Supporting Information

Atomic Level Design of Single Iron Atom Embedded Mesoporous Hollow Carbon Spheres as Multi-effect Nanoreactors for Advanced Lithium-Sulfur Batteries

Qinjun Shao, Lei Xu, Decai Guo, Yan Su and Jian Chen**

[a] Advanced Rechargeable Battery Laboratory, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

[c] Key Laboratory of Materials Modification by Laser, Ion and Electron Beams (Ministry of Education), Dalian University of Technology, Dalian, 116024, China.

* Corresponding author. Email address: chenjian@dicp.ac.cn;

Email address: su.yan@dlut.edu.cn.

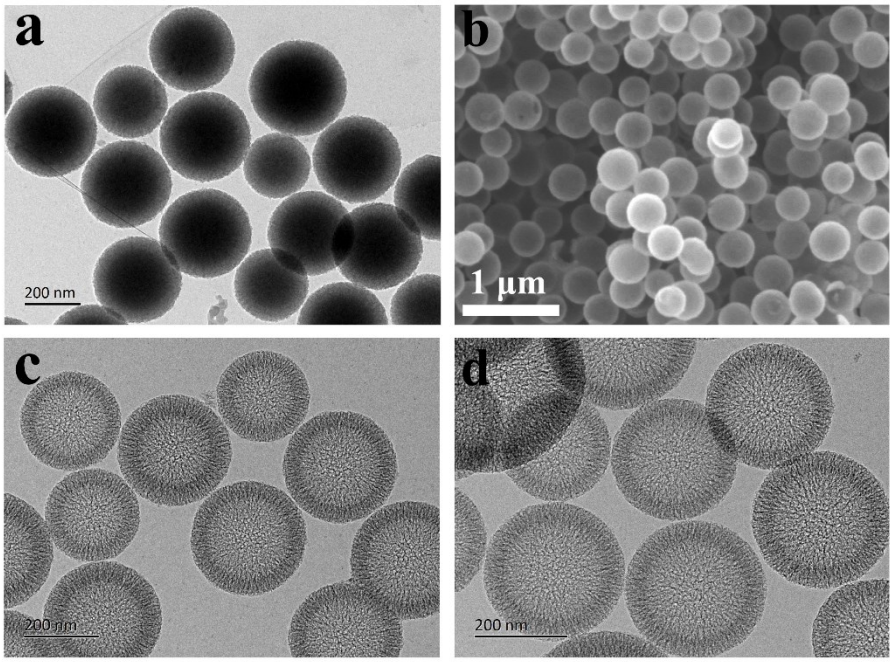

Figure S1. (a) TEM image of the SiO_2@C spheres; (b) SEM and (c) TEM images of MHCS. (d) TEM image of N/MHCS.

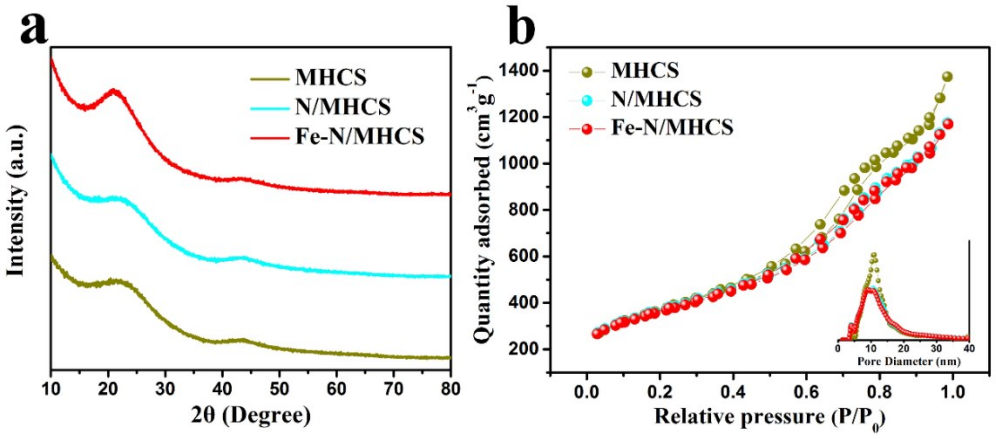

Figure S2. (a) XRD patterns and (b) N_2 adsorption-desorption isotherms of MHCS, N/MHCS and Fe-N/MHCS.

