Experimental

1. Chemicals

Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2·6H_2O$, AR), iron(III) nitrate nonahydrate ($Fe(NO_3)_3·9H_2O$, 98%), potassium hydroxide (KOH) were obtained from Sinopharm Chemical Reagent Co., Ltd. Urea (AR), zinc acetate ($Zn(CH_3COO)_2·2H_2O$, AR) were purchased from Aldrich. Nafion (5 wt%) and 20% Pt/C were purchased from HESEN. Ruthenium (IV) oxide (RuO_2, 99.9%) was obtained from Alfa Aesar.

2. Characterizations

A Bruker D8 Advance X-ray polycrystalline diffractometer (Bruker, Billerica, MA, USA) was also used to record the X-ray diffraction (XRD) spectra with a scanning range of 10°–80° and a scanning speed of 4° min^{-1}. The JEOL JSM-7100F scanning electron microscope (Japan Electron Optics Laboratory, Tokyo Akishima Station, Tokyo, Japan) was also used to analyze the particles and morphology of the catalyst, The FEI Talos-S transmission electron microscope (Frequency Electronics, Inc., Columbia, MD, USA) was used to analyze the particle size and morphology of the catalyst. Raman spectroscopy was detected at 514 nm using Horiba Scientific LabRAM HR Evolution Raman spectrometer (HORIBA Scientific, Palaiseau, France). The model of the automatic specific surface and porosity analyzer is Mike 2460 (Micromeritics, Atlanta, GA, USA). We also used X-ray photoelectron spectroscopy analyzer Thermo

Scientific ESCALAB 250Xi (Thermo Scientific, Thermo Scientific, Waltham, MA, USA) to analyze elements.

3. Electrochemical experiments

All electrochemical tests were performed on the IVIUM instrument (Lvium Technologies BV, Eindhoven, Netherlands) at 25 °C. The electrolytic cell used a traditional five-port electrolytic cell with an electrolyte of 0.1 M KOH. A platinum wire and Ag/AgCl electrode were used as the counter electrode and the reference electrode, and the salt bridge used a saturated KCl solution. The working electrode was a rotating disk electrode (RDE), and the electrode was a 5 mm glass-carbon disk. For typically preparing the catalyst ink, 5 mg of the FeNi@NC sample was put into the mixture containing 0.90 mL of ethanol, 0.10 mL of water, and 10 μL of 5 wt%Nafion. Next, the mixture was ultrasonicated for at least 30 min to obtain a homogeneous suspension. After that, 10 μL of the catalyst ink was dropped onto the RDE with a catalyst loading of 0.25 mg cm^{-2}. In the controls, commercial Pt/C and RuO_2 catalysts modified electrodes were constructed in a similar way. The linear sweep volt-ampere (LSV) curve is 0.2–1.2 V (vs. RHE), and the sweep rate is 5 mv s^{-1}.

The conversion of Ag/AgCl electrode and standard hydrogen electrode is as follows:

$$V_{RHE} = V_{Ag}/AgCl + 0.059pH + 0.197$$

The Koutecky-Levich (K-L) equation is used to calculate the number of electrons transferred in the ORR process. Obtain the LSV curves of the relevant catalysts at 400, 625, 900, 1225, 1600 rpm. Based on these curves, calculate the electron transfer number (N) of each oxygen molecule involved in the ORR process according to the Koutecky-Levich (K-L) equation as follows:

$$1/i = 1/i_k + 1/i_d = 1/i_k + 1/\left(B\omega^{1/2}\right) \qquad (1)$$

$$B = 0.2nFC_0D_0^{2/3}v^{-1/6} \qquad (2)$$

Where i is the experimentally measured current, i_k is the kinetic current, i_d is the diffusion-limiting current, ω is the rotating speed, n is the number of transferred electrons, F is the Faraday constant (96485 C mol^{-1}), C_0 is the oxygen solubility (1.26×10^{-3} mol L^{-1}), D_0 is the oxygen diffusivity (1.93×10^{-5} cm^2 s^{-1}), and v is the kinetic viscosity of the electrolyte (0.01 cm^2 s^{-1}).

The OER measurements were conducted in the O_2-saturated 1.0 M KOH solution. The electrocatalytic activity was critically examined by LSV at 1600 rpm and 5 mV s^{-1}. All of the OER data were corrected with the iR compensation (90%).

4. Zn–air battery test

The homemade rechargeable Zn-air batteries were assembled by using a freshly-polished Zn plate as the anode, a 6.0 M KOH solution containing 0.2 M $Zn(CH_3COO)_2$ as the electrolyte, and the catalyst coated on a carbon paper as the cathode. The air cathode was typically prepared by sequentially casting the catalyst ink (5 mg of the FeNi@NC powder, 1 mL of ethanol and 50 μL of a Nafion solution (5 *wt*%)) on the carbon paper with an average catalyst loading of 1.0 mg cm^{-2}, combined by drying at 60 °C for 4 h. For comparison, the air electrodes based on Pt/C (20 *wt*%) + RuO_2 were also fabricated similarly with the identical mass loading.

The polarization curves of the charge and discharge processes were acquired by LSV at a sweep rate of 5 mV s^{-1}. The charge-discharge cycling test was conducted at a current density of 10 mA cm^{-2}. Each cycle contained one discharge process at 10 mA cm^{-2} for 15 min, and another charge process for 15 min. All of the Zn–air batteries were tested in ambient atmosphere on a CHI 660E electrochemical workstation.

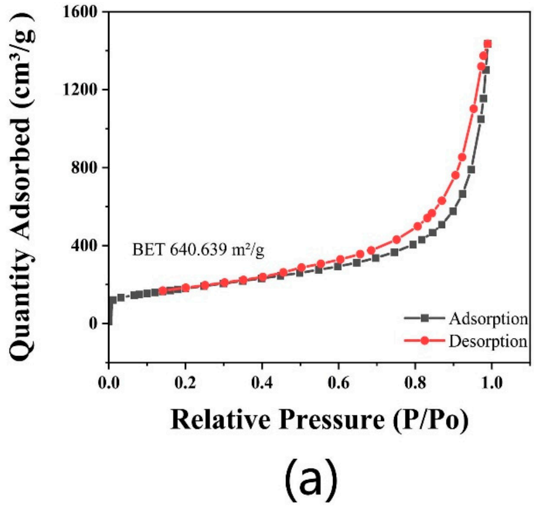

Figure. S1 (a) N_2 sorption isotherms of FeNi@NC.

Table S1. Comparison of the ORR/OER catalytic data of the FeNi@NC with other FeNi-based catalysts early published.

Catalysts	$E_{1/2}$ (V)	$E_{j=10}$ (V)	ΔE	References
FeNi@NC	**0.84**	**1.59**	**0.75**	**This work**
FeNi-NC	0.83	1.64	0.81	[1]
Fe-enriched-$FeNi_3$/NC	0.79	1.59	0.80	[2]
FeNi/NC	0.81	1.58	0.77	[3]
FeNi@NCNT-CP	0.85	1.58	0.73	[4]
NiCoFe@N-CNFs	0.81	1.50	0.69	[5]
$Fe_{0.5}Ni_{0.5}$@N-GR	0.83	1.44	0.61	[6]
CoFeNi@CNT	0.82	1.67	0.85	[7]
NiFe@NCNT	0.79	1.56	0.77	[8]
NiFe/N-CNT	0.75	1.52	0.77	[9]
FeNi@NCSs	0.84	1.54	0.70	[10]

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