Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Boosting Electrocatalytic Activity of Single Atom Iron Catalysts through Sulfur-Doping Engineering for Liquid and Flexible Rechargeable Zn-air Batteries

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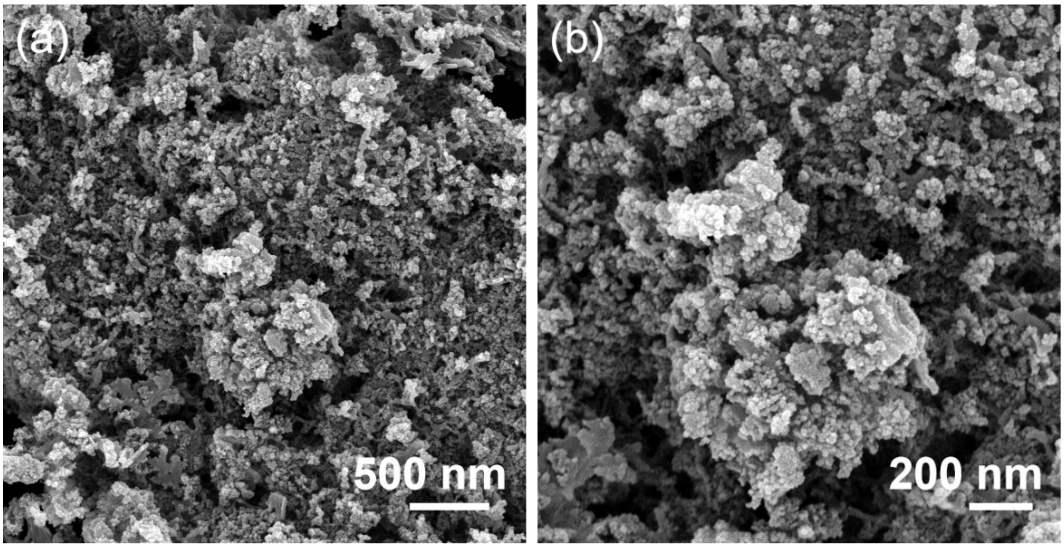

Fig. S1. (a) FE-SEM images of Fe SAs@N-C catalyst.

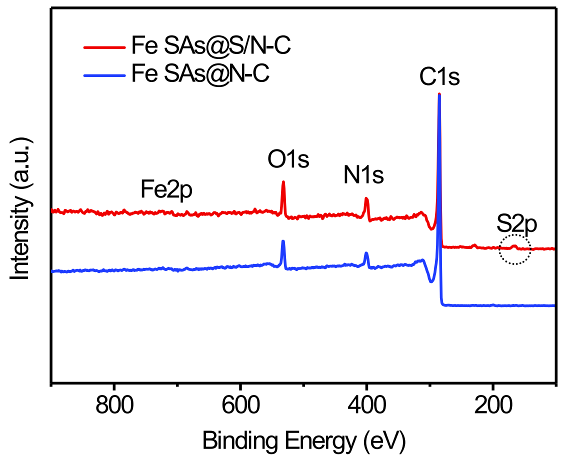

Fig. S2. XPS survey spectra of Fe SAs@S/N-C.

