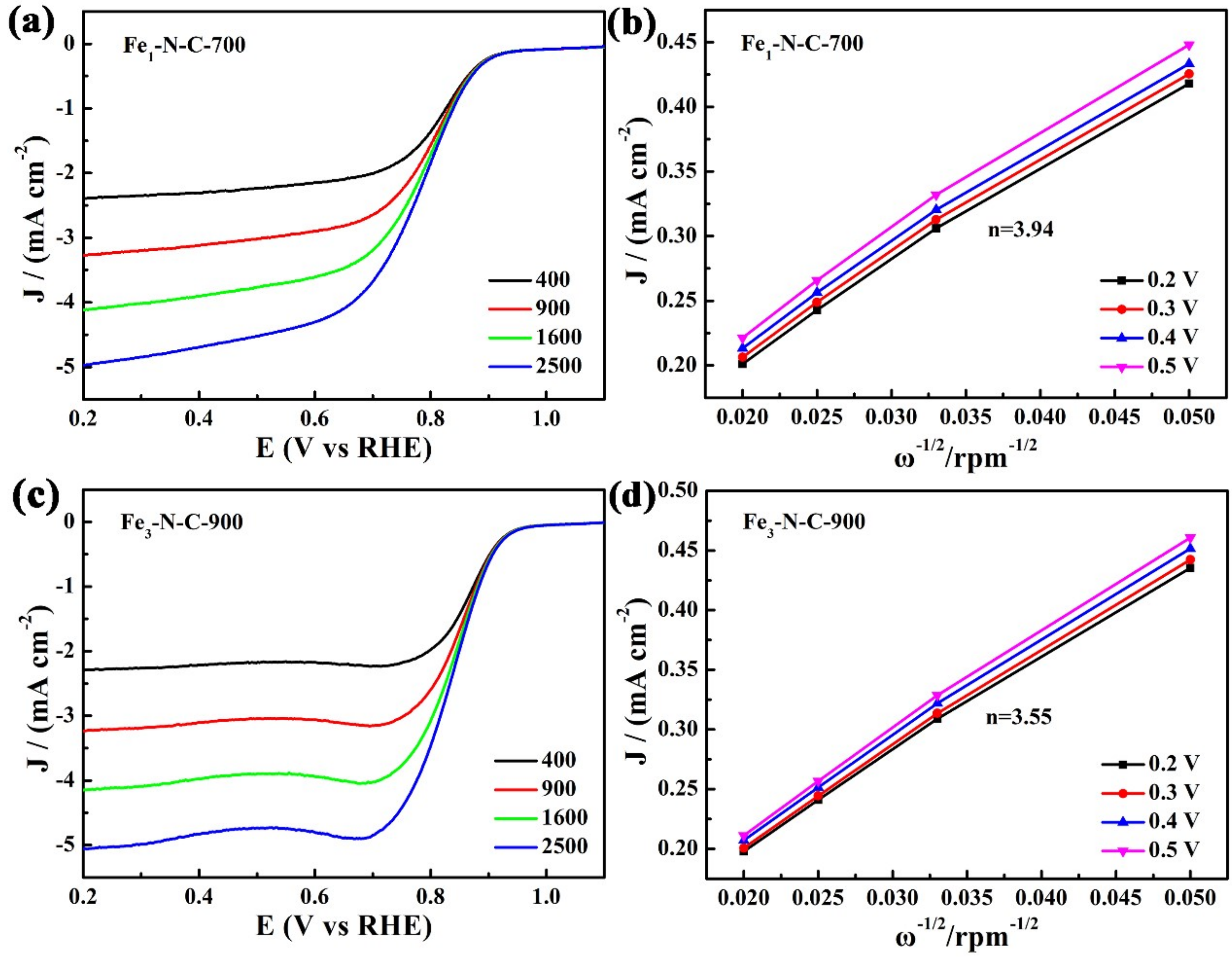

Fig. S7 LSV curves of the (a) Fe_3-N-C-700 and (c) Fe_3-N-C-900 in O_2-saturated 0.1 M KOH solution with various rotation rates. The K-L plots of (b) Fe_3-N-C-700 and (d) Fe_3-N-C-900 at different potentials.

