

Supplementary Information

Stress-Adaptive Conductive Network and Ion-Segregated Polymeric-Inorganic Interphases Enable Durable Room-Temperature Silicon-Based Solid-State Batteries

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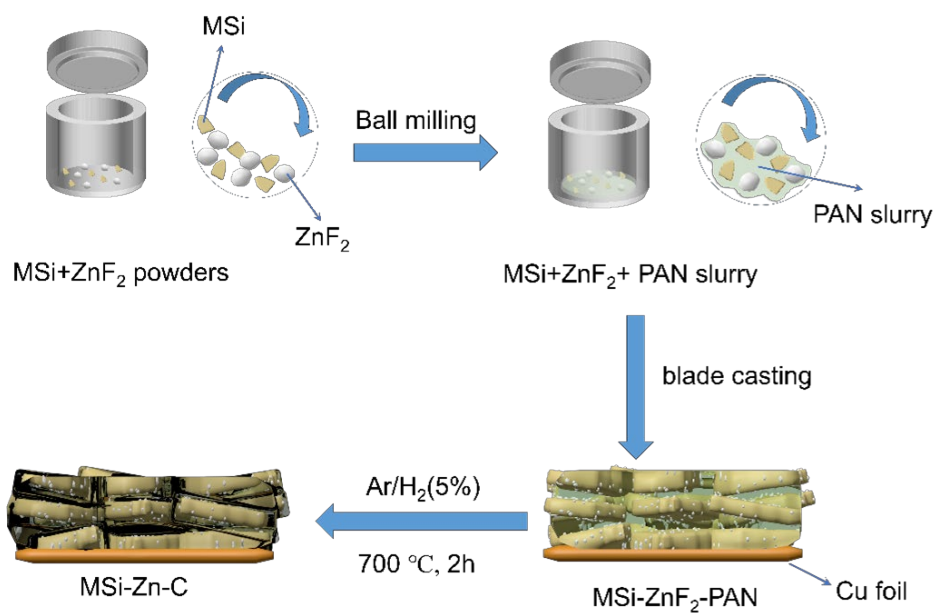


Figure S1. Fabrication process of free-standing and monolithic MSi-Zn-C negative electrode. The Zn nanoparticles decorated embedded in the continuous a-C network is expected to enhance electronic conductivity.

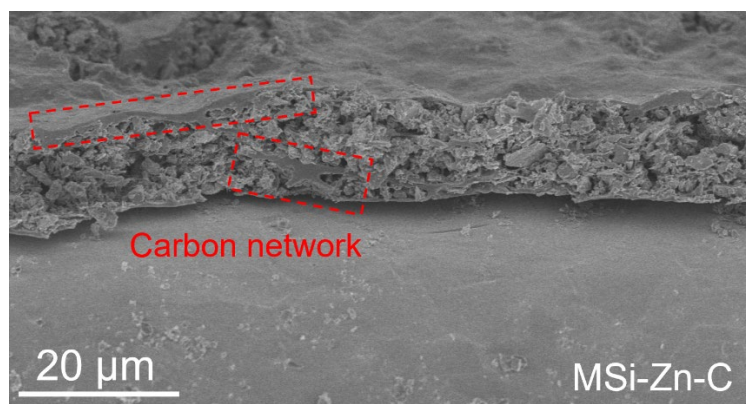


Figure S2. Cross-sectional SEM image of MSi-Zn-C negative electrode, revealing the uniform carbon coating and the interconnected carbon network.

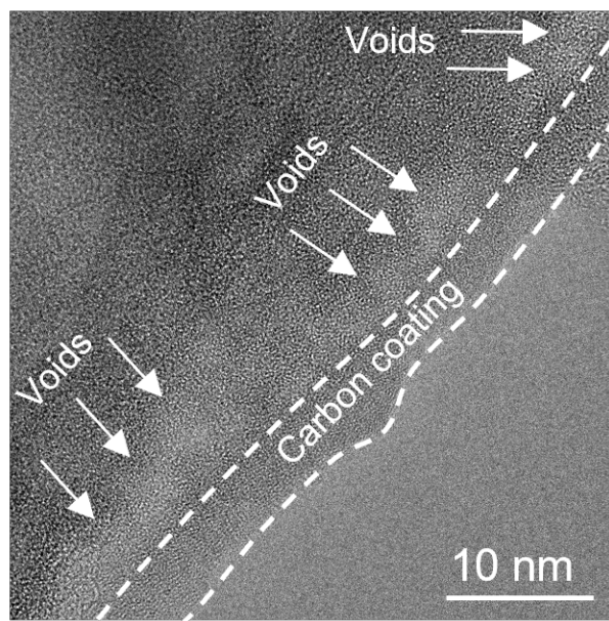


Figure S3. High-resolution TEM image of MSi-Zn-C particle, revealing the formed voids and weak bonded nature.

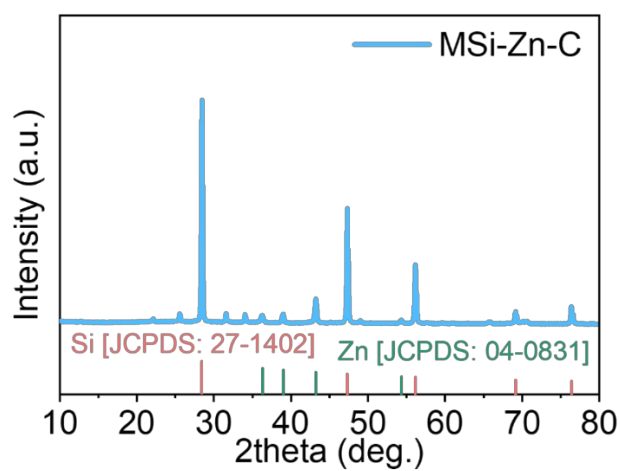


Figure S4. X-ray diffraction patterns of MSi-Zn-C electrode, indicating the decomposition of ZnF_2 and formation of metallic Zn.

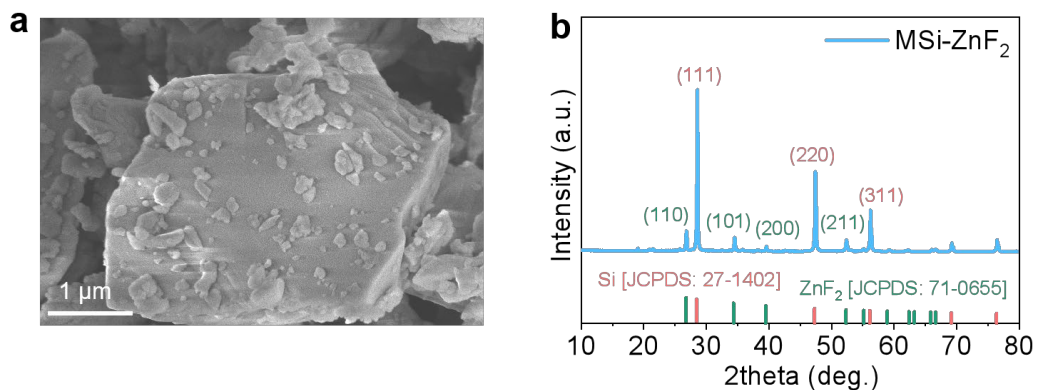


Figure S5. (a) SEM image of MSi-ZnF₂ powder. (b) XRD pattern of MSi-ZnF₂ powder.