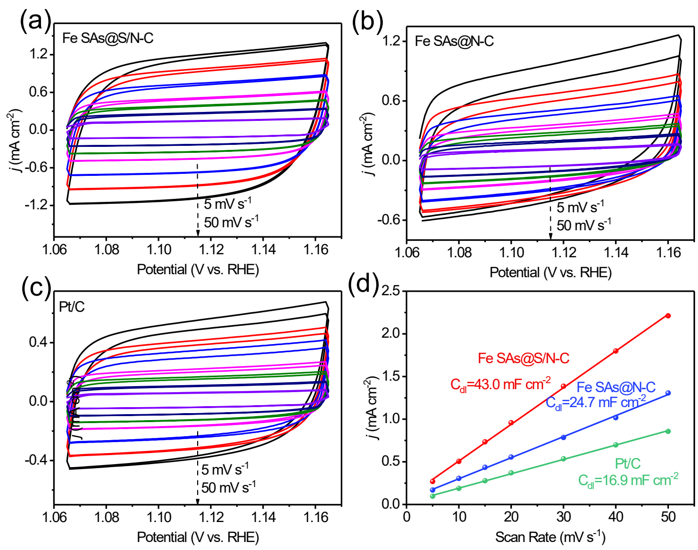

Fig. S3. The measurement of electrochemical double-layer capacitance (C_{dl}). CV curves of (a) Fe SAs@S/N-C, (b) Fe SAs@N-C, (c) Pt/C in 0.1 mol L^{-1} KOH solution at the scan rates of 5, 10, 15, 20, 30, 40 and 50 mV s^{-1}. (d) C_{dl} values at different scanning rates.

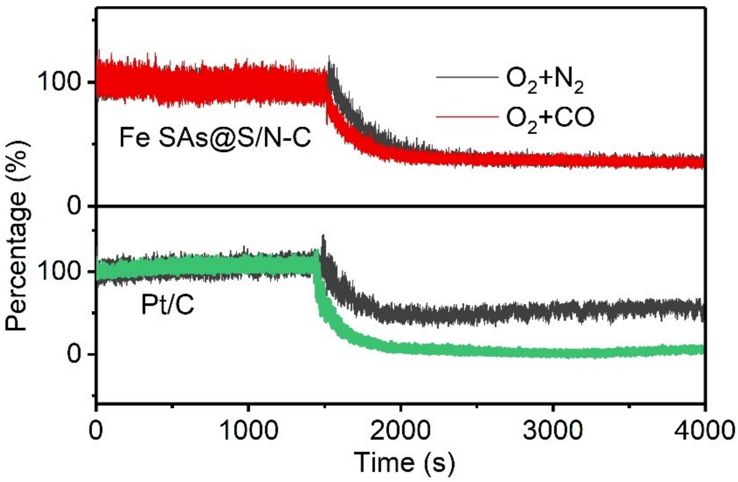

Fig. S4. The CO tolerance test by Chronoamperometric response of Fe SAs@S/N-C and Pt/C.

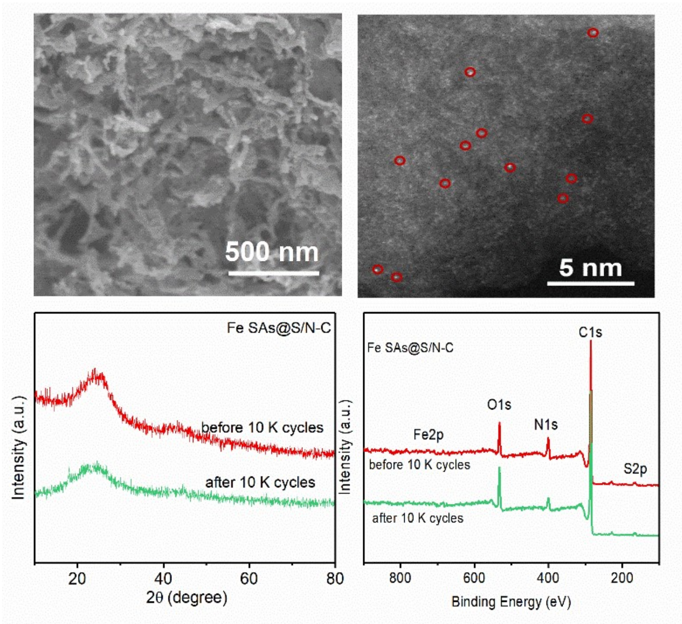

Fig. S5. (a) SEM images, (b) AC HAADF-STEM image, (c) XRD patterns, XPS survey spectra of Fe SAs@S/N-C after 10 K cycles