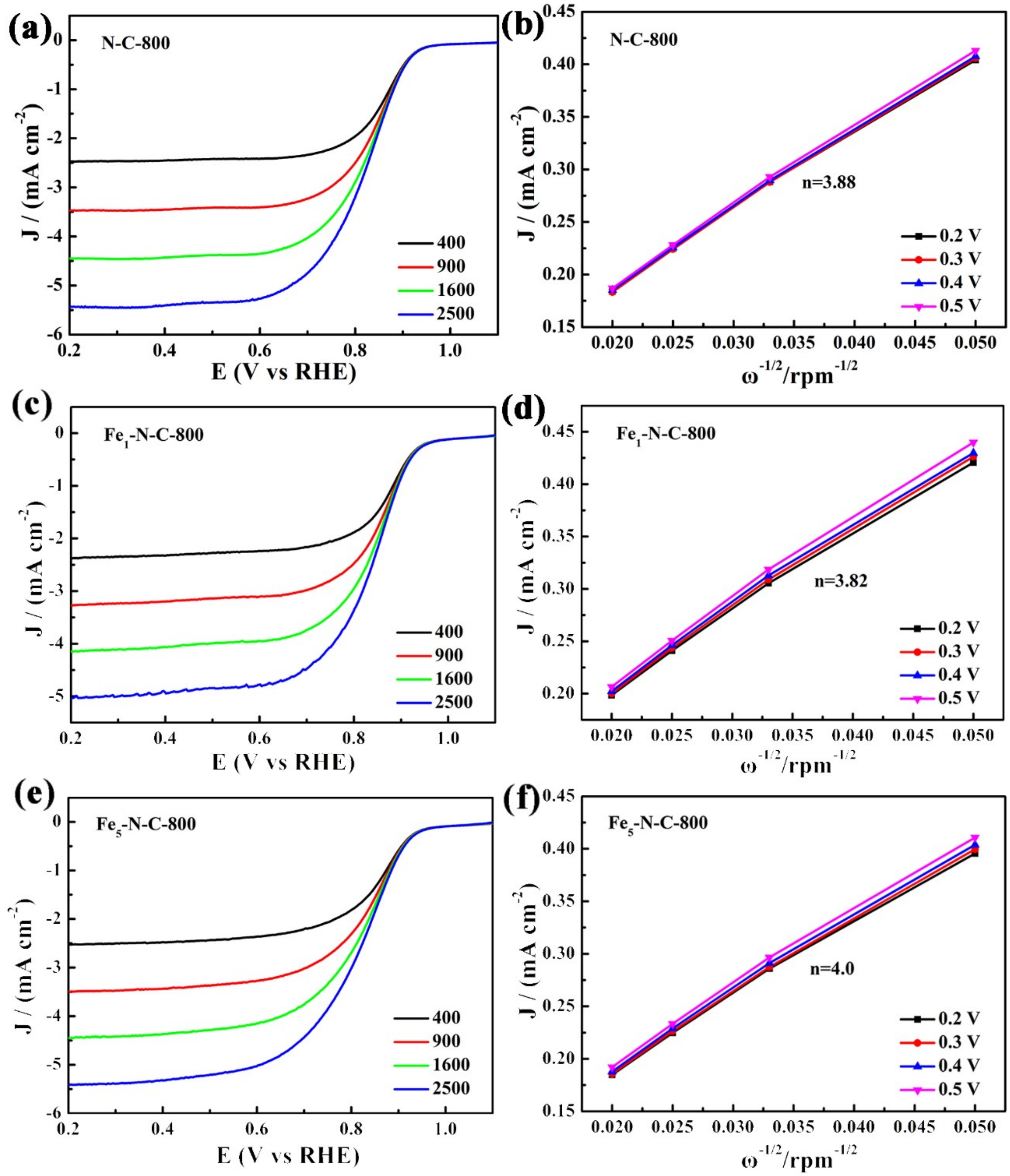

Fig. S8 LSV curves of the (a) N-C-800, (c) Fe_1-N-C-800 and (e) Fe_5-N-C-800 in O_2-saturated 0.1 M KOH solution with various rotation rates. The K-L plots of (b) N-C-800, (d) Fe_1-N-C-800 and (f) Fe_5-N-C-800 at different potentials.