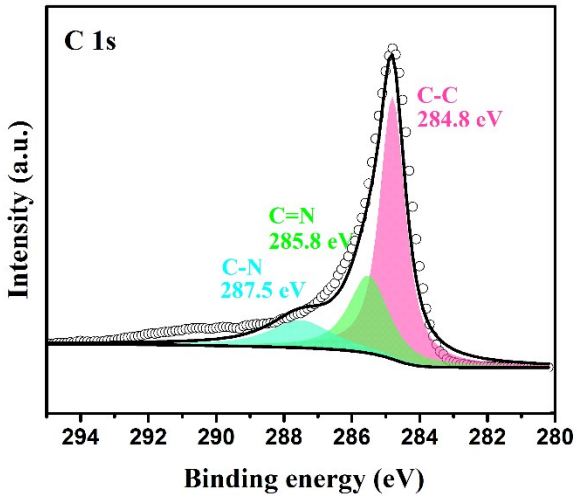

Figure S3. C 1s XPS spectrum of Fe-N/MHCS.

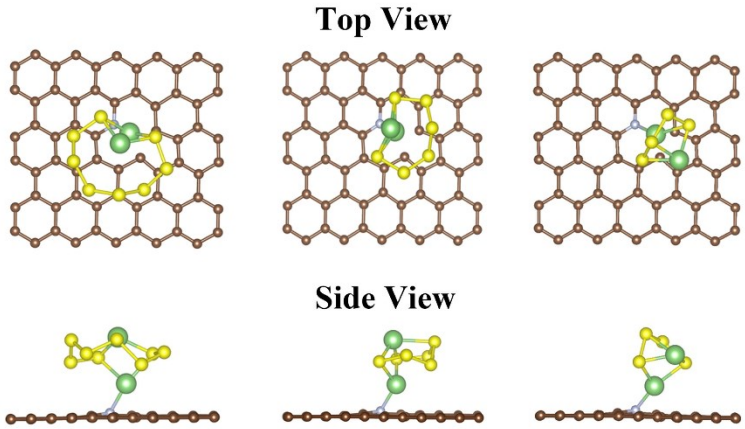

Figure S4. The strongest adsorption energy configurations of polysulfides on N-C substrate.

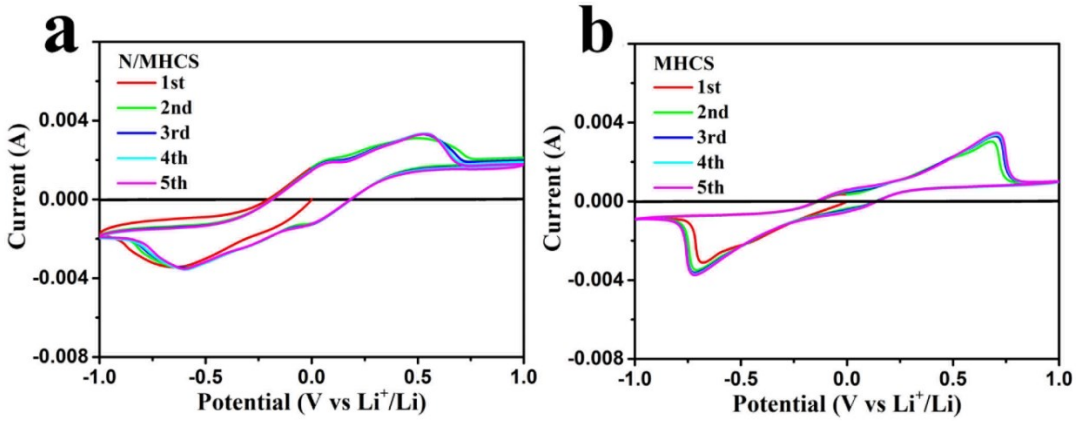

Figure S5. CV curves of (a) N/MHCS and (b) MHCS symmetric cells in 0.5 mol L^{-1} Li_2S_6 electrolyte at 1 mV s^{-1}.

