

Electronic Supplementary Information

In-situ green architecture of 3D FeZn-N-C based electrocatalyst for efficient oxygen reduction

Kui Fu,^{a,‡} Biao Ma,^{a,‡} Jianling Liu,^a Meng Zhou,^a Yihai Xing,^a Xiangfeng Wei,^a
Fancheng Meng,^a and Jiehua Liu^{*ab}

^a Future Energy Laboratory, School of Materials Science and Engineering, Hefei University of Technology Hefei 230009, China

^b Key Laboratory of Advanced Functional Materials and Devices of Anhui Province, Engineering Research Center of High-Performance Copper Alloy Materials and Processing, Ministry of Education, Hefei 230009, China.

*Email: liujh@hfut.edu.cn and liujh@iccas.ac.cn

Experimental sections

Preparation of MOF-5

According to the previous report,¹ MOF-5 was synthesized. Configuration solution A: 0.507 g Terephthalic acid (TPA, Shanghai Macklin Biochemical Co., Ltd) and 0.85 mL triethylamine (TEA, Sinopharm Chemical ReagentCo., Ltd) were dissolved in 40 mL of N, N-dimethylformamide (DMF, Shanghai Aladdin Biochemical Technology Co., Ltd). Then 1.699 g zinc acetate dihydrate ($\text{Zn}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$, Sinopharm Chemical ReagentCo., Ltd) was dissolved in 50 mL DMF, slowly added to solution A for 2.5 h under magnetic stirring at room temperature, and further transferred to a polytetrafluoroethylene liner. The crystal growth was promoted by solvothermal treatment at 120°C for 6 h. After the reaction was cooled to room temperature, the precipitate was collected by centrifugation, washed several times with DMF, and dried in vacuum at 60°C to obtain MOF-5.

Preparation of KFC@MOF-5-120

Then 20 mg potassium ferrocyanide (KFC, Shanghai Aladdin Biochemical Technology Co., Ltd) and 200 mg MOF-5 were added to 20 mL deionized water (DI) and stirred evenly. The obtained solution was transferred to a hydrothermal reactor at 120°C for 12 hours. After cooling to room temperature, the deionized water and ethanol were centrifuged and washed several times. After vacuum drying at 60 °C, the KFC@MOF-5-120 sample was obtained.

Preparation of FeZn-N-C-800

The PFC@MOF-5-120 sample obtained in the previous step was ground and mixed with melamine (Shanghai Aladdin Biochemical Technology Co., Ltd) at a mass ratio of 1:10, and then pyrolyzed at 800°C under N_2 flow. The obtained black powder was the target product, named FeZn-N-C-800.

Materials characterizations

The samples were subjected to XRD testing by a D/MAX2500V diffractometer with Cu-K α radiation. FESEM and TEM images were obtained by SU8020 (HITACHI) and JEM 2100F. N_2 adsorption-desorption isotherms were performed on an autosorb-IQ3 analyzer at 77 K. XPS measurements were performed by ESCLAB250 with a monochromatic Al K α X-ray source with the power of 150 W.

Raman spectra were collected by using Lab Raman HR Evolution.

Electrochemical measurements

Electrochemical measurements were performed on three-electrode cells at room temperature using an electrochemical workstation (CHI760E and DH7000) and a rotating disk electrode. Pt wire and KCl-saturated Hg/HgCl₂ electrodes were used as counter and reference electrodes, respectively. Activity evaluations were performed in a 0.1 M KOH electrolyte system. Rotating disk electrode (RDE) measurements were performed using glassy carbon (GC) disks. Before testing, the GC discs were polished to avoid contamination. The catalyst ink was prepared by adding 5 mg of the resulting catalyst and 40 µl of Nafion solution (5 wt.%, DuPont) to 960 µl of water/isopropanol (3:1) solvents. After ultrasonic treatment for 30 minutes, a homogeneous suspension was obtained. The 5 µl catalytic ink is then applied to the surface of the GC disk and dried at room temperature.

