Supporting Information

N-doped hierarchical porous carbon nanoscrolls towards efficient oxygen reduction reaction in Zn-air batteries via interior and exterior modification

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 works reported previously

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1.1 Chemicals and materials

All the reagents were of analytical grade and used as received without further purification. Pyrrole (98%) was purchased from Sigma–Aldrich Co., Ltd. Urea (99%) was bought from Shanghai Aladdin Biochemical Technology Co., Ltd. Ammonium persulphate (≥98%) was bought from Shanghai Shiyicr Co., Ltd. Ultrapure water was used in this study.

1.2 Characterization

The morphology and microstructure of the obtained samples were measured by scanning electron microscope (FE-SEM, JEOL, JSM-6330f) and transmission electron microscope (TEM, JEOL, JEM–2100). The crystalline structure and defect nature of these samples were detected by X-ray diffraction (XRD, Rigaku, Ultima IV) and Raman spectroscopy (Jobin Yvon, Labram–010). X–ray photoelectron spectroscopy (XPS) equipped with an ESCALAB250 XPS spectrometer were used to analyze the chemical composition of these samples. The specific surface area and pore structure of these samples were tested on an analyzer (Micromeritics, ASAP 2020 HD) by recording the N₂ adsorption/desorption curves.

1.3 Electrochemical measurement

1.3.1 ORR performance

The whole electrochemical performance was tested in 0.1 M KOH electrolyte with a typical three-electrode system on rotating disk electrode (Gamry Instruments, RDE 710). A platinum foil and Ag/AgCl electrode full of saturated KCl solution were adopted as auxiliary electrode and reference electrode, respectively. The working

electrode was prepared as follows. Specifically, 10 μ L of 2 mg mL⁻¹ dispersed sample ink was dropped onto a polished glassy carbon electrode (GCE, Φ =5 mm). Then, 6 μ L of 0.05 *wt.*% Nafion solution was overlain on GCE to acquire the final working electrode. All potentials in this work was calibrated to reversible hydrogen electrode (RHE) by the equation: $E_{RHE} = E_{Ag/AgC1} + 0.97$ V in 0.1 M KOH electrolyte [S1]. Before ORR tests, the electrolyte saturated with N₂ or O₂ was realized by bubbling with pure N₂ or O₂ for at least 30 mins. Cyclic voltammetry (CV) was conducted in saturated N₂ or O₂ aura within the voltage range between 1.17 V and -0.03 V. Linear sweep voltammetry (LSV) was measured at a scanning rate of 10 mV s⁻¹ within the voltage range between 1.05 V and 0.02 V at different rotation speeds from 400 to 1600 rpm. The ORR kinetic parameters can be calculated by typical Koutechy–Levich (K–L) equation [S2–S3]:

$$\frac{1}{J} = \frac{1}{0.62nFC_0 D_0^{2/3} v^{-1/6} \omega^{1/2}} + \frac{1}{J_k}$$
(1)

Where *J* represents tested current density, $J_{\rm K}$ is kinetic current density. *n* is electron transfer number, *F* refers to Faraday constant (96485 C mol⁻¹), C_0 is O₂ bulk concentration (1.2×10⁻³ M), D_0 stands for oxygen diffusion coefficient (1.9×10⁻⁵ cm² s⁻¹), *v* is electrolyte kinetic viscosity (0.01 cm² s⁻¹) and ω is disk angular velocity.

The H_2O_2 generation of the carbon samples was measured by rotating ring-disk electrode (RRDE-3A, ALS). The H_2O_2 yield (% H_2O_2) and electron transfer number were calculated by the following equations [S4]:

% H₂O₂=
$$\frac{200 I_r/N}{(I_d + I_r/N)}$$
 (2)

$$n = \frac{4I_d}{I_d + I_r / N} \tag{3}$$

Where I_d is disk current, I_r is ring current, N is current collection efficiency of the Pt ring (N=0.37) and n refers to the electron transfer number during ORR process.

1.3.2 Zn-air batteries performance

The Zn–air battery tests were conducted in home–made electrochemical cells. The Zn–air battery tests were conducted in home–made electrochemical cells. The EN–PCNS or Pt/C catalyst (De Nora Elettrodi Co. Ltd., 20 *wt.*% Pt on carbon black) was loaded on carbon cloth with a mass loading of ~1.0 mg cm⁻² to prepare the air cathode. A piece of polished Zn foil with the thickness of 0.1 mm and polymer gel were utilized as the anode and electrolyte, respectively. The preparation of the polymer gel electrolyte was described as follows. Firstly, 0.5 g of acrylic acid and 0.075 g N, N' –methylene–bisacrylamide (MBA) were sequentially added into 5 mL of 11.25 M KOH solution containing 0.25 M ZnO. After stirring for over 0.5 h, the existing white precipitate was filtered out, and then 75 μ L of saturated K₂S₂O₄ as the initiator was added into the residual solution. In the last step, a certain amount of the obtained mixed solution was transferred into the void of acrylic tape. Once the solution completed polymerization process, the polymer gel electrolyte could be successfully made. The battery measurements were performed on a LAND battery testing system and an electrochemical workstation (CHI 760E).