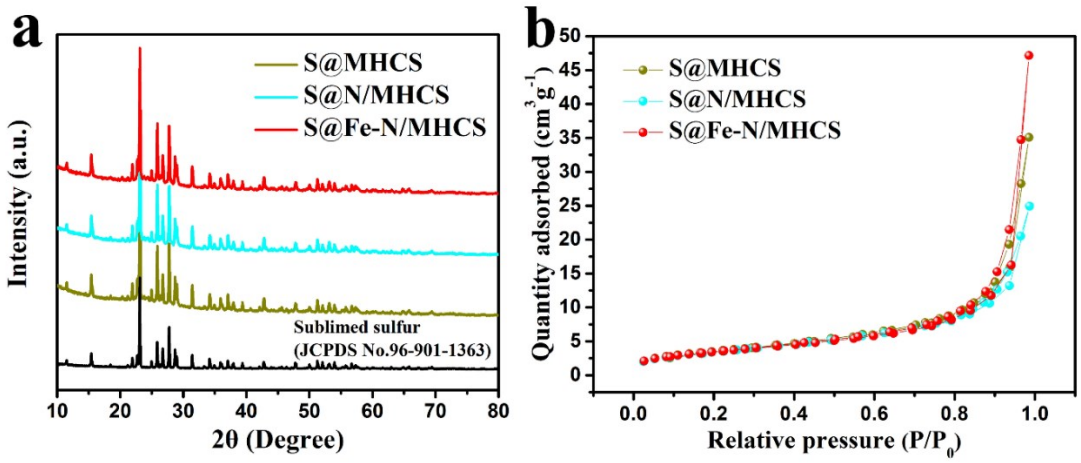

Figure S6. (a) XRD patterns and (b) N_2 adsorption-desorption isotherms of S@MHCS, S@N/MHCS and S@Fe-N/MHCS.

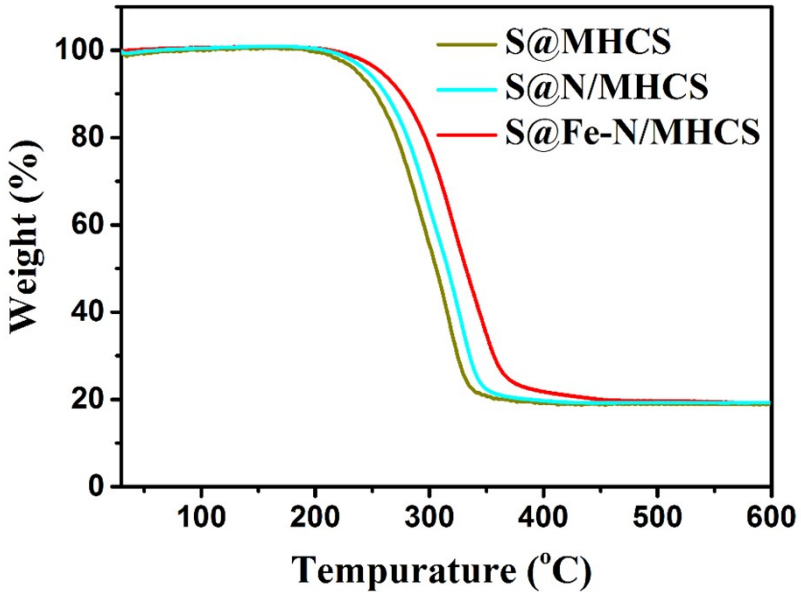

Figure S7. TGA curves of S@MHCS, S@N/MHCS and S@Fe-N/MHCS in Ar atmosphere.

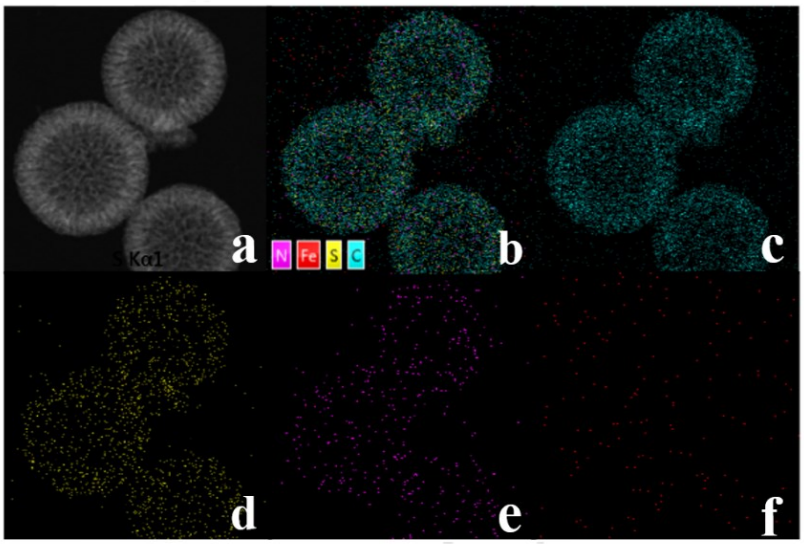

Figure. S8 (a) STEM image of S@Fe-N/MHCS. (b) EDX elemental mapping of (c) carbon (blue), (d) sulfur (yellow), (e) nitrogen (purple) and (f) iron (red).