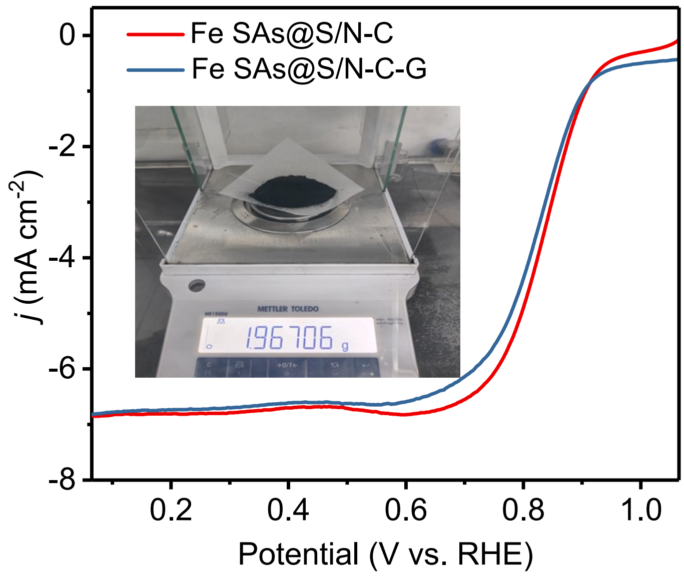

Fig. S6. LSV curves of the Fe SAs@S/N-C and Fe SAs@S/N-C-G.

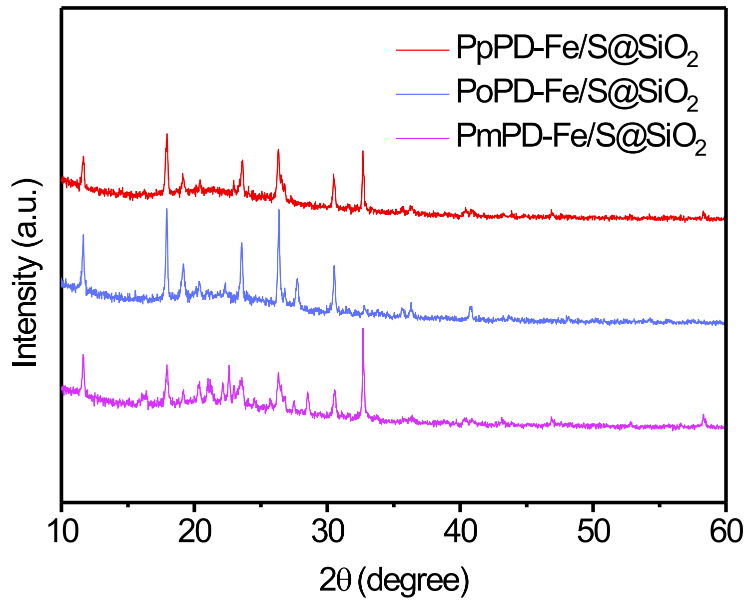

Fig. S7. XRD patterns of PpPD-Fe/S@SiO_2, PoPD-Fe/S@SiO_2 and PmPD-Fe/S@SiO_2.

