

## Supporting Information

### Zinc Ferrum energy storage chemistries with high efficiency and long cycling life

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#### EXPERIMENTAL SECTION

**Preparation and improvement of carbon fibers:** Polyacrylonitrile (Mw = 80,000) was vacuum dried at 60°C for 6 h before use. Then it was dissolved in dimethylformamide to make a solution with concentration of 8 wt.%. The solution was stirred for 1 h using high energy ball mill and stirred for 12 h by magnetic stirring at room temperature. The polyacrylonitrile solution was then loaded into glass capillary (0.5 mm diameter), which as an anode was 20 cm distant from cathode stuck on a drum whose rotation speed was 300 rpm. An aluminum sheet was attached on the drum to collect the

polyacrylonitrile nanofibrous film under a voltage of 20.0 kV. The prepared polyacrylonitrile nanofibrous was carbonized at 200°C for 2h in air and 1000°C for 3h in argon atmosphere, which was abbreviated as CF. Then it was sent into a horizontal tube furnace treated at 1000°C under ammonia atmosphere (30 sccm) for 2h. Then it was processed with O<sub>2</sub>-plasma (PDC-32G-2, Harrick Plasma) for 2h, which was abbreviated as CF-N-O.

**Characterization:** Nitrogen adsorption-desorption isotherms at 77 K were conducted on a Micromeritics Tristar 3000 system using vacuum-degassed samples (180°C for at least 6 h). The specific surface area was calculated by desorption branch of the isotherms using the Brunauer-Emmett-Teller (BET) method. The pore size distribution (PSD) plot was recorded from the adsorption branch of the isotherm based on the Barrett-Joyner-Halenda (BJH) model. Transmission electron microscope (TEM) and high resolution transmission electron microscope (HRTEM) images were obtained by JEOL 2100F. The morphology of porous carbon was observed by a Hitachi S-4800 field emission scanning electron (SEM) microscope. The crystallinity of synthesized carbon materials were measured by X-ray diffraction (XRD, Bruker D8) with a monochromatized source of Cu K<sub>α1</sub> radiation ( $\lambda = 1.541841 \text{ \AA}$ ) at 1.6 kW (40 kV, 40 mA). Raman spectra were collected in a Thermal Dispersive Spectrometer using a 10 mW laser with an excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) was collected in an RBD upgraded PHI-5000C ESCA system (Perkin Elmer) with Mg K $\alpha$  radiation ( $h\nu=1253.6 \text{ eV}$ ). Binding energies were calibrated using containment carbon (C 1s =284.6 eV).

**Preparation of the electrodes and electrolytes:** Zn plate was used as negative electrode. CF and CF-N-O were used as positive electrode, respectively. The electrolyte was made of 5 M ZnSO<sub>4</sub>, 3.1 M glycine, 0.08 M Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> • 5H<sub>2</sub>O and 0.12 M FeSO<sub>4</sub>•7H<sub>2</sub>O, here glycine is introduced as the complexing agent to prevent hydrolysis and crossover of the iron ions in ZFBs.

**Preparation of the coin-cell devices:** The electrodes were assembled in standard CR2032 coin cells using electrode discs (14 mm in diameter) and Φ19 mm paper separator (MPF30AC-100, NKK). Φ14 mm Zn plate was used as negative electrode, and Φ14 mm CF-N-O discs as positive electrode. Here, the porous paper membrane was as separator. The coin-cell was assembled in air.

**Electrochemical test:** A series of electrochemical tests including cyclic voltammetry test (CV) at different scan rate were tested on the electrochemical working station (CHI760E, CH Instruments) using two-electrode systems. The three-electrode systems were also conducted with a Pt wire and an Ag/AgCl (KCl saturated) electrode as counter and reference electrodes. Galvanostatic charge and discharge (GCD) and cycling performance for the total battery were carried out by using a Land cyler (Wuhan, China).

