

Supplementary information

Sulfur-doped Silicon Oxycarbide by Facile Pyrolysis Process as an Outstanding Stable Performance Lithium-Ion Battery Anode

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- Fig. S1** N_2 adsorption/desorption isotherms of (a) SiOC and (b) S-SiOC. (BET surface area of SiOC, S-SiOC is $0.257 \text{ m}^2 \text{ g}^{-1}$, $2.033 \text{ m}^2 \text{ g}^{-1}$ respectively.) (c) BJH pore size distribution for the SiOC and S-SiOC.
- Fig. S2** Morphology and microstructure of SiOC.
- Fig. S3** Quantitative analysis spectra and atomic percentage of (a) SiOC and (b) S-SiOC corresponding from EDS analysis (inset).
- Fig. S4** XRD patterns of SiOC and S-SiOC.
- Fig. S5** High resolution XPS spectra of (a) C 1s, (b) O 1s, (c) Si 2p and (d) S 2p in SiOC.
- Fig. S6** XPS spectra of (a) F 1s, (b) O 1s, and (c) C 1s in SiOC and S-SiOC anode after initial cycle.
- Fig. S7** Voltage profile of (a) SiOC and (b) S-SiOC during GITT analysis. (c) Demonstration of a single titration with ΔE_v , ΔE_s parameters. (d) Relationship between the voltage and square root of the pulse time at a single current pulse during GITT analysis of both electrodes.
- Fig. S8** Cycle performance and coulombic efficiency of S-SiOC electrode at 1 A g^{-1} for 2000 cycles (0.7 mg cm^{-2} of loading mass).
- Fig. S9** SEM images of S-SiOC (a) before and (b) after cycling test. (c) TEM image of S-SiOC after cycling test.
- Table S1** EIS fitting results of SiOC and S-SiOC electrodes.
- Table S2** Comparison of electrochemical performances between the S-SiOC electrode and other reported SiOC-based electrodes.