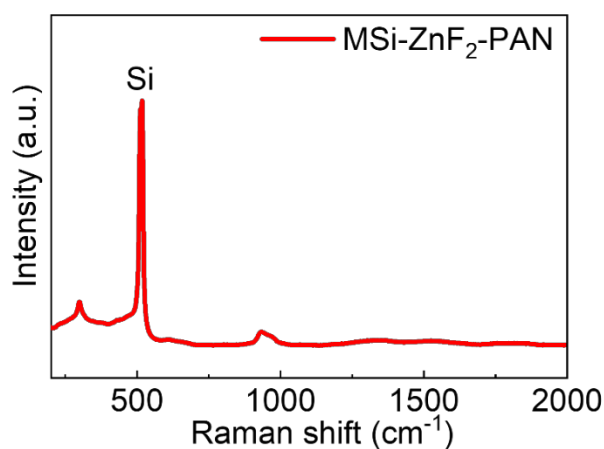


Figure S6. Raman spectrum of MSi-ZnF₂-PAN electrode before carbonization.

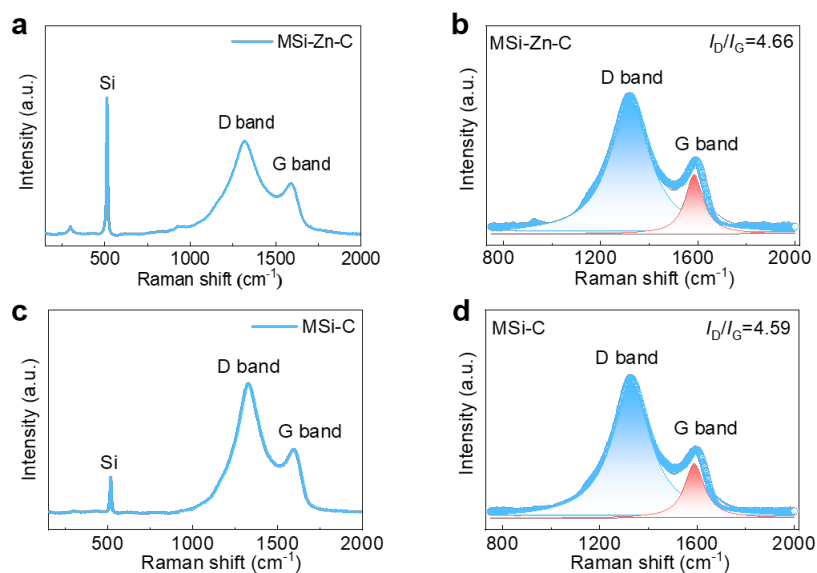


Figure S7. (a) Raman spectra of MSi-Zn-C and (b) its fitting curve of D and G bands. (c) Raman spectra of MSi-C and (d) its fitting curve of D and G bands, confirming the same quality of the coated carbon layer.

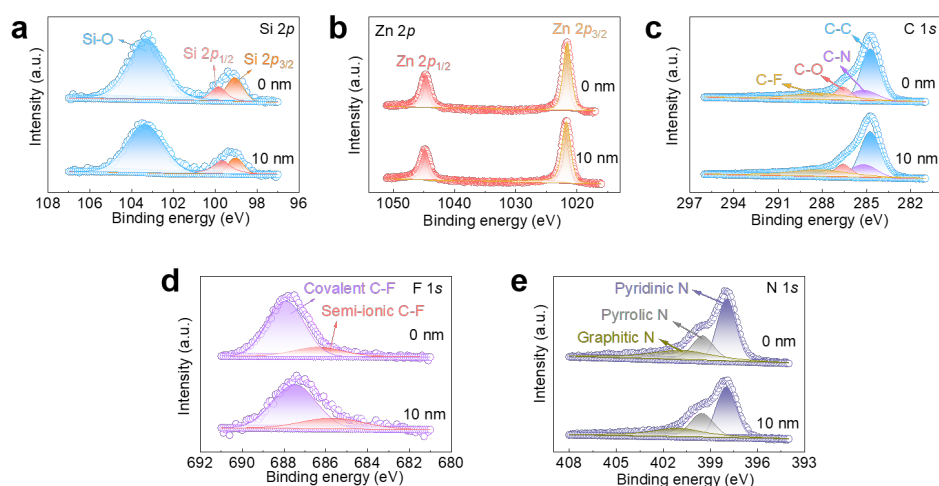


Figure S8. High resolution XPS spectra: (a) Si 2p, (b) Zn 2p, (c) C 1s, (d) N 1s and (e) F 1s.

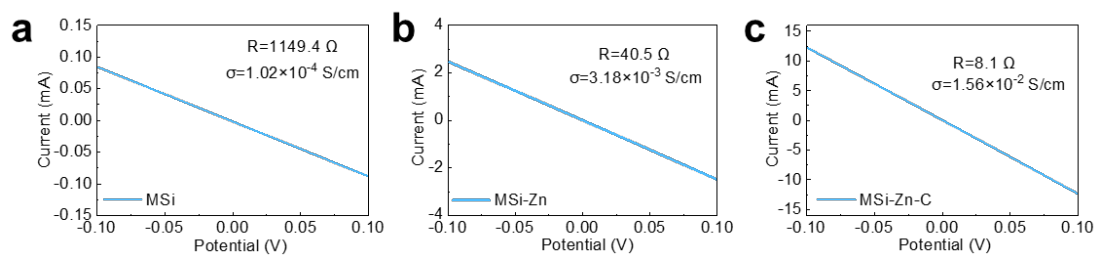


Figure S9. I-V curve test of the (a) MSi, (b) MSi-Zn, and (c) MSi-Zn-C composites, revealing that Zn enhanced the conductivity of Si.

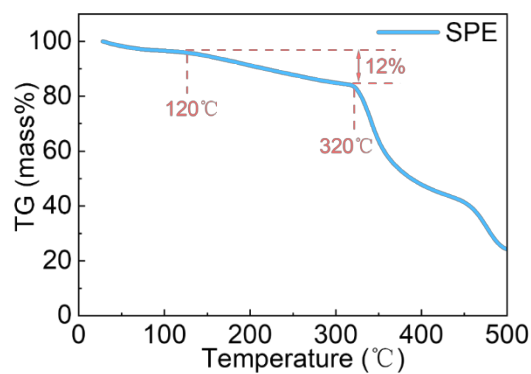


Figure S10. Thermogravimetric analysis (TGA) curves of the SPE, implying 12% residual solvents in the SPE.