The mass based specific capacitance ( $C_s$ ) was calculated from the galvanostatic discharge process using equation (1):

$$C_s = \frac{I \times \Delta t}{m} \quad (1)$$

where  $I$  (mA) corresponds to the constant discharge current,  $\Delta t$  (h) represents the discharge time, and  $m$  (g) refers to the mass of cathode. The energy density ( $E$ ) and

power density (P) were calculated using equation (2) and (3).

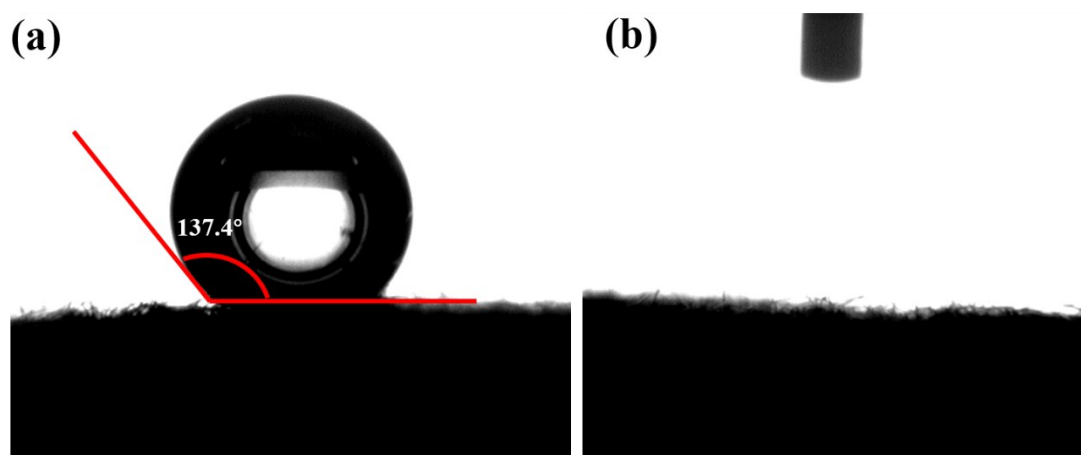
$$E = C_s \times V_p \quad (2)$$

$$P = \frac{E}{\Delta t} \quad (3)$$

Where  $V_p$  (V) is the platform voltage of discharge,  $\Delta t$  (h) is the discharge time,  $E$  (Wh  $\text{kg}^{-1}$ ) is the mass based-energy density,  $P$  (W  $\text{kg}^{-1}$ ) is the average power density.

**Table S1.** Elemental composition (at.%), obtained by XPS

Sample	C (at.%)	N (at.%)	O (at.%)
CF	77.69	1.79	20.52
CF-N-O	70.91	5.57	23.52



**Fig. S1** Contact angle of CF (a) and CF-N-O (b).

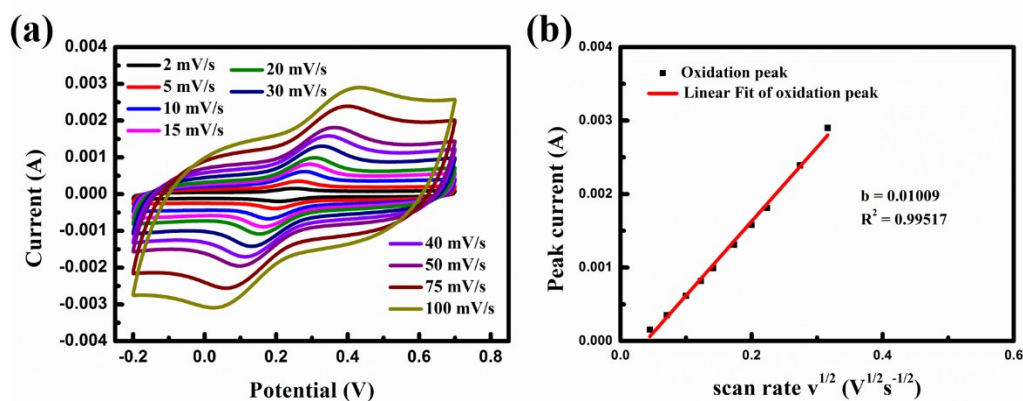
In this work, the electrochemical active surface area of CF-N-O was measured by cyclic voltammetry test (CV) in  $1 \times 10^{-3} \text{ mol L}^{-1} \text{ K}_3[\text{Fe}(\text{CN})_6]$  and  $0.1 \text{ mol L}^{-1} \text{ KCl}$ , using Randles–Sevcik equation (1).<sup>1,2</sup> A couple of obvious redox peaks was observed due to the presence of ferricyanide/ferrocyanide. The oxidation peak currents of CV