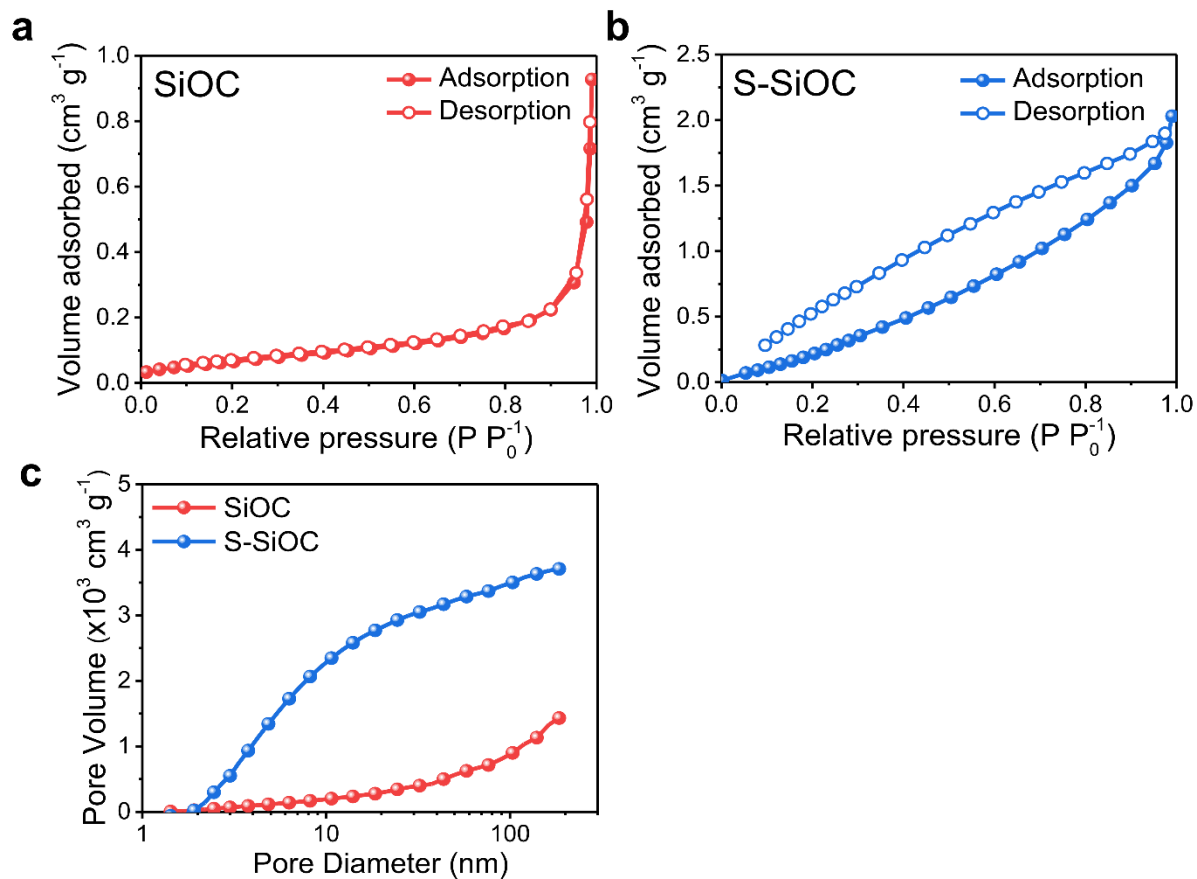


Fig. S1. N₂ adsorption/desorption isotherms of (a) SiOC and (b) S-SiOC. (BET surface area of SiOC, S-SiOC is 0.257 m² g⁻¹, 2.033 m² g⁻¹ respectively.) (c) BJH pore size distribution for the SiOC and S-SiOC.