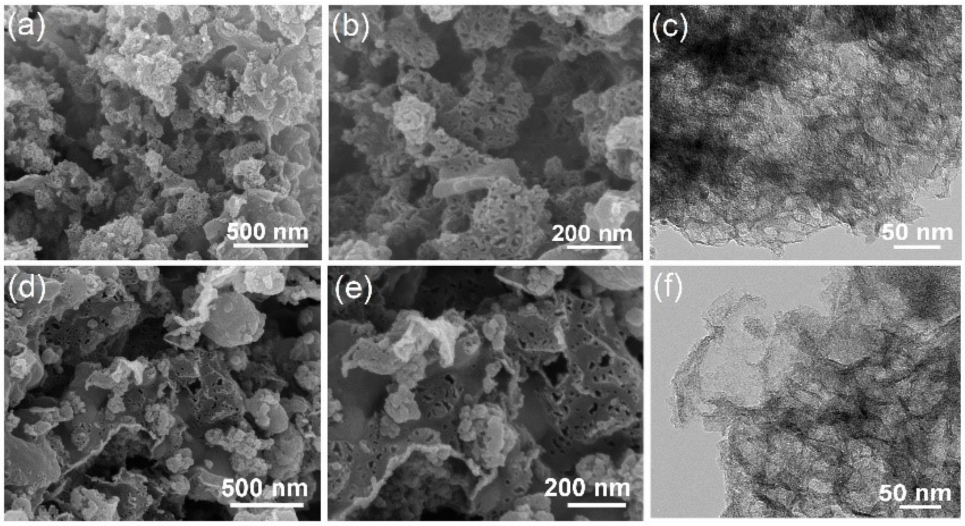

Fig. S8. (a-b) FE-SEM images, (c) TEM image of Fe SAs@S/N-C_{PoPD}. (d-e) FE-SEM images, (f) TEM image of Fe SAs@S/N-$C_{PmPD.}$

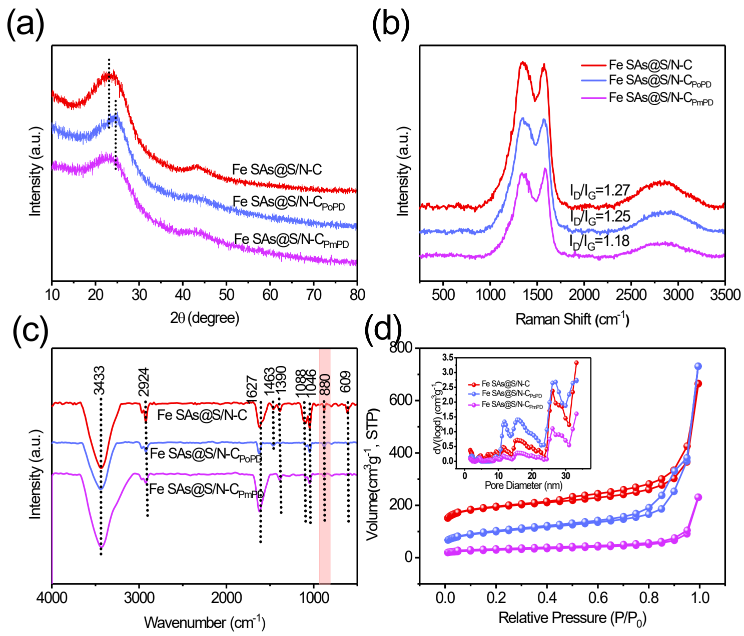

Fig. S9. (a) XRD patterns, (b) Raman spectra, (c) FT-IR spectra, (d) N_2 adsorption-desorption isotherms (inset is the pore size distribution curves) of Fe SAs@S/N-C, Fe SAs@S/N-C_{PoPD} and Fe SAs@S/N-$C_{PmPD.}$