Before ORR evaluation, the CV curves in O₂-saturated KOH were obtained at a scan rate of 20 mV s⁻¹. The ORR LSV curves were obtained at different rotation speeds (900, 1225, 1600, 2025, and 2500 rpm) at a scan rate of 5 mV s⁻¹ in an O₂-saturated 0.1 M KOH electrolyte. The K-L equations applied to investigate the ORR kinetic.²

$$1/j = 1/j_L + 1/j_K \quad (1)$$

$$j_L = \frac{0.2nFC_0D_0}{\nu^{1/6}} * \frac{1}{\omega^{1/2}} = B * \frac{1}{\omega^{1/2}} \quad (2)$$

where J, J_K, and J_D represent electrode current density, dynamic current density, and diffusion limiting current density, respectively; n is the number of electron transfers per O₂ molecule; F is Faraday's constant with a Value of 96485 C mol⁻¹; k is the electron transfer rate constant; C_{O₂}, D_O, and ν is the oxygen concentration in the electrolyte, the diffusion coefficient of oxygen molecules and the kinematic Viscosity of the electrolyte, respectively. In 0.1 M KOH, the oxygen concentration is 1.2×10⁻⁶ mol cm⁻³ and the diffusion coefficient is 1.9×10⁻⁵ cm s⁻¹, the kinematic Viscosity is 0.01 cm² s⁻¹, A is the electrode area, about 0.07068 cm², and ω is the electrode rotation speed.

Battery test

Zn-air batteries were tested using a homemade cell. The working electrode with the catalyst of 2 mg cm⁻² was prepared by casting the above catalyst ink onto the carbon paper, and the polished Zn plate (0.2 mm thickness) was used as the anode. 6

M KOH solution was used as the electrolyte.

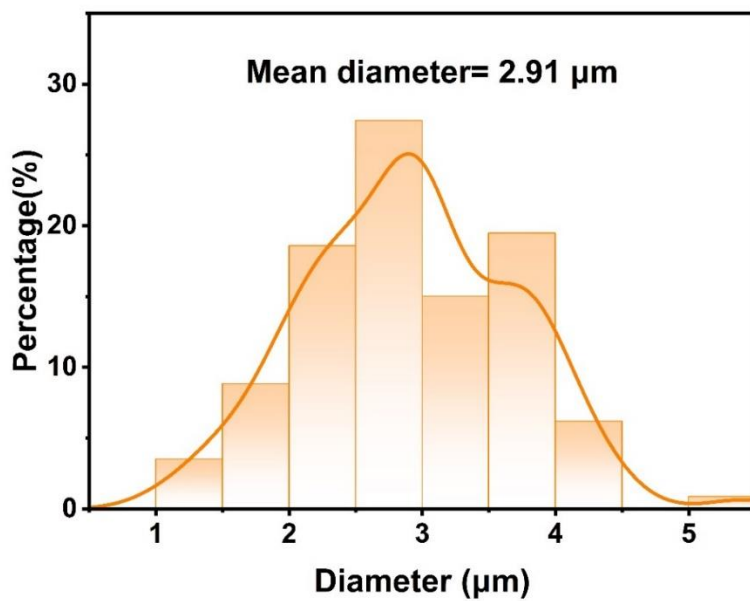


Fig. S1. particle size statistics of MOF-5

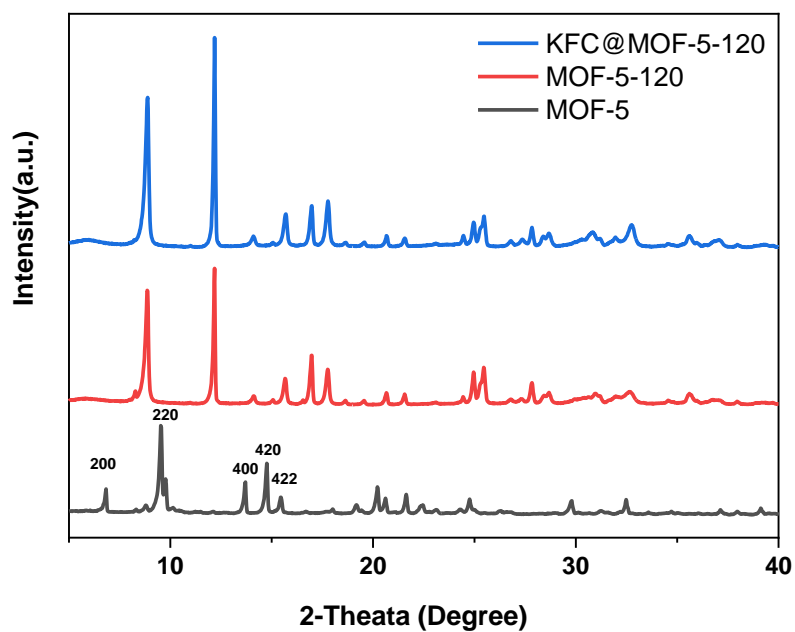


Fig. S2. XRD patterns of MOF-5, MOF-5-120, and KFC@MOF-5-120.