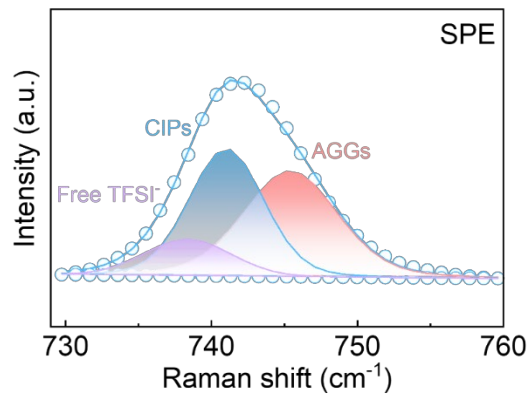


Figure S11. The Raman spectra of the SPE.

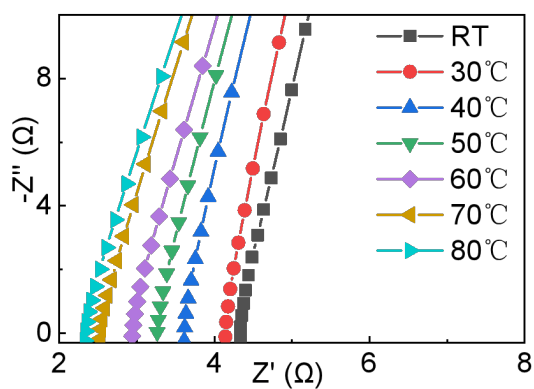


Figure S12. Nyquist plots of SS|SPE|SS cell in a temperature range from room temperature to 80 °C.

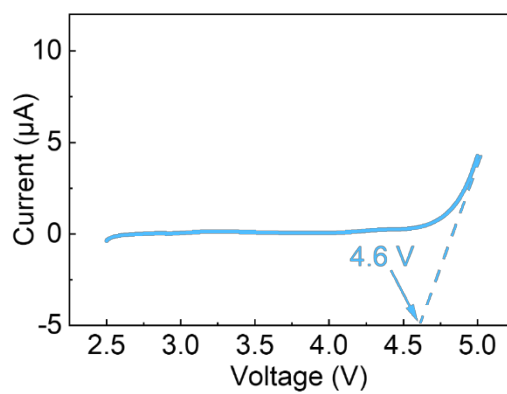


Figure S13. LSV curve of Li|SPE|SS cell, revealing the high antioxygenation voltage of 4.6 V.

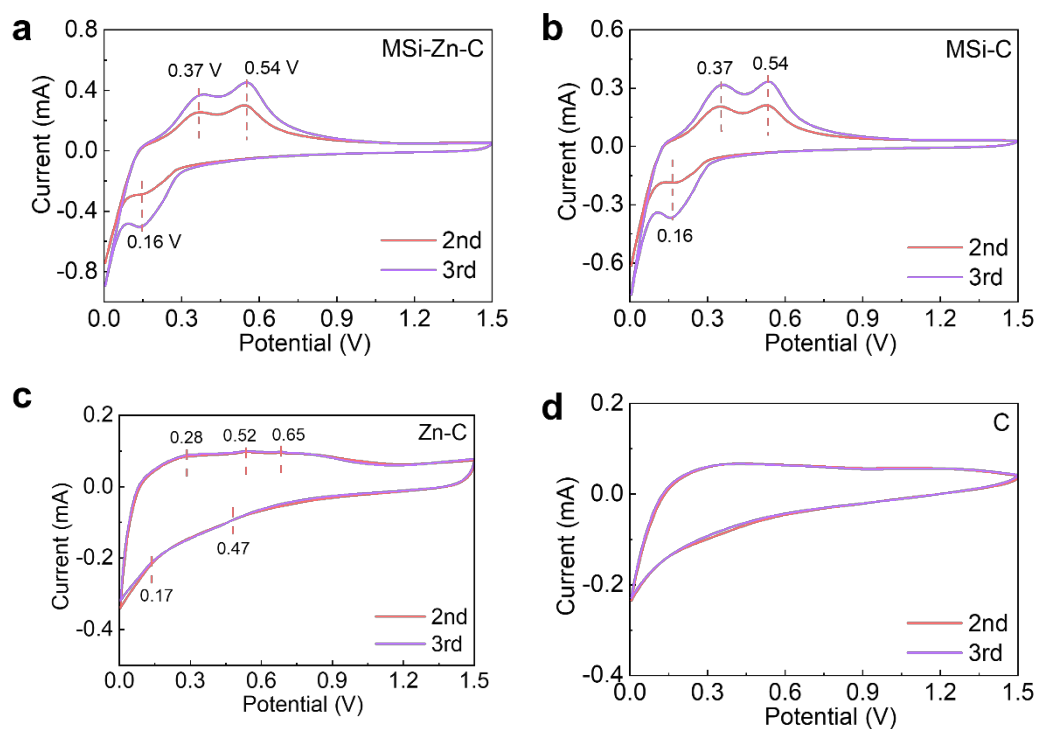


Figure S14. The CV curves of (a) MSi-Zn-C, (b) MSi-C, (c) Zn-C, and (d) C negative electrodes in solid-state batteries.

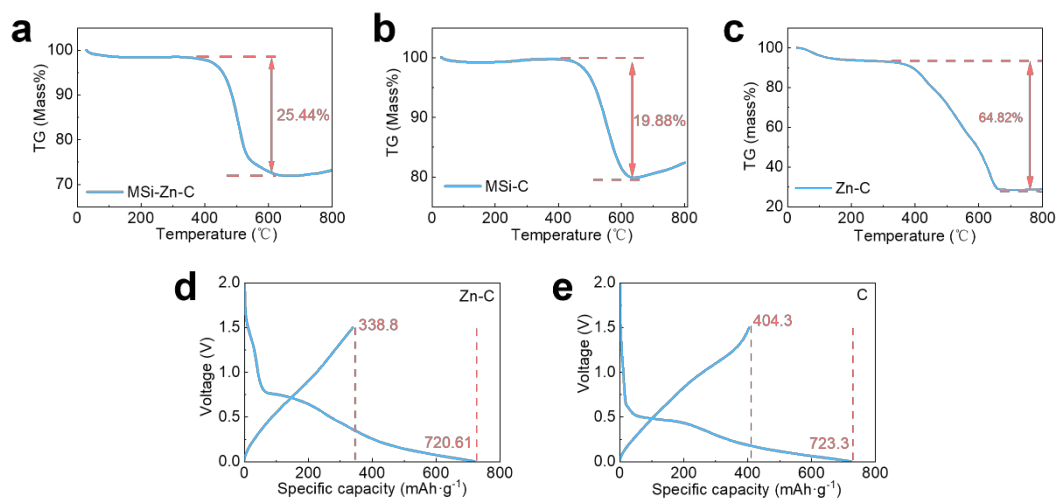


Figure S15. Thermogravimetric analysis (TGA) curves of (a) MSi-Zn-C, (b) MSi-C and (c) Zn-C negative electrodes. The initial specific capacity of (d) Zn-C and (e) C negative electrodes.