curves from 2 mV s<sup>-1</sup> to 100 mV s<sup>-1</sup> were used to analyze the the electrochemical active surface area of CF-N-O, using the Randles-Sevick equation (1).

$$I_p = 0.4463(F^3/RT)^{1/2}n^{3/2}AD^{1/2}Cv^{1/2}$$

$$= 2.69 \times 10^5 n^{3/2}AD^{1/2}Cv^{1/2} \quad (1)$$

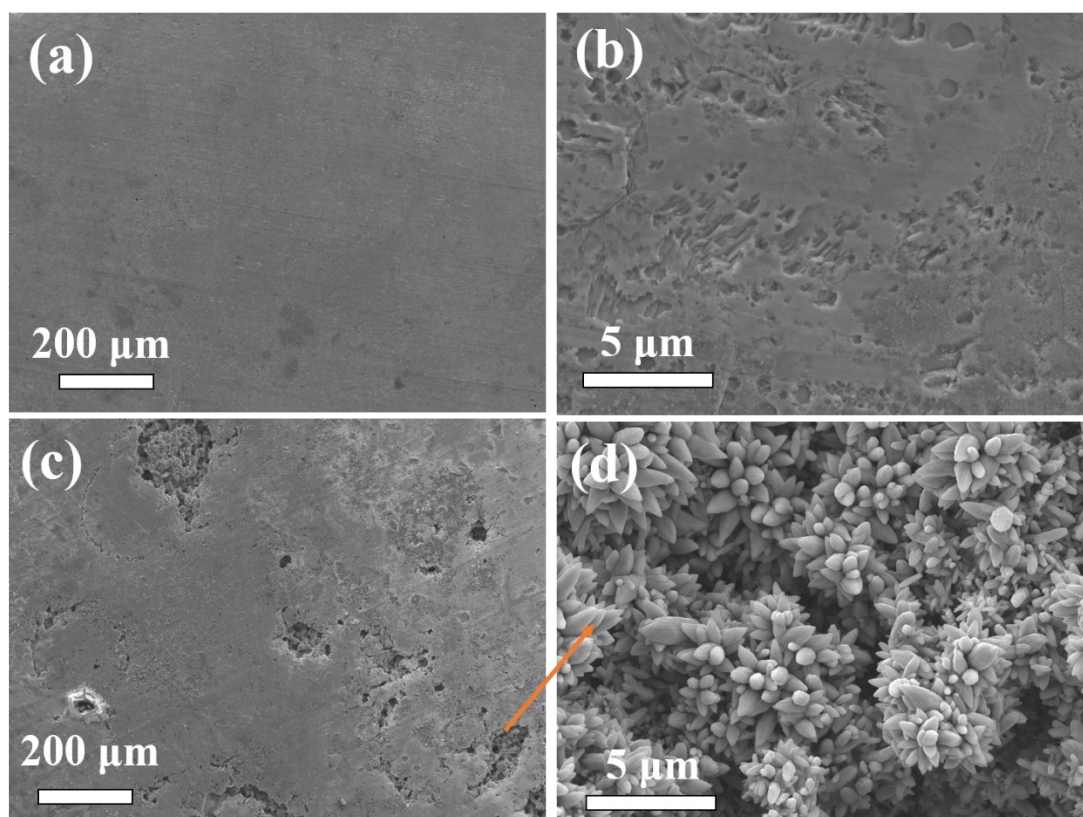
where F is Faraday constant [96485 C mol<sup>-1</sup>], R is the universal gas constant [8.314 J mol<sup>-1</sup> K<sup>-1</sup>], A is the electrochemical active surface area [cm<sup>2</sup>],  $I_p$  refers to the oxidation peak currents [A], n is the number of electrons involved in the redox reaction (n = 1 for K<sub>3</sub>[Fe(CN)<sub>6</sub>]), T is the absolute temperature [298 K], D is diffusion coefficient of K<sub>3</sub>[Fe(CN)<sub>6</sub>] [7.2 × 10<sup>-6</sup> cm<sup>2</sup> s<sup>-1</sup>], v is scan rate [V s<sup>-1</sup>], and C is the concentration of K<sub>3</sub>[Fe(CN)<sub>6</sub>] [1 × 10<sup>-3</sup> mol L<sup>-1</sup>]. Thus, the value of A can easily be calculated from the slope of  $I_p$  vs  $v^{1/2}$  plot, and the electrochemical active surface area was evaluated as 5.2 cm<sup>2</sup>.