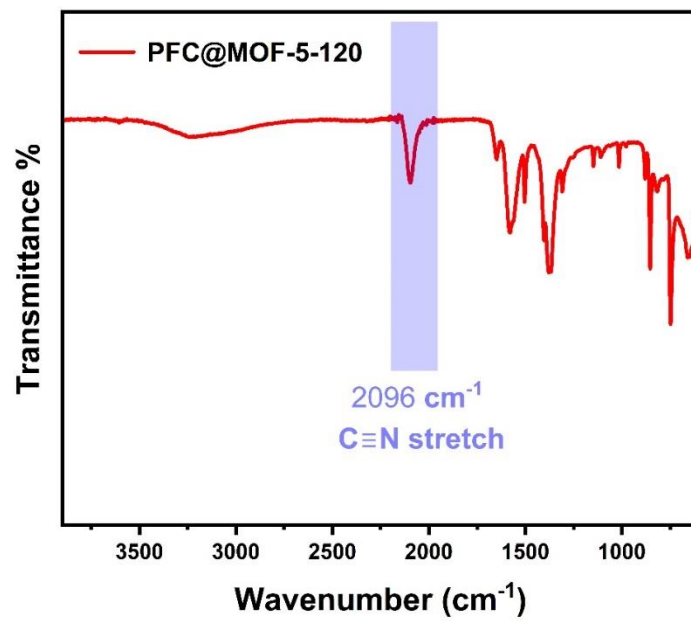


Fig. S3. FT-IR spectrum of KFC@MOF-5-120

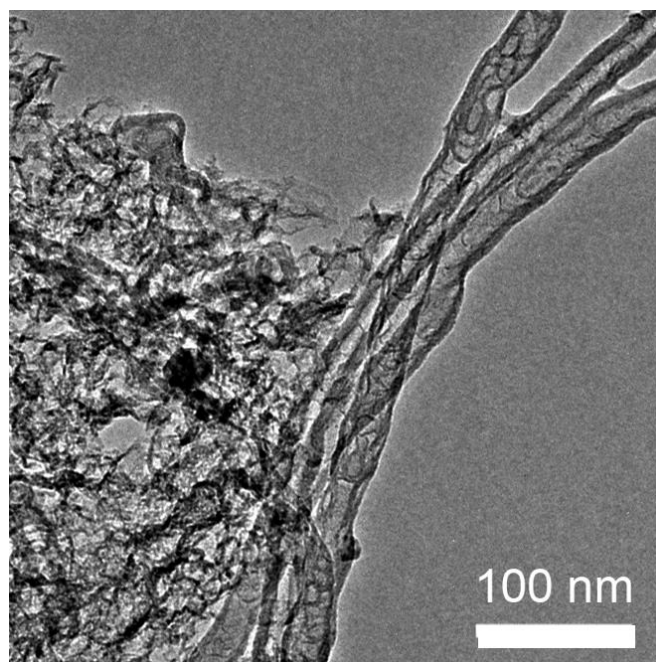


Fig. S4. TEM image of FeZn-N-C-800

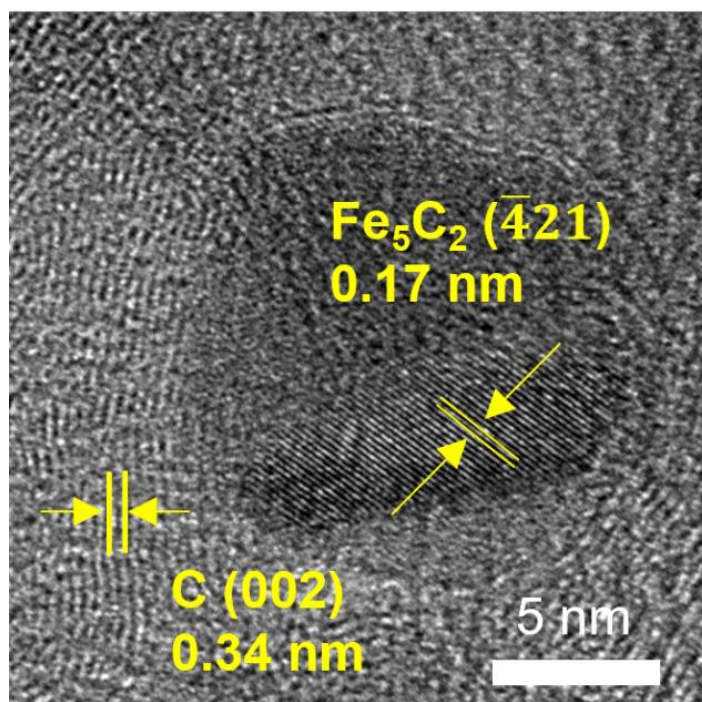


Fig. S5. HRTEM image of FeZn-N-C-800.

