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Supporting Information

Core-shell Fe-N-C nanocatalyst with ultrathin porous carbon shell as a robust

electrocatalyst for oxygen reduction reaction

Bin Yue^a, Kang Yang^a, Huaming Xie^a, Ying Lei^{*a}, Jianying Li^a, Yujun Si^b

^aCollege of Chemical Engineering, Sichuan University of Science and Engineering,

Zigong 643000, PR China

^bCollege of Chemistry and Environmental Engineering, Sichuan University of Science and Engineering, Zigong 643000, PR China



Figure. S1 TEM image of Fe-ZIF-8@PVP

Sample	surface area	ace area pore volume pore diamet	
	$(m^2 g^{-1})$	(cm ³ g ⁻¹)	(nm)
Fe-N-C@NC	1163.9619	1.1459	3.9379
Fe-N-C	579.2399	0.9750	6.7330

Table S1. Pore structure characteristics of Fe-N-C@NC and Fe-N-C



Figure. S2 High-resolution XPS spectra of (a) survey, (b) C 1s and (c) O 1s for Fe-N-C@NC and Fe-N-C.



Figure. S3 (a) LSV curves of Fe-N-C with different molar of metallic iron (0.3 mmol, 0.5 mmol and 0.7 mmol), (b) LSV curves of Fe-N-C@NC with different grams of polyvinylpyrrolidone (0.5g, 1g, 1.5g, 2g, with optimal metallic iron additions) and (c) LSV curves of Fe-N-C@NC with different pyrolysis temperatures (900 °C, 950 °C and 1000 °C)



Figure. S4 LSV curves at various rotation rates for the ORR and the corresponding K-L plots for (a, b) $Fe_{0.3}$ -N-C, (c, d) $Fe_{0.5}$ -N-C, and (e, f) $Fe_{0.7}$ -N-C in the O₂-saturated 0.1 M KOH solution, respectively.



Figure. S5 LSV curves at various rotation rates for the ORR and the corresponding K-L plots for (a, b) Fe-N-C@NC_{0.5}, (c, d) Fe-N-C@NC₁, (e, f) Fe-N-C@NC_{1.5}, and (g, h) Fe-N-C@NC₂ in the O₂-saturated 0.1 M KOH solution, respectively.



Figure. S6 LSV curves at various rotation rates for the ORR and the corresponding K-L plots for (a, b) Fe-N-C@NC-950 and (c, d) Fe-N-C@NC-1000 in the O₂-saturated 0.1 M KOH solution, respectively



Figure. S7 LSV curves at various rotation rates for the ORR and the corresponding K-L plots for 20% Pt/C in the O_2 -saturated 0.1 M KOH solution.



Figure. S8 LSV curves of Fe-N-C@NC before and after adding 5 mM NaSCN into $0.05M H_2SO_4$. Electrode rotation speed, 1600 rpm; scan rate, 10 mV/s.



Figure. S9 CV at scan rates of 10, 20, 30, 40 and 50 mV s⁻¹ in 0.1 M KOH electrolyte for (a) Fe-N-C@NC, (b) Fe-N-C and (c) 20% Pt/C.



Figure. S10 LSV curves of Fe-N-C@NC and Fe-N-C after ADT.



Figure. S11 voltage-energy density curves for different current densities.



Figure. S12 TEM was used to test the Fe-N-C@NC material after cycling, and it was found that its morphology and structure were well preserved.

Sam	ple	C (at%)	N (at%)	O (at%)	Fe (at%)
	initial	80.87	3.27	14.65	1.21
Fe-IN-C@INC -	after 150 h	79.97	0.65	18.35	1.03
Fe-N-C -	initial	80.54	2.97	14.44	2.05
	after 150 h	74.94	0.64	24.24	0.18

 Table S2 Elemental analysis parameters of samples

Catalyst	Catalyst loading (mg cm ⁻²)	Peak power density (mW cm ⁻²)	Cycling time (h)	Referenc e
Fe-N-C@NC	1.0	170.8	150	This work
FeS/Fe ₃ C@NS-C- 900	1.25	90.9	865	1
CeO ₂ -FeNC-5	4.0	169	200	2
Fe-N-C/2rGO	1.0	164	30	3
FeNC-0.04	1.0	165	-	4
NiFe(1:2)P/Pi	2.0	395	100	5
Fe-KJB-3-60A	0.15	251	156	6
Co SAs@PNCN	1.0	220	89	7
Fe-N/S-HPC	1.0	188.4	240	8
Fe/Co/Zn-CNZIF	-	156.7	137	9

 Table S3 Electrochemical performance of Zn-air batteries with our catalysts and other

 advanced catalysts reported recently.

Reference

- Y. W. Li, W. J. Zhang, J. Li, H. Y. Ma, H. M. Du, D. C. Li, S. N. Wang, J. S. Zhao, J. M. Dou and L. Xu, Fe-MOF-Derived Efficient ORR/OER Bifunctional Electrocatalyst for Rechargeable Zinc-Air Batteries, ACS Appl. Mater. Interfaces, 2020, 40, 44710-44719.
- Y. Huang, Y. Zhang, J. Hao, Y. Wang, J. Yu, Y. Liu, Z. Tian, T. S. Chan, M. Liu, W. Li and J. Li, Tuning the coordination environment of Fe atoms enables 3D porous Fe/N-doped carbons as bifunctional electrocatalyst for rechargeable zinc-air battery, J. Colloid Interface Sci., 2022, 628, 1067-1076.
- X. Zhao, L. Shao, Z. Wang, H. Chen, H. Yang and L. Zeng, In situ atomically dispersed Fe doped metal-organic framework on reduced graphene oxide as bifunctional electrocatalyst for Zn-air batteries, J. Mater. Chem. C, 2021, 34, 11252-11260.
- Z. Meng, N. Chen, S. Cai, J. Wu, R. Wang, T. Tian and H. Tang, Rational design of hierarchically porous Fe-N-doped carbon as efficient electrocatalyst for oxygen reduction reaction and Zn-air batteries, Nano Res., 2021, 12, 4768-4775.
- N. Thakur, M. Kumar, D. Mandal and T. C. Nagaiah, Nickel Iron Phosphide/Phosphate as an Oxygen Bifunctional Electrocatalyst for High-Power-Density Rechargeable Zn-Air Batteries, ACS Appl. Mater. Interfaces, 2021, 44, 52487-52497.
- M. Wang, B. Huang, N. Jiang, T. Liu, J. Huang and L. Guan, An Fe-N-C electrocatalyst with dense active sites synthesized by expeditious pyrolysis of a natural Fe-N₄ macrocyclic complex, J. Mater. Chem. A, 2022, 43, 23001-23007.
- M. Zhang, H. Li, J. Chen, F. X. Ma, L. Zhen, Z. Wen and C. Y. Xu, Transition Metal (Co, Ni, Fe, Cu) Single-Atom Catalysts Anchored on 3D Nitrogen-Doped Porous Carbon Nanosheets as Efficient Oxygen Reduction Electrocatalysts for Zn-Air Battery, Small, 2022, 34, 2202476.
- M. Wang, X. Du, M. Zhang, K. Su and Z. Li, From S-rich polyphenylene sulfide to honeycomb-like porous carbon with ultrahigh specific surface area as bifunctional electrocatalysts for rechargeable Zn-air batteries, Carbon, 2022, 198, 264-274.

 Z. Guo, Y. Ma, Y. Zhao, Y. Song, S. Tang, Q. Wang and W. Li, Trimetallic ZIFsderived porous carbon as bifunctional electrocatalyst for rechargeable Zn-air battery, J. Power Sources, 2022, 542, 231723.