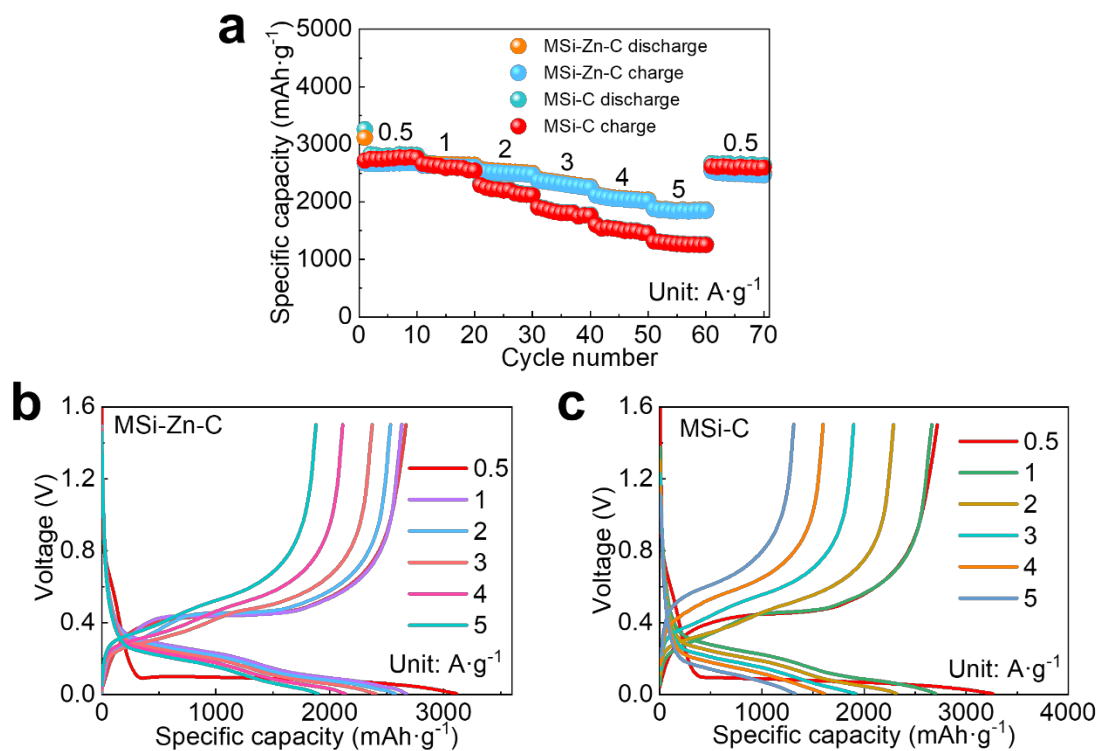


Figure S16. (a) Rate capability of MSi-Zn-C and MSi-C negative electrodes in solid-state batteries. The charge-discharge profiles of (b) MSi-Zn-C and (c) MSi-C at various current rates.

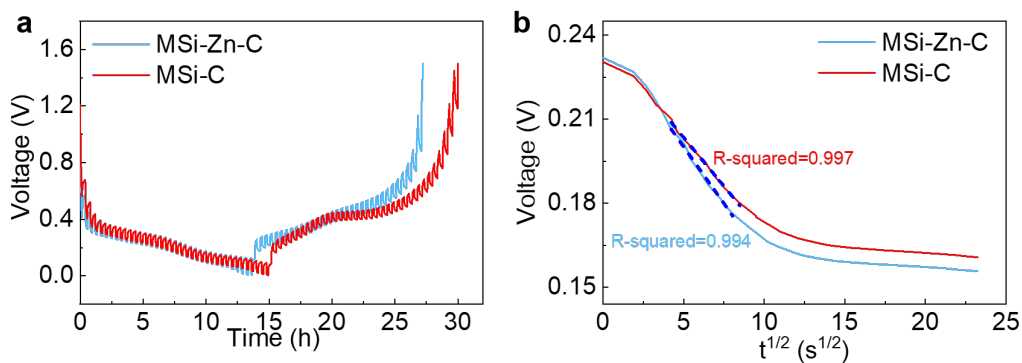


Figure S17. (a) GITT curves of MSi-Zn-C and MSi-C negative electrodes. (b) Linear relationship between voltage and $t^{1/2}$ for representative GITT pulses of MSi-Zn-C and MSi-C.

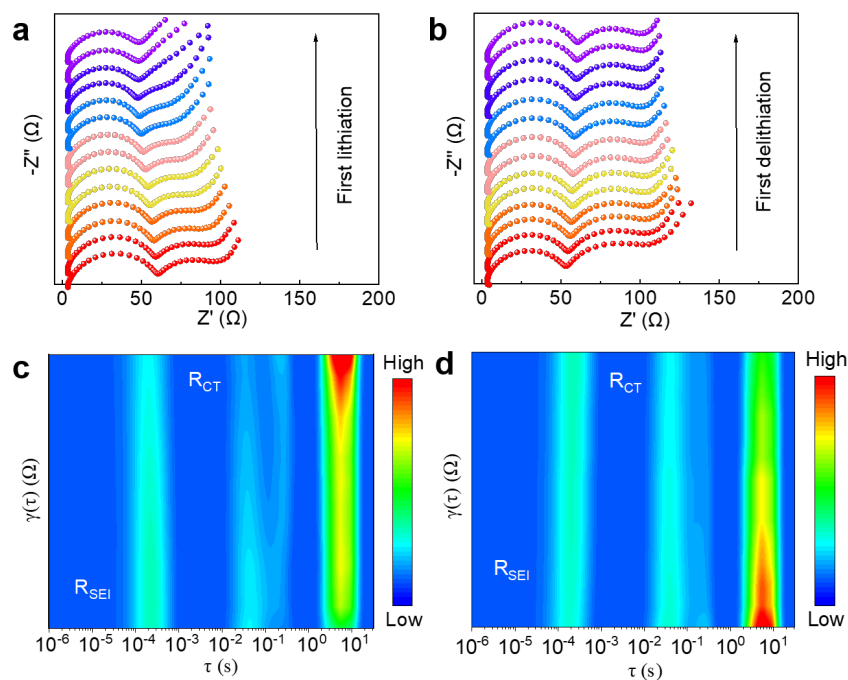


Figure S18. (a) The EIS test of MSi-Zn-C negative electrode in a half cell for the first lithiation process at 0.5 A g^{-1} and 26°C . (b) The EIS test of MSi-Zn-C negative electrode in a half cell for the first delithiation process at 0.5 A g^{-1} and 26°C . (c) The DRT transformation of EIS spectra in (a). (d) The DRT transformation of EIS spectra in (b).