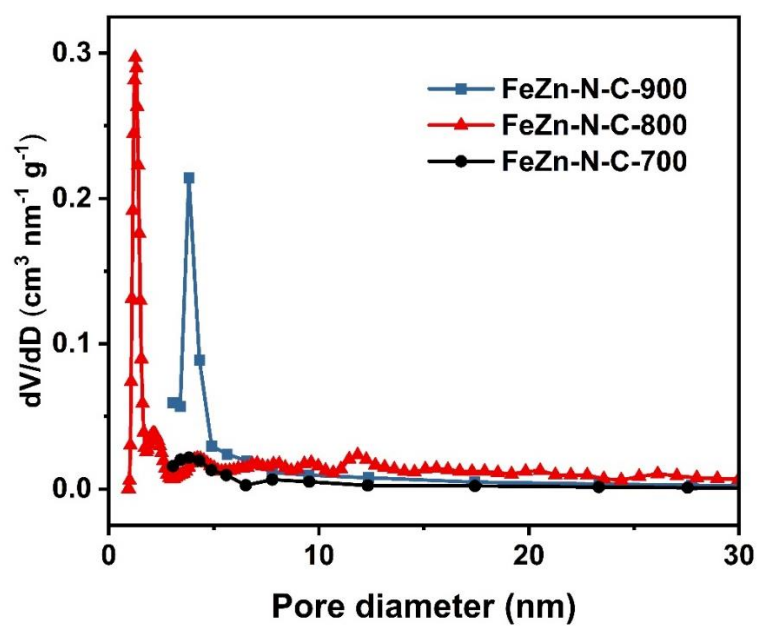


Fig. S6. Pore size distribution of FeZn-N-C-800

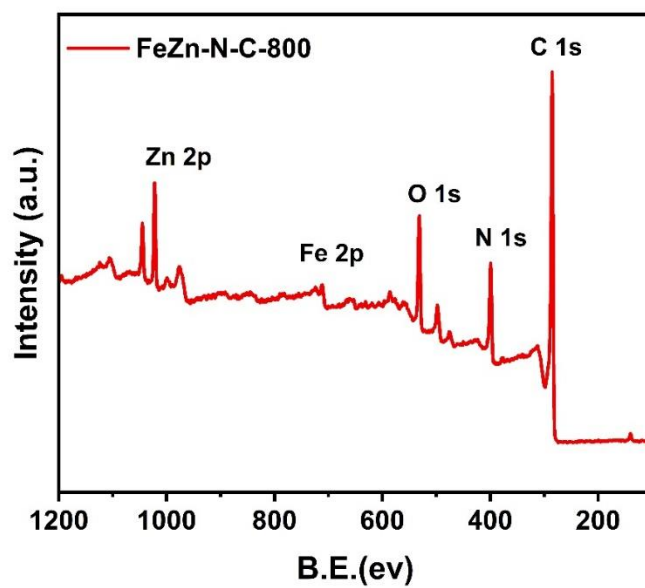


Fig. S7. XPS survey spectra of FeZn-N-C-800

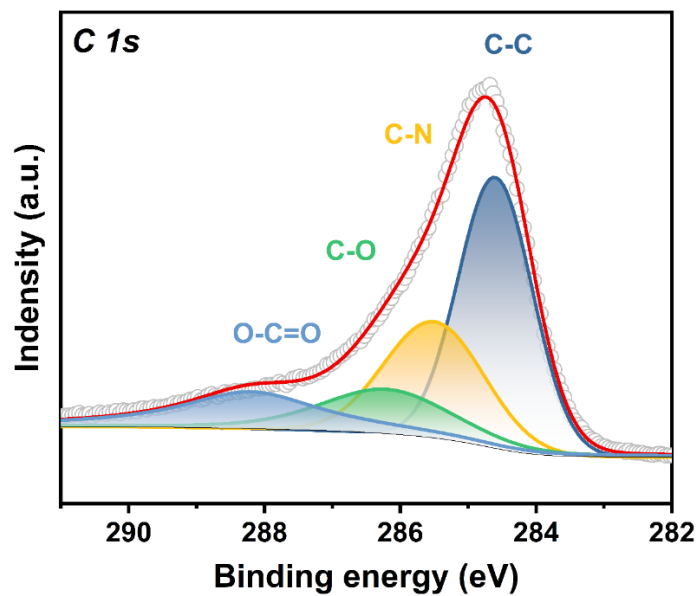


Fig. S8. High-resolution XPS spectra of C 1s of FeZn-N-C-800