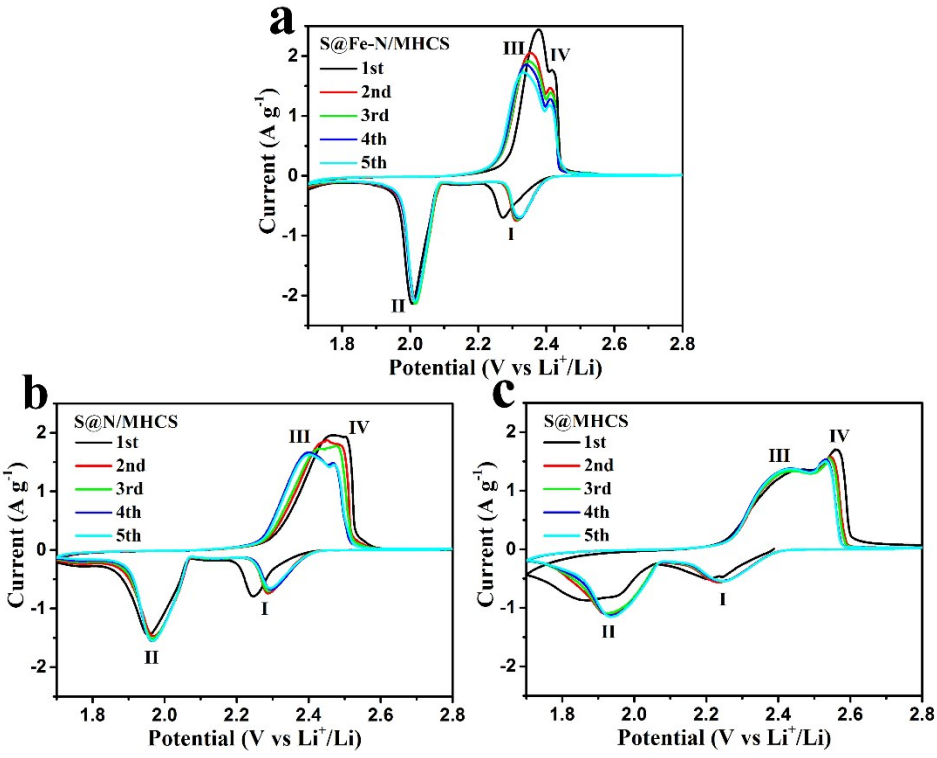

Figure. S9 CV curves of (a) S@Fe-N/MHCS (b)S@N/MHCS and (c) S@MHCS cells at 0.1 mV s^{-1}.

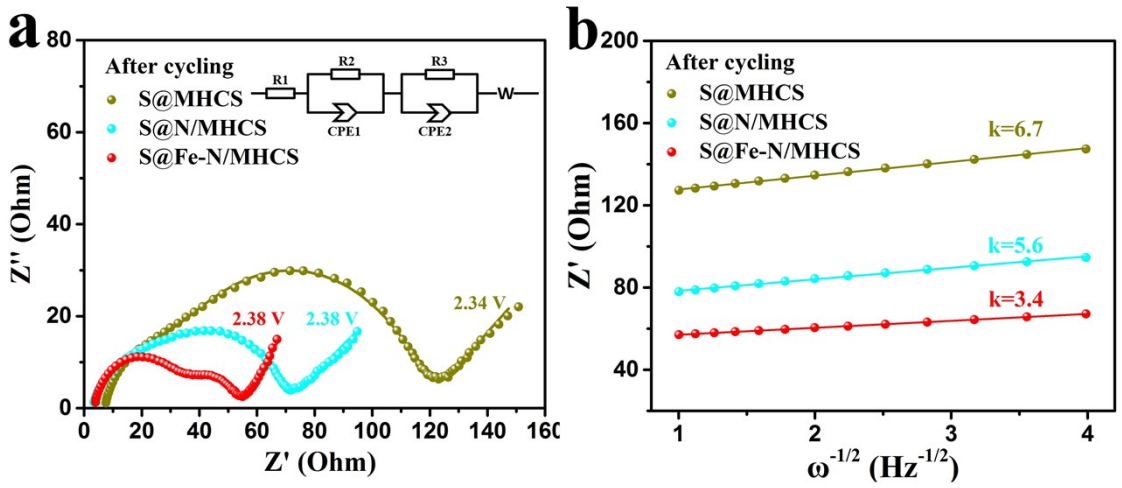

Figure. S10 (a) EIS curves and (b) the relationship between Z' and $\omega^{-1/2}$ of the three cells with frequency range between 1 and 0.01 Hz after cycling (symbols, real data; lines, fitting curves).