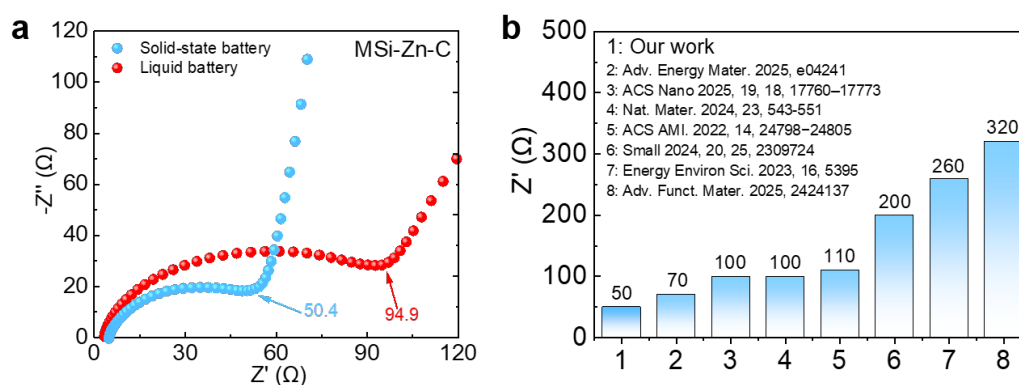


Figure S19. (a) The impedance of MSi-Zn-C negative electrode in solid-state battery and liquid battery. (b) Comparison of impedance in solid-state batteries here with other published works.

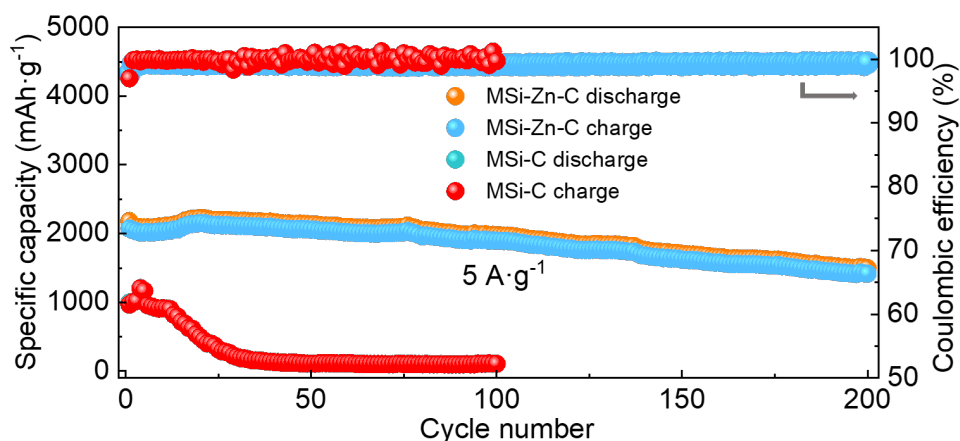


Figure S20. Long-term cycling performance comparison of MSi-Zn-C and MSi-C negative electrodes in solid-state batteries at 5 A g^{-1} .

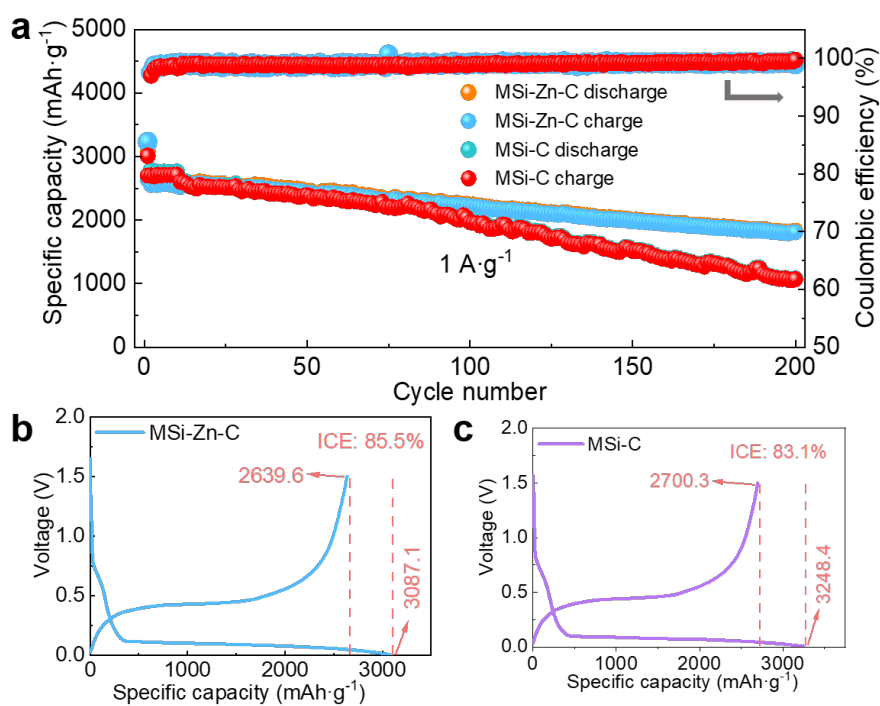


Figure S21. (a) Long-term cycling performance comparison of MSi-Zn-C and MSi-C negative electrodes in solid-state batteries at 1 A g^{-1} . The initial specific capacity and initial Coulombic efficiency (ICE) of (b) MSi-Zn-C and (c) MSi-C negative electrodes.

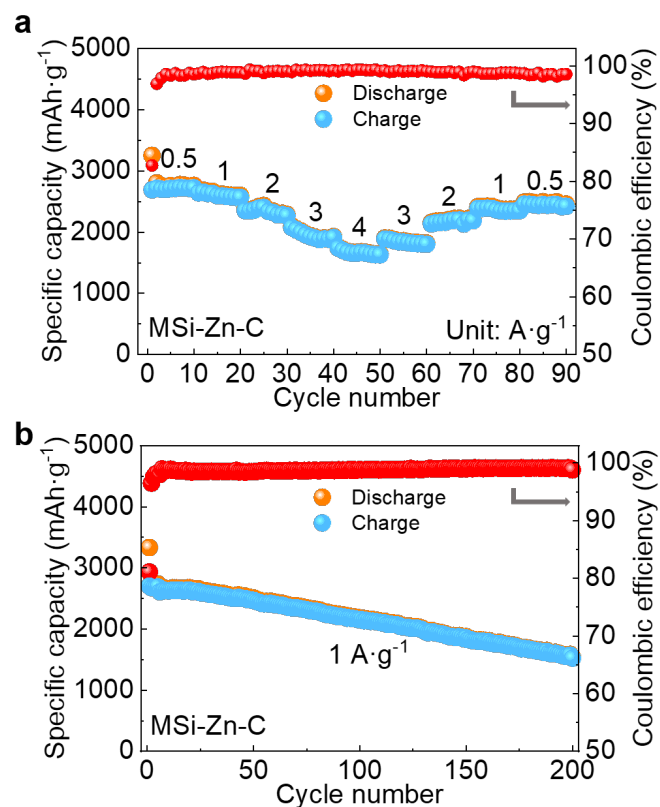


Figure S22. The cycling performance in liquid batteries of MSi-Zn-C negative electrode: (a) Rate capability and (b) Long-term cycling performance at 1 A g⁻¹.