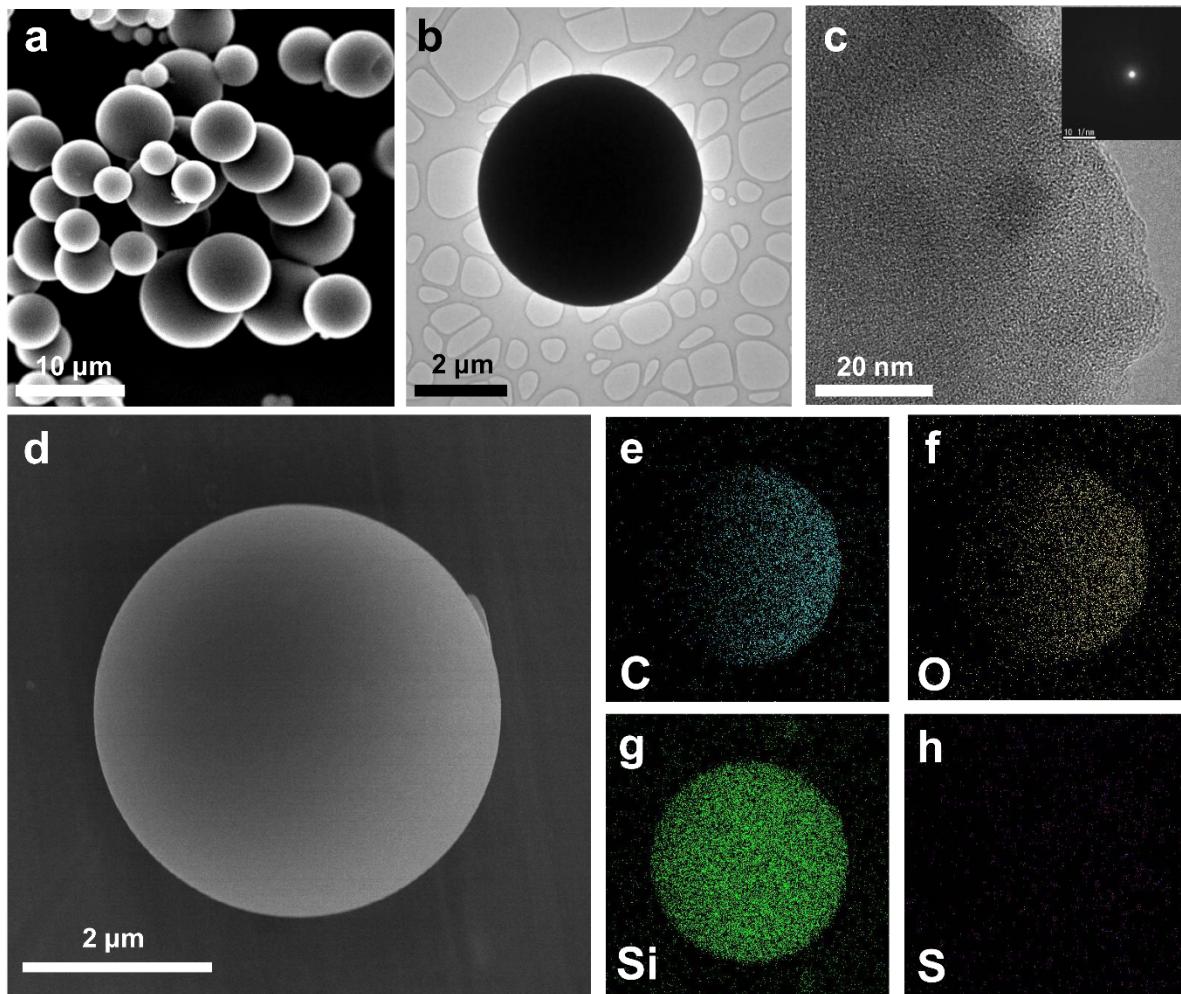


Fig. S2. Morphology and microstructure of SiOC. (a) SEM image of SiOC; (b) TEM and (c) HRTEM images of SiOC (SAED pattern inset); (e) Carbon, (f) oxygen, (g) silicon, (h) sulfur elemental mappings of SiOC corresponding (d).

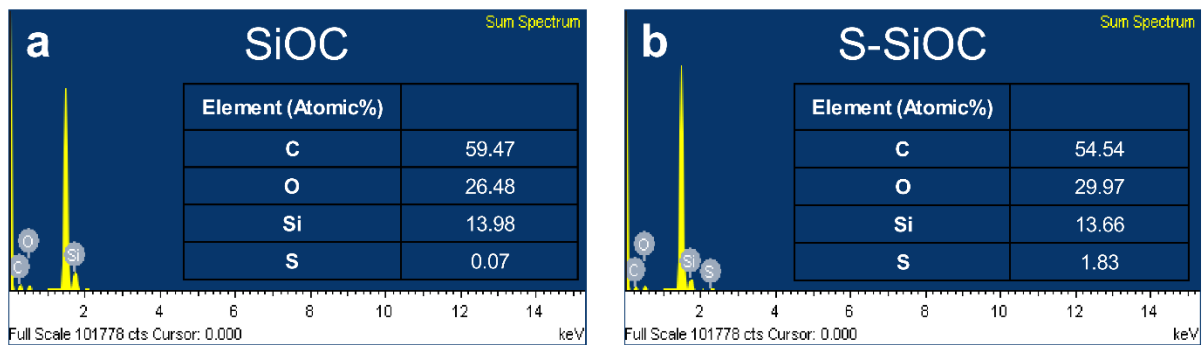


Fig. S3. Quantitative analysis spectra and atomic percentage of (a) SiOC and (b) S-SiOC corresponding from EDS analysis (inset).

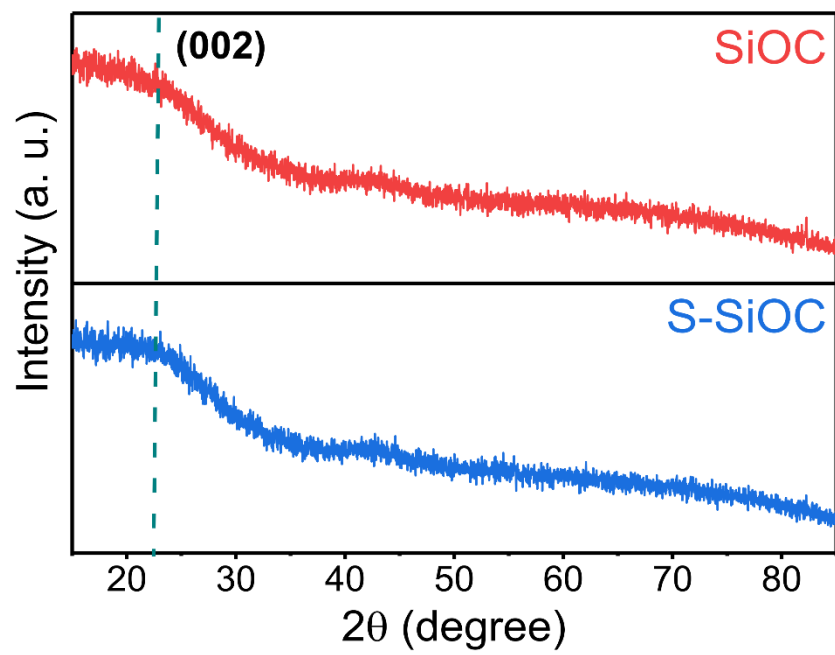


Fig. S4. XRD patterns of SiOC and S-SiOC.

