FeS encapsulated hierarchical porous S, N-dual-doped carbon for oxygen reduction reaction facilitation in Zn-air battery

Hao Xu,^a Dan Wang,^a Peixia Yang,^{*a} Anmin Liu,^{*b} Ruopeng Li,^a Lihui Xiao,^a Jinqiu

Zhang,^a Zhenshen Qu^c and Maozhong An^a

^a MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001 China. *E-mail: yangpeixia@hit.edu.cn;

^b State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian, 116000 China. *E-mail: <u>liuanmin@dlut.edu.cn</u>.

^c Aerospace College, Harbin Institute of Technology. Harbin, 150001 China. E-mail: miraland@hit.edu.cn



Fig. S1 The SEM image of Fe NPs/SNC.



Fig. S2 (a) The SAED pattern of Fe-S, N-C-950. (b) the size distribution of FeS nanoparticles.



Fig. S3 (a) High resolution spectra of C 1s of Fe-S, N-C-950. (b) High resolution spectra of C 1s of Fe NPs/SNC.



Fig. S4 (a) High resolution spectra of Fe 2p of Fe-S, N-C-950. (b) High resolution spectra of Fe 2p of Fe NPs/SNC.



Fig. S5 (a) High resolution spectra of S 2p of Fe-S, N-C-950. (b) High resolution spectra of S 2p of Fe NPs/SNC.



Fig. S6 Cyclic voltammograms (CV) of the prepared catalysts at a scan rate of 50 mv s⁻¹ in 0.1 M KOH.



Fig. S7 ORR polarization LSV curves of NC, Fe-S, N-C-950, Fe NPs/SNC and 20% Pt/C in 0.1 M HClO₄; rotation rate of 1600 rpm, scan rate of 10 mVs⁻¹.



Fig. S8 CV curves for (a) Fe-S, N-C-950 and (b) Fe NPs/SNC at various scan rates.



Fig. S9 (a) LSV curves of Fe-S, N-C-950 for rotation speeds from 400 to 2500 rpm. (b) Fitted K–L plots at different potentials.



Fig. S10 ORR polarization curves of Pt/C before and after 5000 cycles in 0.1 M KOH.



Fig. S11. Discharge curves of primary Zn-air batteries using Fe-S, N-C-950 as ORR catalyst.



Fig. S12 H_2O_2 yield and electron transfer number (n) for 20% Pt/C.



Fig. S13 ORR polarization curves of Fe-S, N-C-950 before and after 5000 cycles in 0.1 M HClO₄.



Fig. S14 Methanol tolerance tests for Fe-S, N-C-950 and 20% Pt/C in 0.1 M KOH at 0.7 V.

Atomic %	Fe-S, N-C-950	Fe NPs/SNC		
С	92.75	90.01		
Ν	3.32	4.37		
0	3.19	3.94		
S	0.19	0.57		
Fe	0.55	1.11		

Table S1 Elemental composition of Fe-S, N-C-950 and Fe NPs/SNC calculated from XPS.

Table S2 The Comparison of ORR performance of non-precious M–N/C catalysts from the recent literature and this work

Catalysts	Electrolyte	Half-wave	Reference
		potential (V vs.	
		RHE)	
Fe-S, N-C-950	0.1 M KOH	0.9	This work
Fe-N/C-155	0.1 M KOH	0.85	J. Mater. Chem.
			A, 2019,
			7,16508.
Fe-N _x -C	0.1 M KOH	0.91	Adv. Funct.
			Mater., 2019,
			29, 1808872.
C-FeZIF-8@g-	0.1 M KOH	0.845	Chem. Eng. J.,
C_3N_4			2020, 390,
			124479.
Fe-N-C/N-OMC	0.1 M KOH	0.93	Appl. Catal. B
			Environ., 2021,
			280, 119411.
Fe-N-C HNSs	0.1 M KOH	0.87	Adv. Mater,
			2018, 31,
			1806312.
Fe-SAC/NC	0.1 M KOH	0.84	Nano Energy,
			2020, 72,
			104670.
Cu SAC	0.1 M KOH	0.81	J. Mater. Chem.
			A, 2019, 7,
			16690.
f-Mn-NC/CNT	0.1 M KOH	0.83	Nanoscale,
			2019, 11, 15900.
Co@hNCTs-800	0.1 M KOH	0.887	Nano Energy,
			2020, 71,
			104592.
Fe-N-S CNN	0.1 M KOH	0.91	Appl. Catal. B
			Environ, 2019,
			250, 143.
Fe-SAs/NSC	0.1 M KOH	0.87	J. Am. Chem.

			Soc., 2019, 141,
			20118.
Fe-NSDC	0.1 M KOH	0.84	Small, 2019, 15,
			1900307.
Fe-S, N-C	0.1 M KOH	0.83	Electrocatalysis,
			2019, 10, 72.