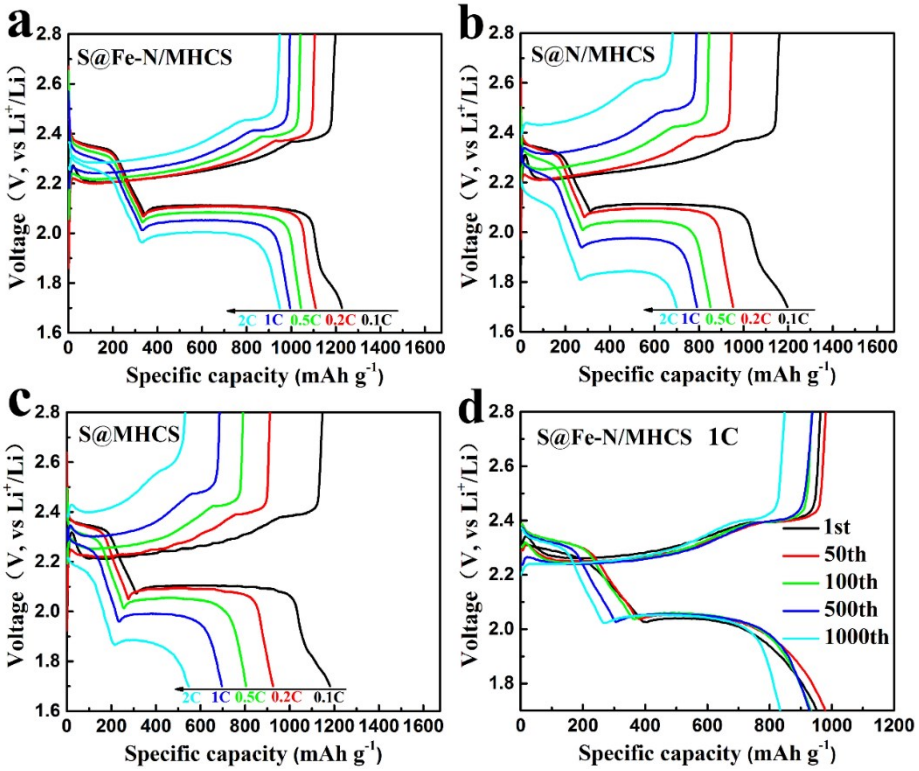

Figure. S11 The charge-discharge profiles of (a) S@Fe-N/MHCS (b) S@N/MHCS and (c) S@MHCS cells at different rate. (d) the charge-discharge profiles of S@Fe-N/MHCS cell at 1 C rate.