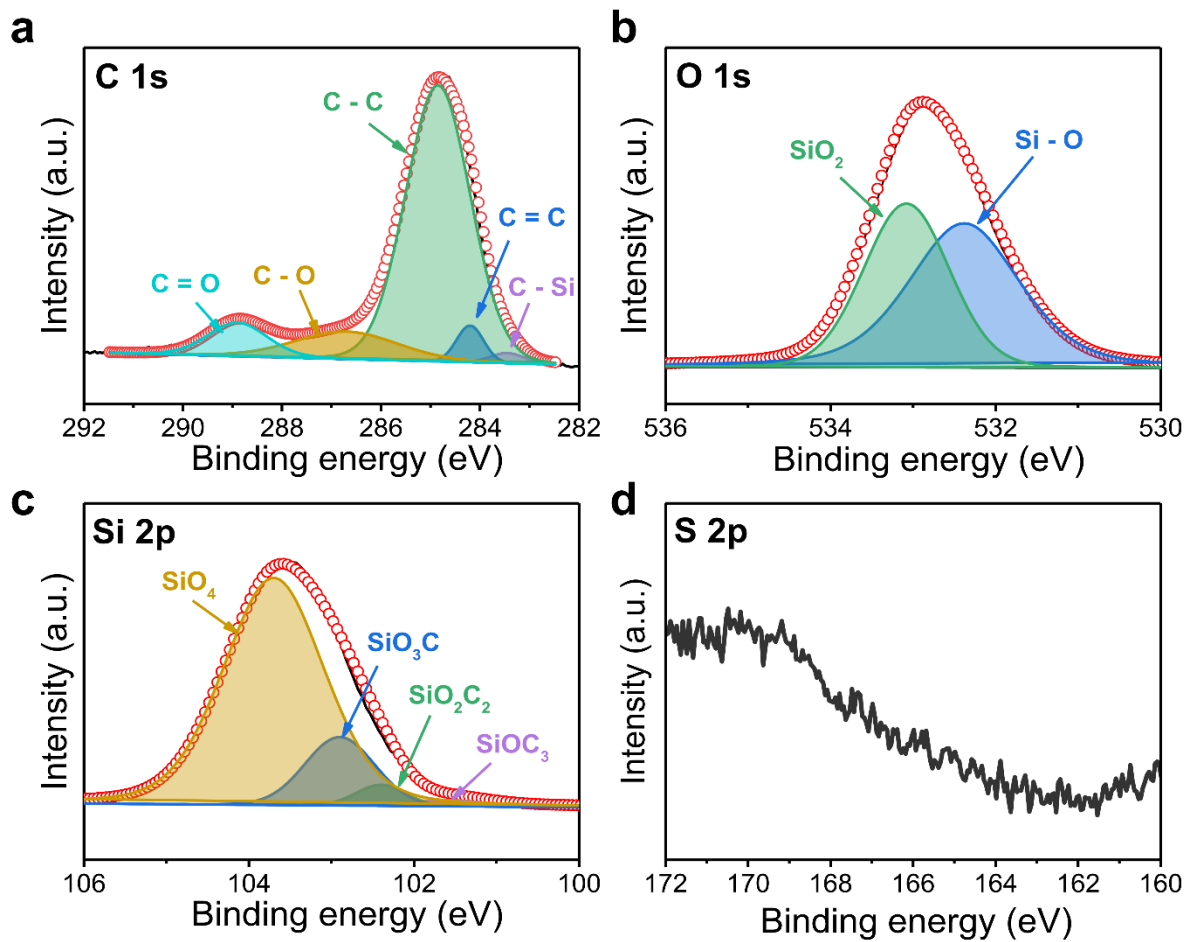


Fig. S5. High resolution XPS spectra of (a) C 1s, (b) O 1s, (c) Si 2p and (d) S 2p in SiOC.