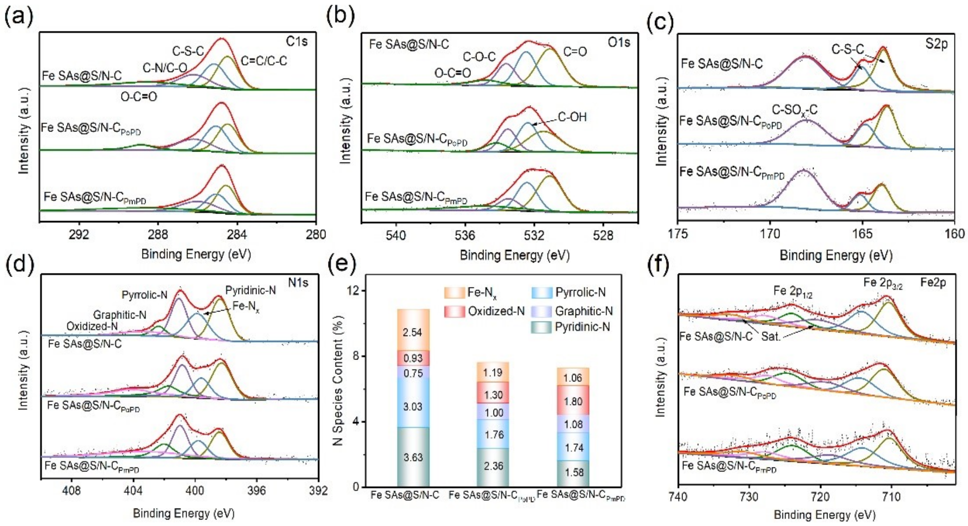

Fig. S10. (a) C 1s XPS spectra, (b) O 1s spectra, (c) S 2p spectra, (d) N 1s XPS spectra, (h) N contents and chemical configurations, (f) Fe 2p XPS spectra of Fe SAs@S/N-C, Fe SAs@S/N-C_{PoPD} and Fe SAs@S/N-C_{PmPD}.

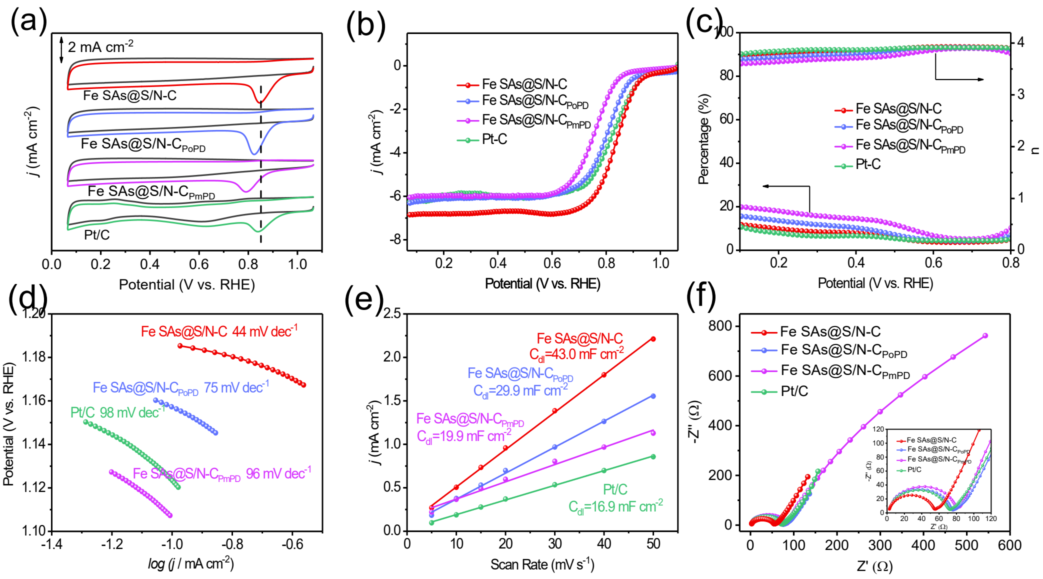

Fig. S11. ORR performance in O_2-saturated 0.1 M KOH: (a) CV curves, (b) LSV curves. (c) H_2O_2 yields and electron numbers, (d) Tafel plots, (e) C_{dl} values at different scanning rates, (f) Nyquist impedance plots of Fe SAs@S/N-C, Fe SAs@S/N-C_{PoPD} and Fe SAs@S/N-C_{PmPD}.