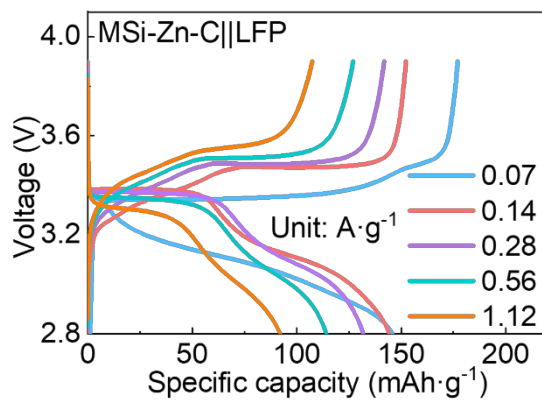


Figure S23. The charge-discharge profile of MSi-Zn-C||LFP full cell at various current densities.

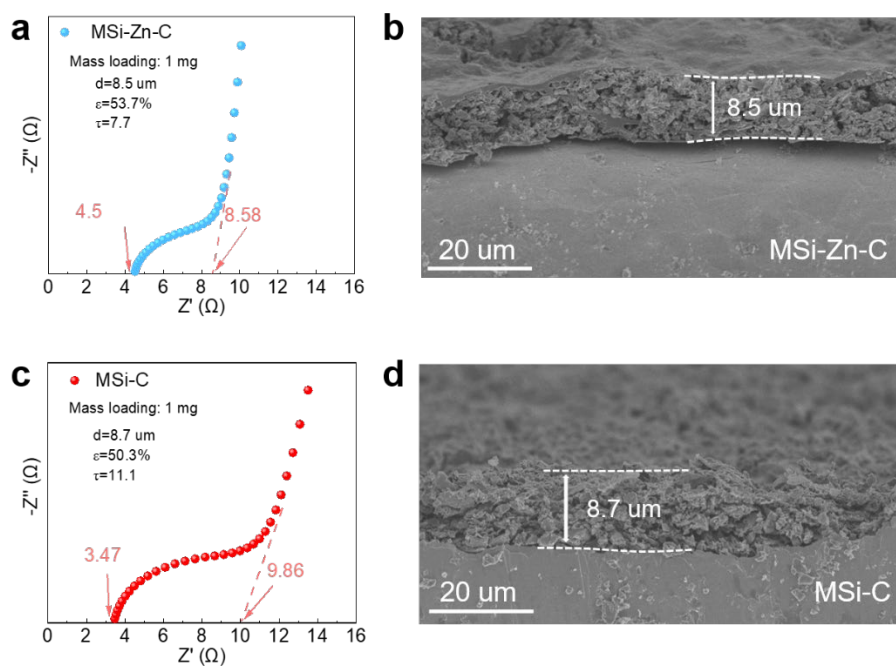


Figure S24. (a) The impedance of MSi-Zn-C||MSi-Zn-C liquid battery. (b) Cross-sectional SEM image of MSi-Zn-C negative electrode. (c) The impedance of MSi-C||MSi-C liquid battery. (d) Cross-sectional SEM image of MSi-C negative electrode.

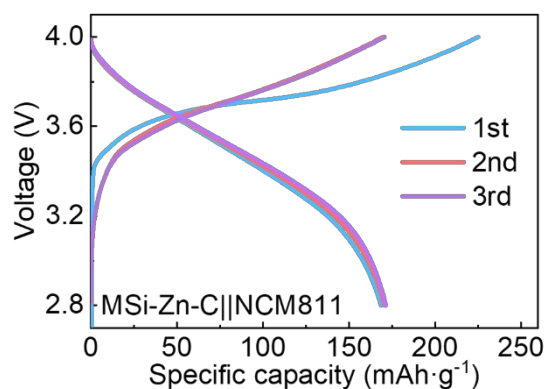


Figure S25. The charge-discharge profile of the first three cycles of the MSi-Zn-C||NCM811 full cell.

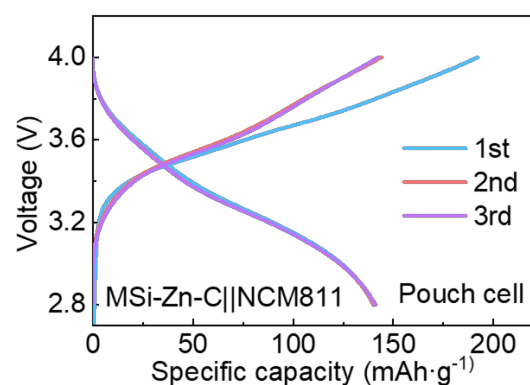


Figure S26. The charge-discharge profile of the first three cycles of the MSi-Zn-C||NCM811 pouch cell.

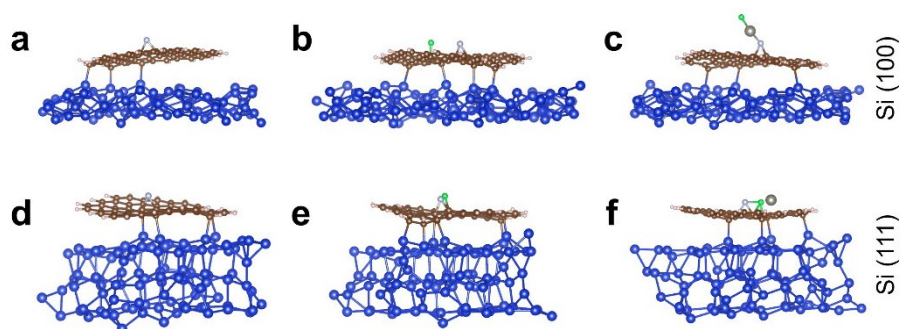


Figure S27. Side view of Si (100)-C combined in (a) N, (b) N-F, (c) Zn-N-F models. Side view of Si (111)-C combined in (d) N, (e) N-F, (f) Zn-N-F models.

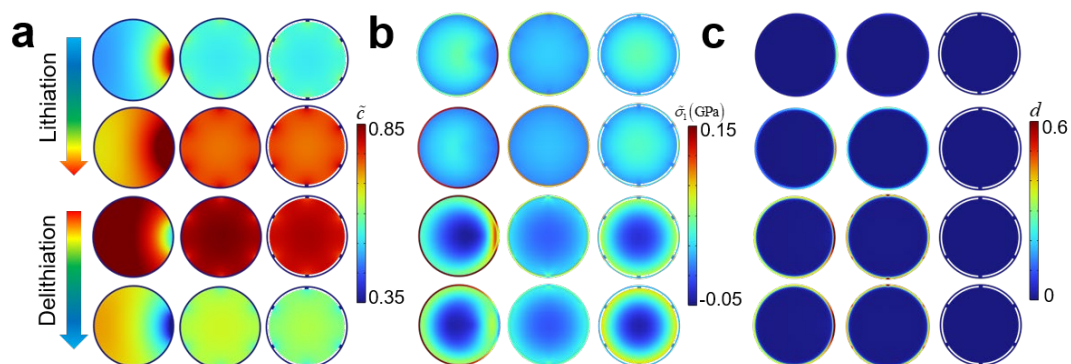


Figure S28. Chemo-mechanical simulated time snapshots of (a) normalized Li concentration, (b) maximum principal stress, and (c) damage of MSi-C (first column), MSi-Zn-C without void space (second column), and MSi-Zn-C (third column) in the undeformed configurations during the initial lithiation and delithiation process.