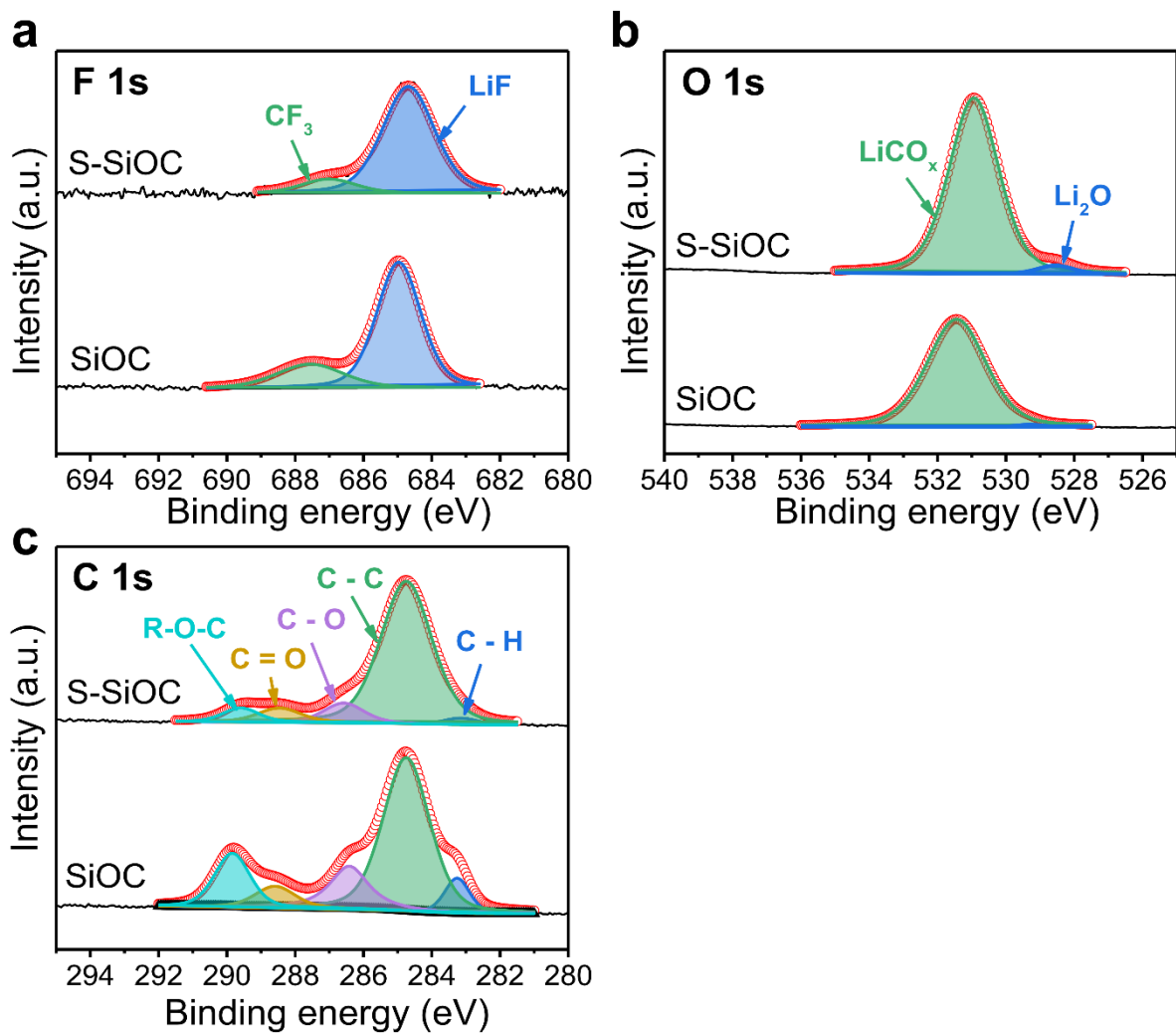


Fig. S6. XPS spectra of (a) F 1s, (b) O 1s, and (c) C 1s in SiOC and S-SiOC anode after initial cycle.