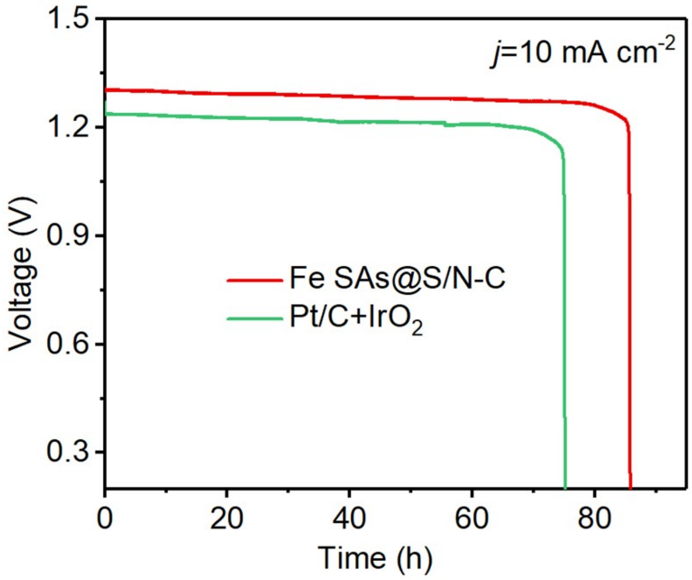

Fig. S12. Discharging polarization curves recorded at 10 mA cm^{-2} of Fe SAs@S/N-C and Pt/C+IrO_2.

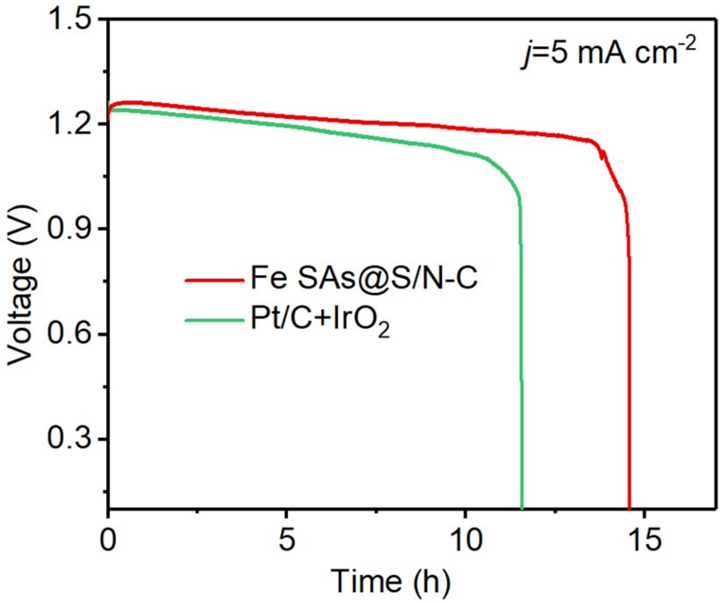

Fig. S13. Discharging polarization curves recorded at 5 mA cm^{-2} of Fe SAs@S/N-C and Pt/C+IrO_2.

Table S1 The intensity ratios of the D band and G band, specific surface area and elemental contents of Fe SAs@S/N-C, Fe SAs@N-C, Fe SAs@S/N-C_{PoPD} and Fe SAs@S/N-C_{PmPD}.

Sample	I_D/I_G	S_{BET} ($m^2\ g^{-1}$)	C (at.%)	N (at.%)	O (at.%)	Fe (at.%)	S (at.%)	Fe (wt%)
Fe SAs@S/N-C	1.27	775.1	77.92	10.87	8.86	0.66	1.69	5.45
Fe SAs@N-C	1.23	363.5	87.04	6.25	6.24	0.46	/	2.05
Fe SAs@S/N-C_{PoPD}	1.15	334.2	78.81	7.61	11.52	0.61	1.45	5.11
Fe SAs@S/N-C_{PmPD}	1.18	98.6	83.86	7.26	7.24	0.50	1.14	2.44

Table S2 Fitting parameters of Fe K-edge FT-EXAFS.

Catalysts	Path	CN	R (Å)	σ^2 (Å^2)	R factor
Fe SAs@S/N-C	Fe-N	4.34	1.98	0.0098	0.0028

CN is the coordination number; R is the interatomic distance (the bond length between central atoms and surrounding coordination atoms); σ^2 is the Debye-Waller factor (a measure of thermal and static disorder in absorber-scatterer distances). R factor is used to value the goodness of the fitting.