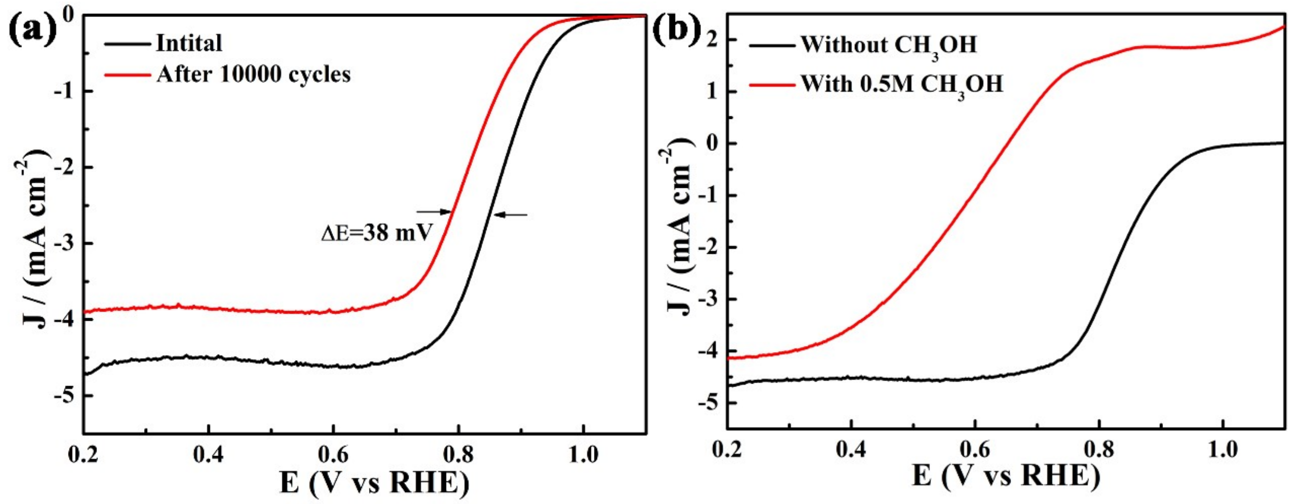

Fig. S9 (a) ORR polarization curve before and after 10000 cycles of the 20% Pt/C. (b) ORR polarization curves of 20% Pt/C in O_2-saturated 0.1 M KOH with and without 0.5 M CH_3OH at 1600 rpm

Table S1. Element content of Fe_3-N-C-800

Samples	Surface atomic concentration (at%)			
	C	N	O	Fe
Fe_3-N-C-800	90.97	2.98	5.90	0.15

Table S2. Comparison of zinc-air battery performance of Fe_3-N-C-800 catalyst with recently reported electrocatalysts.

Catalyst	Cycling conditions (mW cm^{-2})	Stability	Power density (mW cm^{-2})	Refs.
Fe_3-N-C-800	10	80 h	80	This work
Fe/Fe_3C@Fe-Nx-C	5	1 h/cycle for 200 h	147	[S1]
L-FeNC	2	5000 s	140	[S2]
Co-POC	2	237 cycles for 79 h	78	[S3]
Co/Co-Nx-PCNSs	5	60 min/cycle for 120 h	140	[S4]
Fe@Fe_{SA}-N-C-900	/	1 h/cycle for 500 h	110	[S5]
Co_3O_4@POF	5	2250 cycles for 375 h	222.2	[S6]
Fe/Fe_3C-N-CNTs	5	1 h/cycle for 195 h	183	[S7]
MnO/Co-CNTs	10	46 h	/	[S8]

References

[S1] L. Zong, X. Chen, S. Liu, K. Fan, S. Dou, J. Xu, X. Zhao, W. Zhang, Y. Zhang, W. Wu, F. Lu, L. Cui, X. Jia, Q. Zhang, Y. Yang, J. Zhao, X. Li, Y. Deng, Y. Chen and L. Wang, J. Energy Chem, 2021, 56, 72-79.

[S2] X. Jiang, J. Chen, F. Lyu, C. Cheng, Q. Zhong, X. Wang, A. Mahsud, L. Zhang and Q. Zhang, J. Energy Chem, 2021, 59, 482-491.

[S3] B. Li, C. Zhao, S. Chen, J. Liu, X. Chen, L. Song and Q. Zhang, Adv. Mater, 2019, 31, 1900592.

[S4] W. Wu, L. Zong, X. Chen, W. Zhang, L. Cui, Y. Yang, X. Wang, S. Li and L. Wang, Appl. Surf. Sci, 2021, 541, 148262.

[S5] W. Zhang, K. Fan, C.-H. Chuang, P. Liu, J. Zhao, D. Qi, L. Zong and L. Wang, J. Energy Chem, 2021, 61: 612-621.

[S6] J. Liu, B. Li, C. Zhao, J. Yu and Q. Zhang, ChemSusChem, 2020, 13, 1529-1536.

[S7] L. Zong, X. Chen, S. Dou, K. Fan, Z. Wang, W. Zhang, Y. Du, J. Xu, X. Jia, Q. Zhang, X. Li, Y. Deng, Y. Chen and L. Wang, Chin Chem Lett, 2021, 32, 1121-1126.

[S8] W. Zhang, L. Zong, K. Fan, L. Cui, Q. Zhang, J. Zhao, L. Wang and S. Feng, J. Alloys Compd, 2021, 874, 159965.