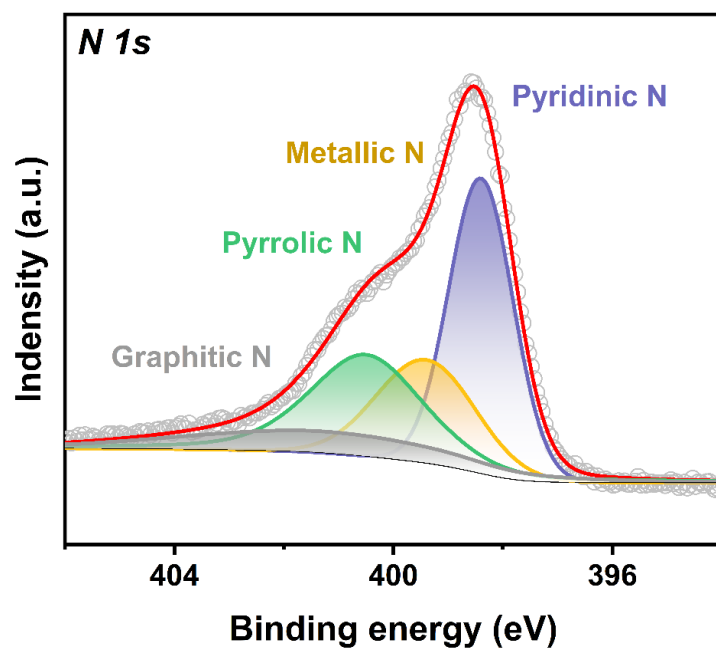


Fig. S9. High-resolution XPS spectra of N 1s of FeZn-N-C-800

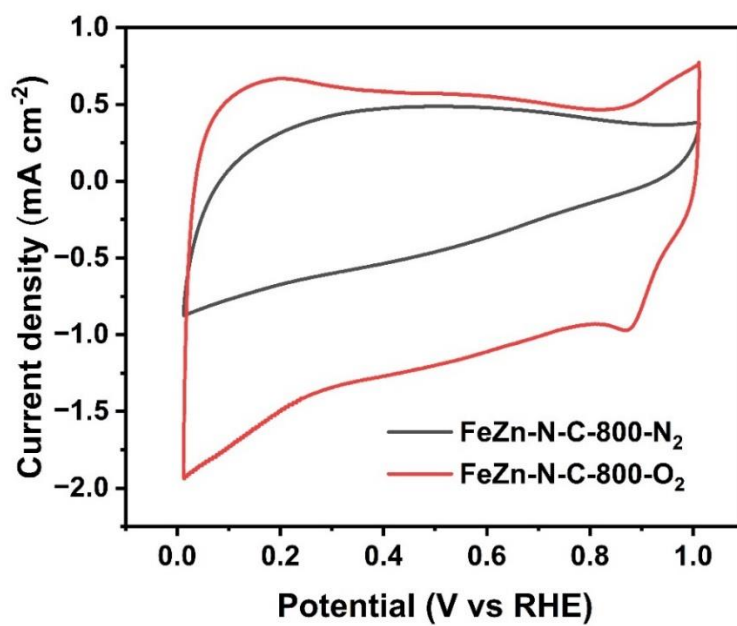


Fig. S10. CV curves in 0.1M KOH solution saturated with oxygen and nitrogen, of FeZn-N-C-800