Table S3. The ORR performance comparison of Fe SAs@S/N-C and other related carbon materials in the recently published works.

Catalysts	E_{onset} (V)	$E_{1/2}$ (V)	References
Fe SAs@S/N-C	0.96	0.84	This work
Fe-BOAc-PNC	0.93	0.84	1
Co-Co_3O_4@NAC	0.93	0.79	2
S-FeNi/$NiFe_2O_4$@NC-800	/	0.84	3
Fe SAs HS	1.0	0.86	4
Ni-N_4/GHSs/Fe-N_4	0.93	0.83	5
Fe-N/C_3	0.89	0.78	6
NiFe-N-C	/	0.87	7
Co/CNT/MCP-850	0.94	0.80	8
PDA-Fe-900	0.92	0.84	9
Co@N-CNTF-2	0.91	0.81	10
FePc@CNF	0.966	0.875	11

Table S4 Comparison of the liquid-state ZABs performance of Fe SAs@S/N-C with recently reported electrocatalysts.

Catalysts	Peak power density (mW cm^{-2})	Specific capacity@10 mA cm^{-2}(mAh g^{-1})	References
Fe SAs@S/N-C	156	794	This work
FeS/Fe_3C@NS-C-900	90.9	750	12
Co/CeO_2–NCNA@CC	123	784.4	13
Fe-N-C/N-OMC	113	711	14
NiFe-N-C	153.04	818	7
Fe-NF-CNTs	144	785	15
PDA-Fe-900	163	802.1	9
Fe_1Co_3–NC-1100	372	/	16
Fe/N-G-SAC	120	/	17
FeP/Fe_2O_3@NPCA	130	717	18
HPFe-N-C	160	672	19

Table S5 Comparison of the flexible ZABs performance of Fe SAs@S/N-C with recently reported electrocatalysts.

Catalysts	Peak power density ($mW\ cm^{-2}$)	Specific capacity@5 mA cm^{-2}($mAh\ g^{-1}$)	References
Fe SAs@S/N-C	122	878	This work
HPFe-N-C	109	/	20
SSHPE-2	95.52	/	21
Fe1Co_3–NC-1100	156	/	16
KI-PVAA-GO	78.6	742	22
CCNF-PDIL	135	700	23
Fe SA/NCZ	101	/	24
FeNS/Fe_3C@CNS	176	/	25
PDA-Fe-900	116.6	800.5	9
FeP/Fe_2O_3@NPCA	40.8	676	18
Fe-BOAc-PNC	93	890	1

1 J. Zhang, Y. Chen, M. Tian, T. Yang, F. Zhang, G. Jia and X. Liu, *Chinese Chemical Letters*, 2023, **34**, 107886.

2 X. Zhong, W. Yi, Y. Qu, L. Zhang, H. Bai, Y. Zhu, J. Wan, S. Chen, M. Yang and L. Huang, *Applied Catalysis B: Environmental*, 2020, **260**, 118188.

3 H. Wang, S. Su, T. Yu, C. Meng, H. Zhou, W. Zhao, S. Yan, T. Bian and A. Yuan, *Applied Surface Science*, 2022, **596**, 153522.

4 Y. Wang, P. Meng, Z. Yang, M. Jiang, J. Yang, H. Li, J. Zhang, B. Sun and C. Fu, *Angewandte Chemie*, 2023, e202304229.

5 J. Chen, H. Li, C. Fan, Q. Meng, Y. Tang, X. Qiu, G. Fu and T. Ma, *Advanced Materials*, 2020, **32**, 2003134.

6 Q.-m. Wu, D.-k. Deng, Y.-l. He, Z.-c. Zhou, S.-b. Sang and Z.-h. Zhou, *Journal of Central South University*, 2020, **27**, 344-355.