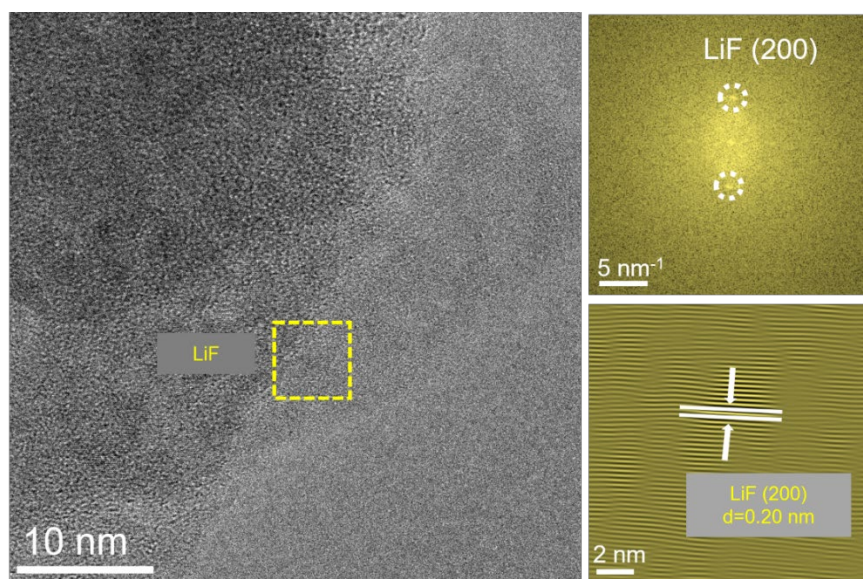


Figure S29. High resolution Cryo-TEM image of cycled MSi-Zn-C and corresponding FFT image.

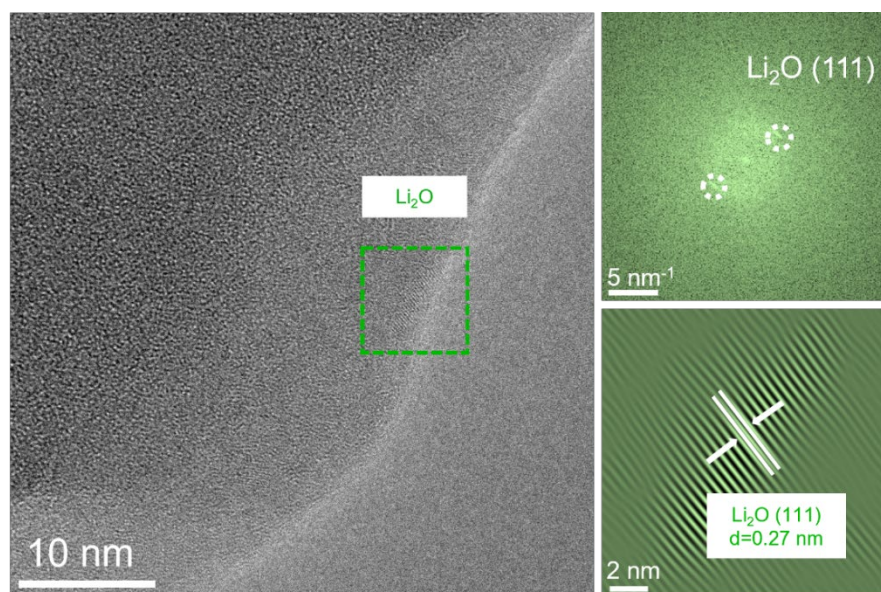


Figure S30. High resolution Cryo-TEM image of cycled MSi-Zn-C and corresponding FFT image.

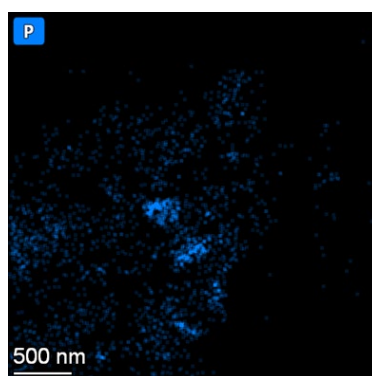


Figure S31. EDS elemental mapping of P for the cycled MSi-Zn-C negative electrode, corresponding to the HAADF image shown in Figure 6. (k).

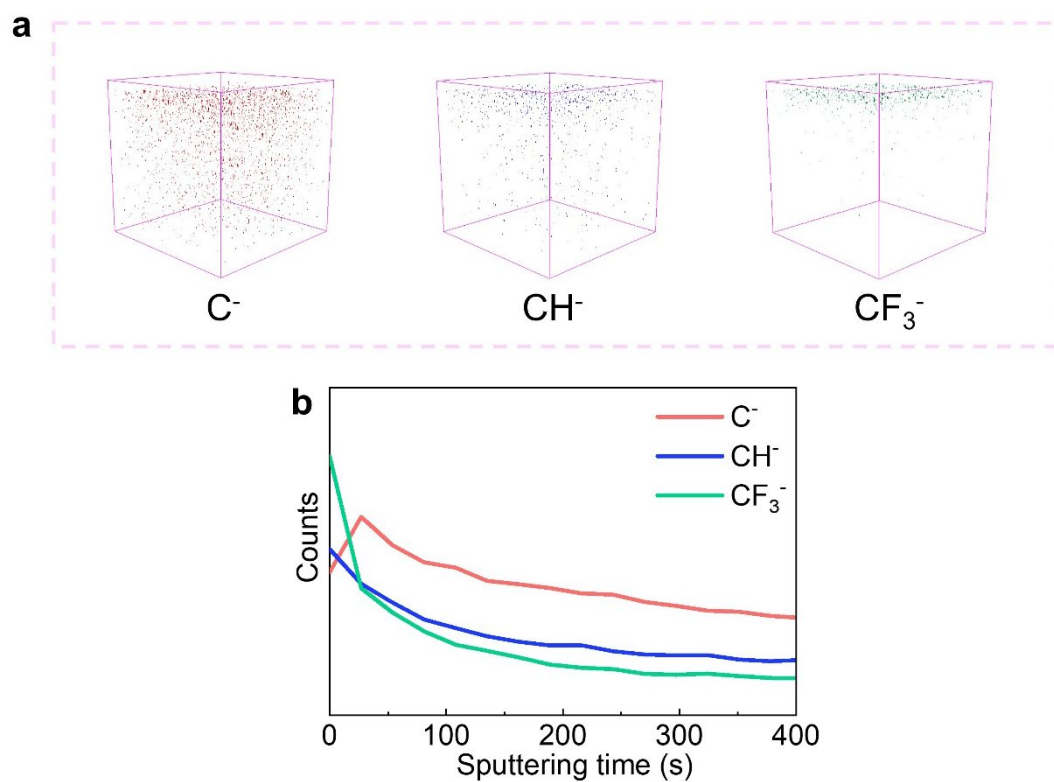


Figure S32. (a) 3D maps showing the distribution of several fragments: C^- , CH^- , CF_3^- for a solid-state cell, sample area $100 \times 100 \mu m$ with 100 nm height. (b) Depth profiles showing normalized intensity of several characteristic molecular fragments on the cycled MSi-Zn-C negative electrode.