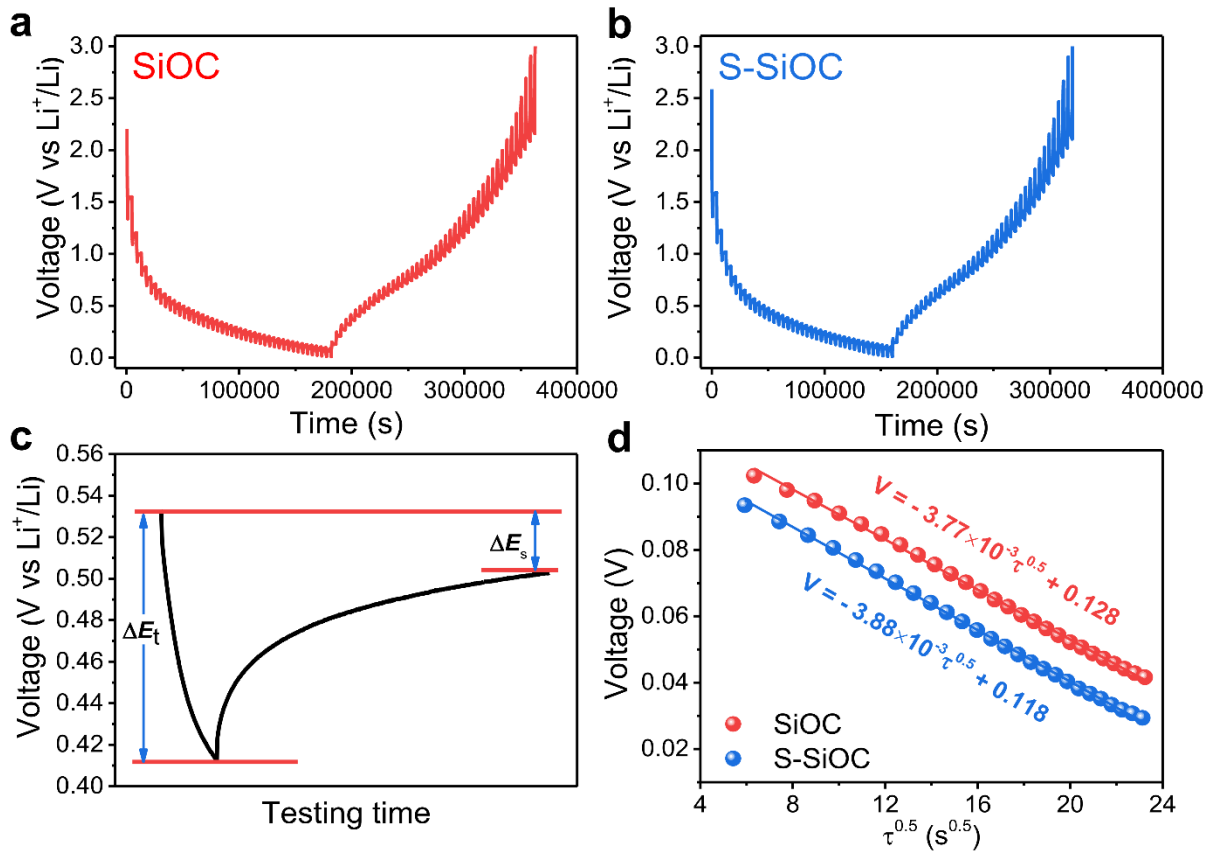


Fig. S7. Voltage profile of (a) SiOC and (b) S-SiOC during GITT analysis. (c) Demonstration of a single titration with ΔE_t , ΔE_s parameters. (d) Relationship between the voltage and square root of the pulse time at a single current pulse during GITT analysis of both electrodes.

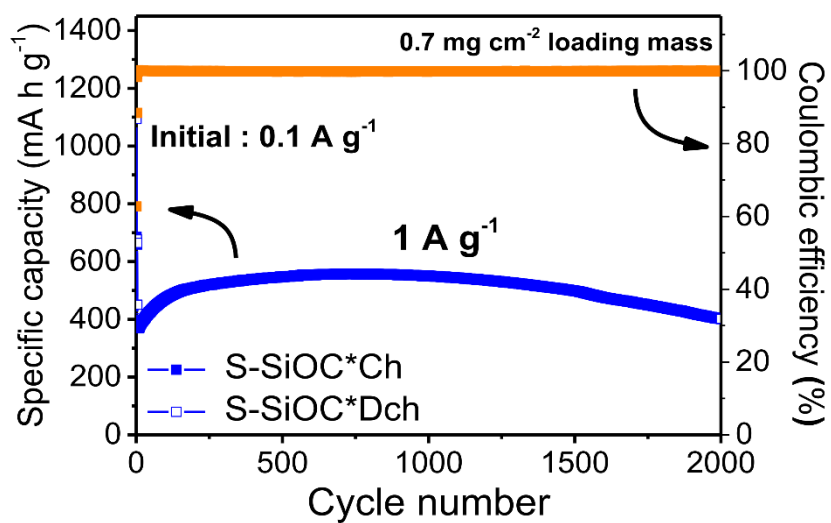


Fig. S8. Cycle performance and coulombic efficiency of S-SiOC electrode at 1 A g^{-1} for 2000 cycles (0.7 mg cm^{-2} of loading mass).