7 H. Meng, B. Wu, D. Zhang, X. Zhu, S. Luo, Y. You, K. Chen, J. Long, J. Zhu and L. Liu, *Energy & Environmental Science*, 2024, **17**, 704-716.

8 X. Zhou, X. Liu, J. Zhang, C. Zhang, S. J. Yoo, J.-G. Kim, X. Chu, C. Song, P. Wang, Z. Zhao, D. Li, W. Zhang and W. Zheng, *Carbon*, 2020, **166**, 284-290.

9 F. Zhang, X. Liu, Y. Chen, M. Tian, T. Yang, J. Zhang and S. Gao, *Chinese Chemical Letters*, 2023,

108142.

10 H. Guo, Q. Feng, J. Zhu, J. Xu, Q. Li, S. Liu, K. Xu, C. Zhang and T. Liu, *Journal of Materials Chemistry A*, 2019, **7**, 3664-3672.

11 Y. Wu, J. Liu, Q. Sun, J. Chen, X. Zhu, R. Abazari and J. Qian, *Chemical Engineering Journal*, 2024, 149243.

12 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, *ACS Applied Materials & Interfaces*, 2020, **12**, 44710-44719.

13 S. Li, H. Zhang, L. Wu, H. Zhao, L. Li, C. Sun and B. An, *Journal of Materials Chemistry A*, 2022, **10**, 9858-9868.

14 J. Han, H. Bao, J.-Q. Wang, L. Zheng, S. Sun, Z. L. Wang and C. Sun, *Applied Catalysis B: Environmental*, 2021, **280**, 119411.

15 Y. Liu, X. Liu, C. Zhang, Y. Chen, Z. Wang, G. Wei, J. Zhang, T. Yang, F. Zhang and S. Gao, *Journal of Alloys and Compounds*, 2023, **941**, 168922.

16 Y. He, X. Yang, Y. Li, L. Liu, S. Guo, C. Shu, F. Liu, Y. Liu, Q. Tan and G. Wu, *Acs Catalysis*, 2022, **12**, 1216-1227.

17 M. Xiao, Z. Xing, Z. Jin, C. Liu, J. Ge, J. Zhu, Y. Wang, X. Zhao and Z. Chen, *Advanced Materials*, 2020, **32**, 2004900.

18 K. Wu, L. Zhang, Y. Yuan, L. Zhong, Z. Chen, X. Chi, H. Lu, Z. Chen, R. Zou and T. Li, *Advanced Materials*, 2020, **32**, 2002292.

19 H. Xu, D. Wang, P. Yang, L. Du, X. Lu, R. Li, L. Liu, J. Zhang and M. An, *Applied Catalysis B: Environmental*, 2022, **305**, 121040.

20 H. Xu, D. Wang, P. Yang, L. Du, X. Lu, R. Li, L. Liu, J. Zhang and M. An, *Appl. Catal. B-Environ.*, 2022, **305**, 121040.

21 X. Fan, R. Zhang, S. Sui, X. Liu, J. Liu, C. Shi, N. Zhao, C. Zhong and W. Hu, *Angewandte Chemie International Edition*, 2023, **62**, e202302640.

22 Z. Song, J. Ding, B. Liu, X. Liu, X. Han, Y. Deng, W. Hu and C. Zhong, *Adv. Mater.*, 2020, **32**, 1908127.

23 M. Xu, H. Dou, Z. Zhang, Y. Zheng, B. Ren, Q. Ma, G. Wen, D. Luo, A. Yu and L. Zhang, *Angew. Chem. Int. Edit.*, 2022, e202117703.

24 C. Jiao, Z. Xu, J. Shao, Y. Xia, J. Tseng, G. Ren, N. Zhang, P. Liu, C. Liu and G. Li, *Advanced*

Functional Materials, 2023, 2213897.

25 Y. Wang, T. Yang, X. Fan, Z. Bao, A. Tayal, H. Tan, M. Shi, Z. Liang, W. Zhang and H. Lin, *Angewandte Chemie International Edition*, 2024, **63**, e202313034.