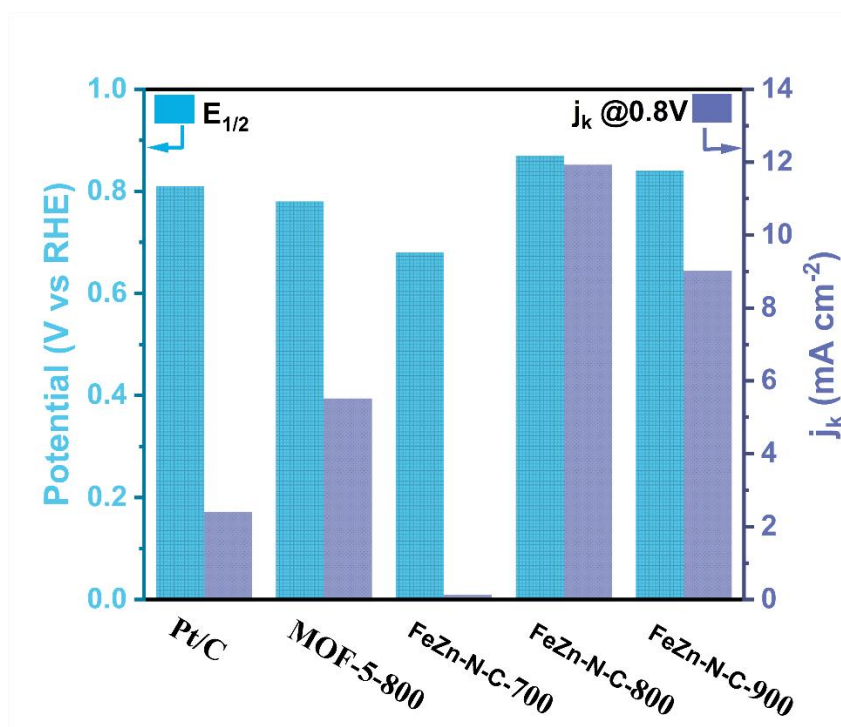


Fig. S11. Comparison of half-wave potential and kinetic current density of FeZn-N-C-X (X represents different pyrolysis temperatures) and Pt/C

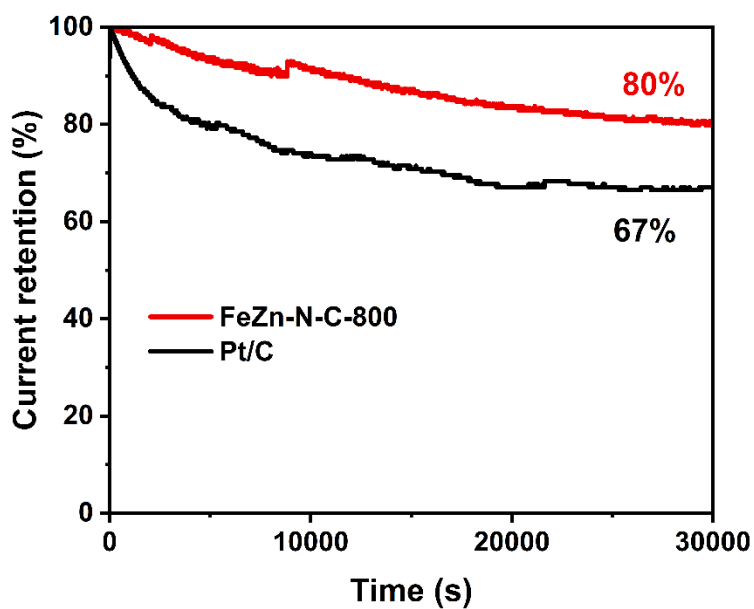


Fig. S12. i-t chronoamperometric experiment of FeZn-N-C-800 and Pt/C catalyst at 0.7 V vs. RHE at 1600 rpm