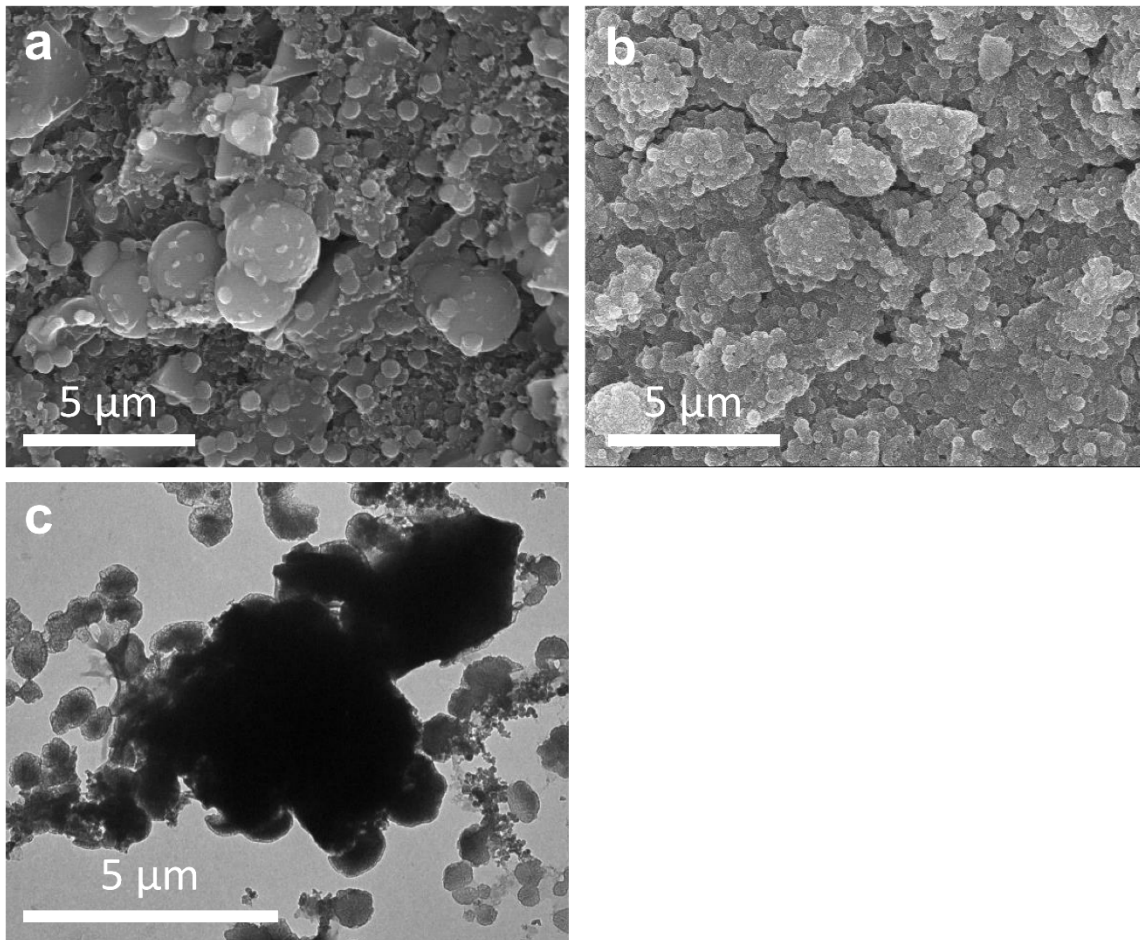


Fig. S9. SEM images of S-SiOC (a) before and (b) after cycling test. (c) TEM image of S-SiOC after cycling test.

Table S1. EIS fitting results of SiOC and S-SiOC electrodes.

Parameter	SiOC	S-SiOC
R_s/Ω	4.69	4.57
R_{SEI}/Ω	12.8	12.2
R_{ct}/Ω	87.2	43.0
$W-R/\Omega$	0.00158	0.00461

Table S2. Comparison of electrochemical performances between the S-SiOC electrode and other reported SiOC-based electrodes.