Figure S1 SEM images of N–PCNS–20 (a), N–PCNS–60 (b) and N–PCNS–80 (c)



Figure S2 SEM images of N-PCNS-40 (a) and EN-PCNS (b); HRTEM images of

N–PCNS–40 (c) and EN–PCNS (d)



Figure S3 High-resolution N 1s spectrum of N-PCNS-20 (a), N-PCNS-60 (b) and

N–PCNS–80 (c)



Figure S4 LSV-RRDE profiles of NC, NMC, N–PCNS–m, EN–PCNS and commercialized Pt/C in O₂–saturated 0.1 M KOH



Figure S5 LSV curves on NC (a), NMC (b), N-PCNS-20 (c) and N-PCNS-40 (d)

electrodes at different rotation speeds in 0.1 M KOH electrolyte



Figure S6 LSV curves on N–PCNS–60 (a), N–PCNS–80 (b) and EN–PCNS (c) electrodes at different rotation speeds in 0.1 M KOH electrolyte; K–L plots on NC, NMC, N–PCNS–m and EN–PCNS electrodes at 0.2 V in 0.1 M KOH electrolyte (d)



Figure S7 K-L plots at different potentials on EN-PCNS electrode



Figure S8 CV curves on EN–PCNS electrode before and after 4500 continuous cycles in 0.1 M KOH electrolyte (a); the *i*–*t* curves on EN–PCNS and commercialized Pt/C electrodes at 0.67 V for 40000 s in O_2 saturated 0.1 M KOH electrolyte (b)



Figure S9 The i-t curves on EN–PCNS and commercialized Pt/C electrodes at 0.67 V

in O₂ saturated 0.1 M KOH electrolyte before and after adding 3 M methanol



Figure S10 Open circuit potential *vs.* time curves of N–PCNS–40, EN–PCNS and commercialized Pt/C catalysts for Zn–air batteries



Figure S11 Charging/discharging cycling curves at 0.5 mA cm⁻² for Zn–air batteries assembled by EN–PCNS and commercialized Pt/C

Samples	Specific surface area (m ² /g)		
NC	21.8		
NMC	256.5		
N-PCNS-40	497.3		
EN-PCNS	945.3		

Table S1 The specific BET result of NC, NMC, N–PCNS–40 and EN–PCNS

Table S2 The XPS result of NMC, N–PCNS–*m* and EN–PCNS

Samples	Samples C (<i>at.</i> %)		O (at. %)	
NMC	86.9	11.1	2.0	
N–PCNS–20	86.0	11.5	2.5	
N-PCNS-40	86.3	11.1	2.6	
N-PCNS-60	88.6	9.1	2.3	
N–PCNS–80	88.6	8.5	2.9	
EN-PCNS	89.8	5.5	4.7	

Samples	Pyridinic-N (%)	Pyrrolic-N (%)	Graphitic–N (%)	Oxygenated-N (%)	
NMC	20.9	12.3	41.0	25.8	
N-PCNS-20	21.6	11.9	42.8	23.7	
N-PCNS-40	23.8	11.9	46.5	17.8	
N-PCNS-60	23.7	16.6	43.9	15.8	
N-PCNS-80	22.0	11.3	43.1	23.6	
EN-PCNS	16.6	10.4	54.5	18.5	

Table S3 The N 1s spectra fitting results of NMC, N–PCNS–m and EN–PCNS

Samples	Electrolyte (KOH)	Limiting current density (mA cm ⁻²)	E _{1/2} (V vs. RHE)	Electron transfer number (<i>n</i>)	loading mass (mg cm ⁻²)	References
N-PCNS-40	0.1 M	4.71	0.79	3.82	0.10	This work
EN-PCNS	0.1 M	5.15	0.82	4.00	0.10	This work
N–CSH	0.1 M	3.40	0.80	4.00	0.10	S 5
N, S–CMTs–800–60	0.1 M	4.60	0.76	3.87	0.32	S6
N, S–CD/rGO	0.1 M	4.51	0.69	3.90	0.34	S7
NPGC-950	0.1 M	4.90	0.75	3.79	0.20	S8
N, S–SMC	0.1 M	5.19	0.81	3.80	0.50	S9
N-C-MOF-5	0.1 M	3.30	0.76	3.80	0.10	S10
NSC/MPA-5	0.1 M	3.30	0.76	3.99	0.25	S11
800–N, P–CNT	0.1 M	6.10	0.80	3.80	0.10	S12
NCN-1000-5	0.1 M	6.43	0.82	3.92	0.20	S13
PNCR	0.1 M	4.30	0.71	3.67	0.20	S14

 Table S4 Comparison of the ORR performance between this work and some other

 works reported previously

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