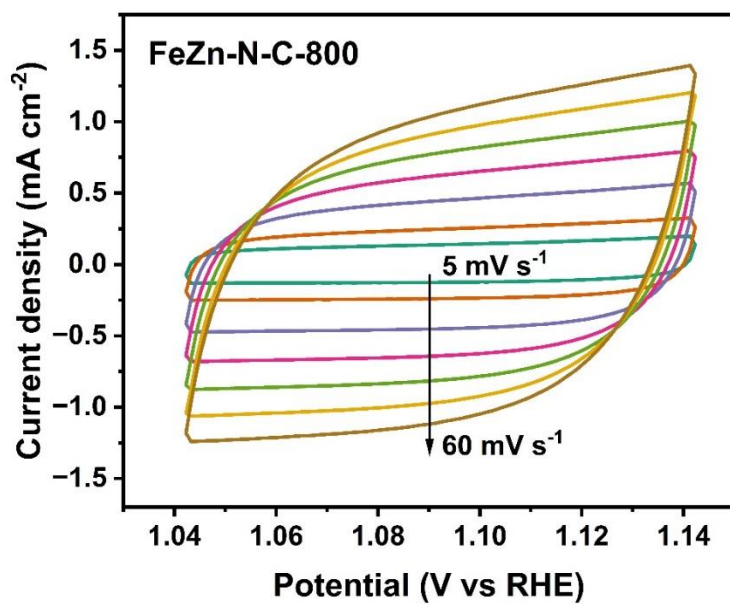


Fig. S13. Cyclic voltammograms at different scan rates of FeZn-N-C-800

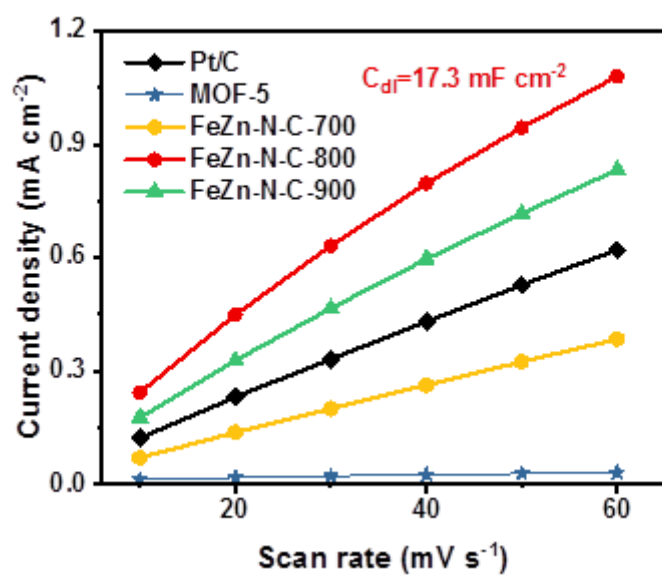


Fig. S14. Dependence of current densities as a function of scan rates for FeZn-N-C-X (X represents different pyrolysis temperatures) and Pt/C

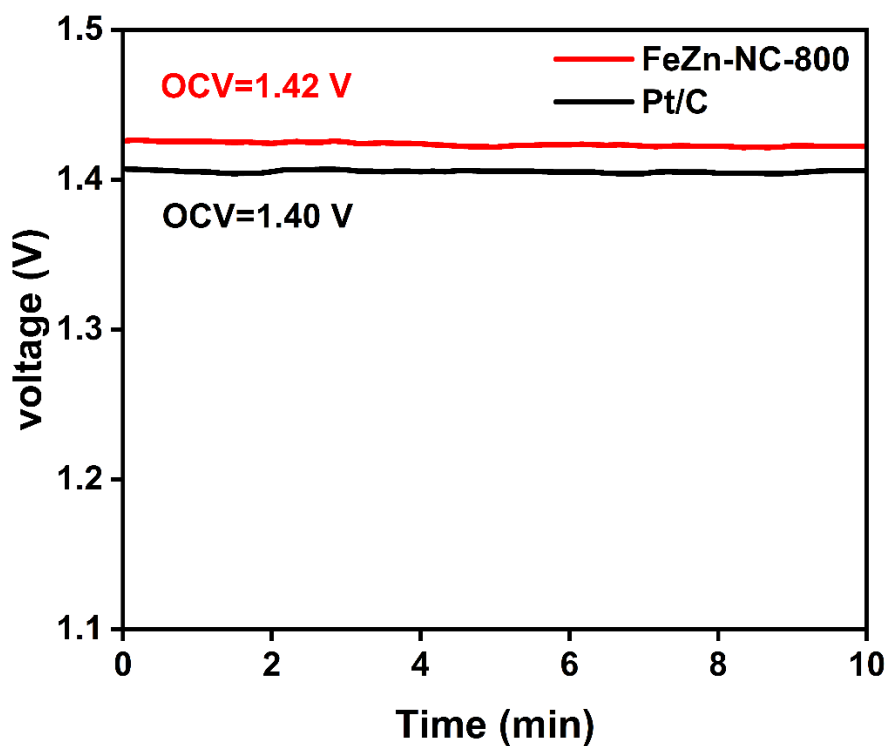


Fig. S15. Open circuit voltage curves of Zn-air batteries with FeZn-N-C-800 material and Pt/C.