**Fig. S2** (a) Cyclic voltammetry curves of CF-N-O in 1 × 10<sup>-3</sup> mol L<sup>-1</sup> K<sub>3</sub>[Fe(CN)<sub>6</sub>] and 0.1 mol L<sup>-1</sup> KCl. (b) The relationships between oxidation peak currents versus the square root of scan rates from cyclic voltammetry curves of CF-N-O (b is the slope of linear fit, R<sup>2</sup> is the goodness-of-fit).

FE-SEM has been conducted to analyze the morphology of anode Zn before and after charge 2000 cycles, as shown in Fig. S3. The surface of Zn undergoes the process

of dissolution and precipitation, and partial surface etching occurs. At the etched portion, the deposited ellipsoidal morphology can be clearly seen (Fig. S3d).



**Fig. S3** FE-SEM images of Zn (a, b) and Zn after charge 2000 cycles (c, d).

**Table S2.** Comparison of Zinc-flow batteries and this work

Battery type	Electrolyte	Separator	Performance	Ref
Zinc-iron redox-flow battery	Positive electrolyte: 1 M FeCl <sub>2</sub> , 1 M HCl Middle electrolyte : 3 M NaCl Negative electrolyte : 0.5 M Na <sub>2</sub> [Zn(OH) <sub>4</sub> ] in 4 M NaOH	Cation-exchange membrane: Nafion® 212 anion-exchange membrane: FAA-3	676 mW/cm <sup>2</sup> at 660 mA/cm <sup>2</sup> 12.5 Ah/L at 80 mA/cm <sup>2</sup>	3
Neutral Zinc-Iron Flow Battery	Catholyte: FeCl <sub>2</sub> , glycine, KCl Anolyte: ZnBr <sub>2</sub> , KCl	A sponge-like polybenzimidazole (PBI) porous membrane	56.30 Wh/L at 40 mA/cm <sup>2</sup>	4
Alkaline zinc-iron flow battery	Catholyte: NaOH Anolyte: Na <sub>3</sub> Fe(CN) <sub>6</sub> , Na <sub>4</sub> Fe(CN) <sub>6</sub> , NaOH	Nafion N-114 separator	between 200 and 300 mA h/cm <sup>2</sup>	5

Neutral zinc-iron battery	5 M ZnSO <sub>4</sub> , 3.1 M glycine, 0.08 M Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·5H <sub>2</sub> O, 0.12 M FeSO <sub>4</sub> ·7H <sub>2</sub> O	Porous separator	352 mAh g <sup>-1</sup> at 2 A g <sup>-1</sup>	This work
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### Notes and references

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