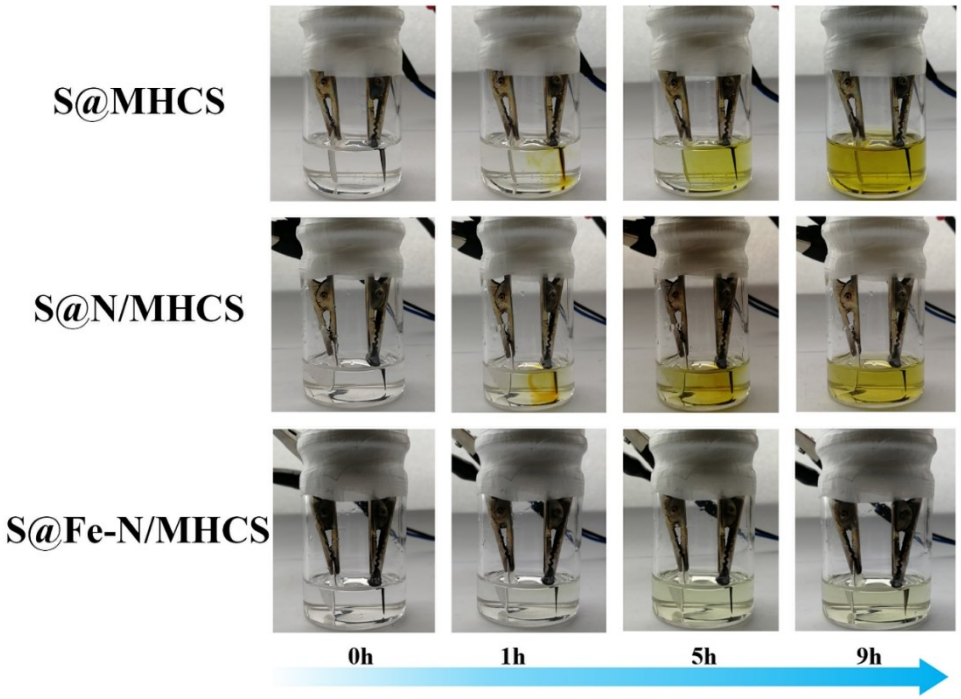

Figure S12. Optical photographs of the visible Li-S electrochemical cells using S@MHCS, S@N/MHCS and S@Fe-N/MHCS as cathodes throughout galvanostatic discharge at 0.1 C for 0, 1, 5 and 9 hours.

Table S1

The fitted Mössbauer parameters and the corresponding assignment to Fe-N/MHCS

Components	δ_{iso}/mm s^{-1}	ΔE_Q/mm s^{-1}	LW/mm s^{-1}	Area/%	Assignment
D1	0.30560	1.04509	0.60406	43.73	$Fe^{II}N_4$-C, low spin
D2	0.59299	2.79304	1.10873	36.13	$Fe^{II}N_{2+2}$-C, medium spin
D3	0.51069	1.40928	0.58209	20.14	N-$Fe^{II}N_{2+2}$-C, high spin

Table S2. EIS fitting results of S@MHCS, S@N/MHCS and S@Fe-N/MHCS cells before/after cycling

Elements	before cycling			after cycling		
	S@MHCS	S@N/MHCS	S@Fe-N/MHCS	S@MHCS	S@N/MHCS	S@Fe-N/MHCS
R_e / Ohm	1.8	3.1	1.8	7.0	2.8	3.4
R_{SEI} / Ohm	10.6	4.7	5.9	18.5	15.4	24.8
R_{ct} / Ohm	**95.8**	**80.2**	**61.0**	**93.2**	**50.4**	**26.4**
D_{Li^+}/cm^2 s^{-1}	**1.5×10^{-10}**	**2.2×10^{-10}**	**3.9×10^{-10}**	**1.3×10^{-9}**	**1.8×10^{-9}**	**5.0×10^{-9}**

The ion diffusion coefficient can be calculated based on the following equation:

$$D = 0.5(RT/An^2F^2C\sigma)^2 \quad (1)$$

(D: diffusion coefficient, $cm^2 \cdot s^{-1}$; R: gas constant, J mol^{-1} K^{-1}; T: absolute temperature, K; A: surface area of the anode, cm^2; n: the charge number of Li^+; F: Faraday constant, C mol^{-1}; C: the concentration of Li^+, mol L^{-1}; σ: the Warburg factor.)

The slope of the lines in Fig. 5d corresponding to the values of σ which can be obtained according to the following equation:

$$Z_{re} = R_e + R_{SEI} + R_{ct} + \sigma\omega^{-1/2} \quad (2)$$

Table S3. Comparison of the cycling performance of previously reported single atom embedded sulfur cathodes in coin cell with similar E/S ratio.

Electrodes	S loading (mg cm^{-2})	Rate (C)	Cycles	Capacity (mAh g^{-1})	Capacity decay (%)	Ref.
S/Co-N-C	1.0	0.5	300	850	0.10	1
S@Co-N/G	2.0	1	500	681	0.053	2
SC-Co	1.2	0.5	300	837	0.086	3
CoSA-N-C@S	1.2	1	1000	675	0.035	4
S@Co-SAs@NC	2.0	1	600	737	0.067	5
Fe-PNC/S	1.3	0.5	300	557	0.2	6
FeSA-CN/S	1.4	4	500	403	0.06	7
Li_2S@NC-SAFe	1.5	2	1000	490	0.04	8
Fe/Co-N@C/S	1.5	2	1000	565	0.029	9
S-SAV@NG	2	0.5	400	551	0.073	10
S@SA-Zn-MXene	~	1	400	706	0.03	11
S@Fe-N/MHCS	**1.5**	**1**	**1000**	**834**	**0.0187**	**This work**

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