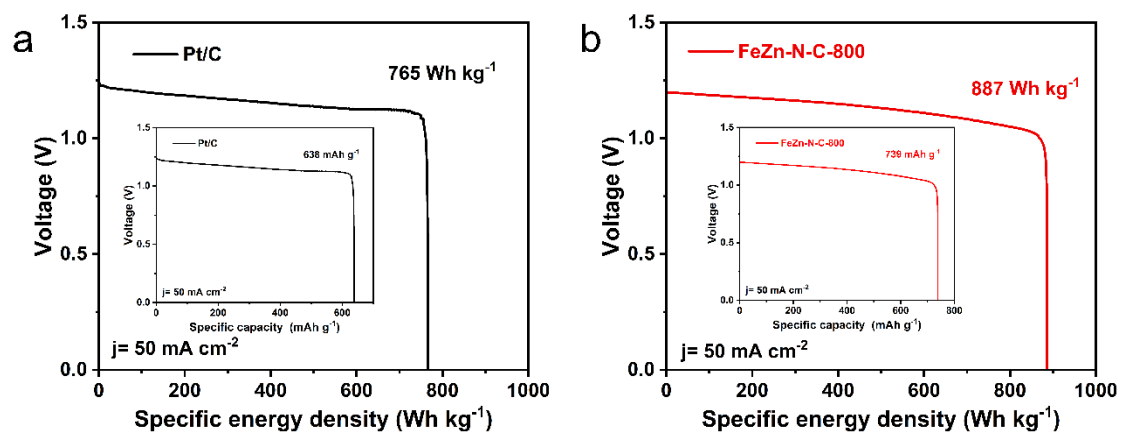


Fig. S16. The specific energy density and specific capacity curves at 50 mA cm^{-2} of a Zn-air battery assembled from (a) Pt/C and (b) FeZn-N-C-800

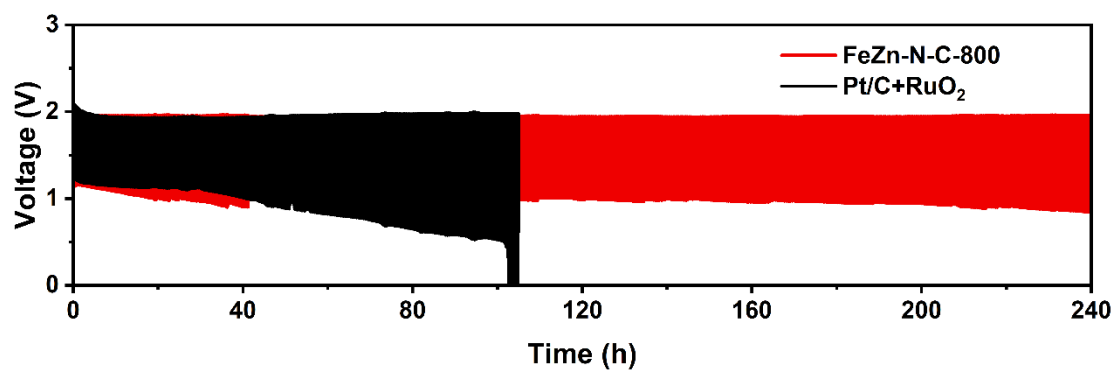


Fig. S17. The long-time cycle performance of a Zn-air battery assembled from FeZn-N-C-800 and Pt/C+RuO₂

Reference

- S1 W. Zhang, Y. L. Hu, J. Ge, H. L. Jiang and S. H. Yu, *J. Am. Chem. Soc.*, 2014, **136**, 16978-16981.
- S2 S. H. Ahn, X. W. Yu and A. Manthiram, *Adv. Mater.* 2017, **29**, 1606534.