Anode	Synthesis method	Initial specific capacity (mAh g ⁻¹)	Initial Coulombic efficiency (%)	Cycle property	Ref.
S-SiOC	Facile one-pot pyrolysis (800°C for 5 hours)	1146 mAh g ⁻¹ at 0.1 A g ⁻¹	69.9	89.2% retention after 2000 cycles at 1 A g ⁻¹	This work
Onion-like pre-SiOC/C spheres	One-step injection pyrolysis (900°C for 30 min)	839.3 mAh g ⁻¹ at 0.1 A g ⁻¹	78.4	82% retention after 500 cycles at 2 A g ⁻¹	[1]
Divinylbenzene and polymethylsilsesquioxane coordinated SiOC (S-DVB-1)	One-step pyrolysis (1200°C for 1 hour)	1273.5 mAh g ⁻¹ at 0.1 A g ⁻¹	64.38	Remaining capacity to 476 mAh g ⁻¹ after 500 cycles at 0.5 A g ⁻¹	[2]
Rambutan-like vertical graphene coated hollow porous SiOC (Hp-SiOC@VG)	Hydrothermal (180°C for 12 hours) + pyrolysis (1000°C for 2 hours)	729 mAh g ⁻¹ at 0.1 A g ⁻¹	75	98% retention after 600 cycles at 1 A g ⁻¹	[3]
Intercalated SiOC/graphene composites	Pyrolysis (800°C for 4 hours)	965 mAh g ⁻¹ at 0.05 A g ⁻¹	63	60% retention after 90 cycles	[4]
Nearly kilogram-scale preparation of SiOC composites	CVD method (1000°C)	988 mAh g ⁻¹ at 0.1 A g ⁻¹	70	88% retention after 2000 cycles at 1	[5]

Amorphous polymer-derived SiOC (NGA-SiOC25)	Pyrolysis (900°C for 1 hour)	1116 mAh g ⁻¹ at 0.037 A g ⁻¹	67.3	A g ⁻¹ 95% retention after 1000 cycles at 1.48 A g ⁻¹	[6]
A SiOC bead mixture of vinyltrimethoxysilane with phenyltrimethoxysilane (Vi-Ph-SiOC)	MicroJet reactor technique + pyrolysis (1100°C for 3 hours)	922 mAh g ⁻¹ at 0.035 A g ⁻¹	76.8	83% retention after 100 cycles at 0.07 A g ⁻¹	[7]

References

- [1] X. Lin, Y. Dong, X. Liu, X. Chen, A. Li, H. Song, In-situ pre-lithiated onion-like SiOC/C anode materials based on metallasilsesquioxanes for Li-ion batteries, *Chem. Eng. J.*, 428 (2022) 132125.
- [2] P. Wu, X. Guo, Z. Su, C. Liu, S. Chen, Z. Zheng, A. Liu, Preparation of silicon oxycarbide (SiOC) anodes for high performance Li-ion batteries using competitive relationship between crosslinking and polymeriz
- [3] K. Li, G. Yuan, X. Liu, Y. Guo, R. Huang, H. Li, H. Zhang, Q. Jia, Z. Xie, S. Zhang, W. Lei, On the practical applicability of rambutan-like SiOC anode with Enhanced reaction kinetics for lithium-ion storage, *Adv. Funct. Mater.*, 33 (2023) 2302348.
- [4] Y. Ren, B. Yang, X. Huang, F. Chu, J. Qiu, J. Ding, Intercalated SiOC/graphene composites as anode material for Li-ion batteries, *Solid State Ion.*, 278 (2015) 198-202.
- [5] S. Fan, J. Zhang, S. Cui, L. Chen, X. Chen, J. Rang, W. Wang, Y. Liu, J.-T. Zhao, Large-

scale synthesis of SiOC composites for stable Li-ion battery anode and denrite-free Li metal deposition, *Chem. Eng. J.*, 479 (2024) 147785.

- [6] G. Shao, D.A.H. Hanaor, J. Wang, D. Kober, S. Li, X. Wang, X. Shen, M.F. Bekheet, A. Gurlo, Polymer-derived SiOC integrated with a graphene aerogel as a highly stable Li-ion battery anode, *ACS Appl. Mater. Interfaces*, 12 (2020) 46045-46056.
- [7] B. Krüner, C. Odenwald, N. Jäckel, A. Tolosa, G. Kickelbick, V. Presser, Silicon oxycarbide beads from continuously produced polysilsesquioxane as stable anode material for lithium-ion batteries, *ACS Appl. Energy Mater.* 1 (2018) 2961-2970.