Table S1 Capacity contribution of MSi, Zn or C in different MSi-based composite negative electrodes.

	Capacity (mAh g ⁻¹)
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C	404.3
Zn-C	338.8
MSi-C	2716.3
MSi-Zn-C	2668.0
	Capacity contribution (mAh g ⁻¹)
C	In Zn-C: $404.3 \times 64.82\% = 262.07$
	In MSi-C: $404.3 \times 19.88\% = 80.37$
	In MSi-Zn-C: $404.3 \times 25.44\% = 102.85$
Zn	In Zn-C: $(338.8 - 262.07) / 35.18\% = 218.11$
	The proportion of Zn in MSi-Zn-C: 4.89%
	In MSi-Zn-C: $218.11 \times 4.89\% = 10.67$
Si	In MSi-C: $(2716.3 - 80.37) / 80.12\% = 3290.0$
	The proportion of Si in MSi-Zn-C: 69.97%
	In MSi-Zn-C: $(2668 - 102.85 - 10.67) / 69.97\% = 3650.82$

Table S2 Specific energy calculation of MSi-Zn-C||LFP cells excluding current collectors at various N/P ratios.

High mass loading		Weight (mg cm ⁻²)	Capacity (mAh g ⁻¹)	Capacity (mAh cm ⁻²)
Positive electrode	LFP (80%)	13.5	147.7	1.994
	PVDF 5% (10%)	3.38		
	Super P (10%)			
Negative	MSi-Zn-C	1.00	2030.7	2.03

electrode				
Current collector		7.80		
SPE		5.0		
N/P				1.02
Voltage				3.45 V
Energy				6.88 mWh
Total mass		30.68		
Specific energy		224.25 Wh kg⁻¹		
Specific energy (excluding current collectors)		300.70 Wh kg⁻¹		
High mass loading		Weight (mg cm ⁻²)	Capacity (mAh g ⁻¹)	Capacity (mAh cm ⁻²)
Positive electrode	LFP (80%)	9.90	141.8	1.404
	PVDF 5% (10%) Super P (10%)	2.47		
Negative electrode	MSi-Zn-C	1.00	2030.7	2.03
Current collector		7.80		
SPE		5.0		
N/P				1.02
Voltage				3.4 V
Energy				4.774 mWh
Total mass		26.17		
Specific energy		182.41 Wh kg⁻¹		

Specific energy (excluding current collectors)		259.89 Wh kg⁻¹		
Low mass loading		Weight (mg cm ⁻²)	Capacity (mAh g ⁻¹)	Capacity (mAh cm ⁻²)
Positive electrode	LFP (80%)	2.80	149.2	0.418
	PVDF 5% (10%) Super P (10%)	0.70		
Negative electrode	MSi-Zn-C	0.24	2668.0	0.64
Current collector		7.80		
SPE		5.0		
N/P				1.53
Voltage				3.39 V
Energy				1.42 mWh
Total mass		16.54		
Specific energy		85.85 Wh kg⁻¹		
Specific energy (excluding current collectors)		162.47 Wh kg⁻¹		
Low mass loading		Weight (mg cm ⁻²)	Capacity (mAh g ⁻¹)	Capacity (mAh cm ⁻²)
Positive	LFP (80%)	1.0	159.5	0.1595

electrode	PVDF 5% (10%) Super P (10%)	0.25		
Negative electrode	MSi-Zn-C	0.24	2668.0	0.64
Current collector		7.80		
SPE		5.0		
N/P				4.01
Voltage				3.35 V
Energy				0.536 mWh
Total mass		14.29		
Specific energy		37.51 Wh kg⁻¹		
Specific energy (excluding current collectors)		82.59 Wh kg⁻¹		

Table S3 Specific energy calculation of MSi-Zn-C||NMC811 cells excluding current collectors at various N/P ratios.

High mass loading		Weight (mg cm ⁻²)	Capacity (mAh g ⁻¹)	Capacity (mAh cm ⁻²)
Positive electrode	NCM811 (80%)	9.0	175.6	1.58
	PVDF 5% (10%) Super P (10%)	2.25		
Negative electrode	MSi-Zn-C	1.00	2030.7	2.03
Current collector		7.80		
SPE		5.0		

N/P				1.28
Voltage				3.68 V
Energy				5.184 mWh
Total mass		25.05		
Specific energy		232.11 Wh kg⁻¹		
Specific energy (excluding current collectors)		337.04 Wh kg⁻¹		
High mass loading		Weight (mg cm ⁻²)	Capacity (mAh g ⁻¹)	Capacity (mAh cm ⁻²)
Positive electrode	NCM811 (80%)	5.10	162.7	0.829
	PVDF 5% (10%) Super P (10%)	1.64		
Negative electrode	MSi-Zn-C	1.00	2030.7	2.03
Current collector		7.80		
SPE		5.0		
N/P				2.45
Voltage				3.6 V
Energy				2.984 mWh
Total mass		20.54		
Specific energy		145.28 Wh kg⁻¹		
Specific energy (excluding current		210.68 Wh kg⁻¹		

collectors)				
Low mass loading		Weight (mg cm ⁻²)	Capacity (mAh g ⁻¹)	Capacity (mAh cm ⁻²)
Positive electrode	NCM811 (80%)	3.00	146.1	0.438
	PVDF 5% (10%) Super P (10%)	0.75		
Negative electrode	MSi-Zn-C	0.24	2668.0	0.64
Current collector		7.80		
SPE		5.0		
N/P				1.46
Voltage				3.65 V
Energy				1.6 mWh
Total mass		16.79		
Specific energy		95.3 Wh kg⁻¹		
Specific energy (excluding current collectors)		177.98 Wh kg⁻¹		
Low mass loading		Weight (mg cm ⁻²)	Capacity (mAh g ⁻¹)	Capacity (mAh cm ⁻²)
Positive electrode	NCM811 (80%)	1.0	159.5	0.1595
	PVDF 5% (10%) Super P (10%)	0.25		
Negative	MSi-Zn-C	0.24	2668.0	0.64

electrode				
Current collector		7.80		
SPE		5.0		
N/P				3.79
Voltage				3.55 V
Energy				0.60 mWh
Total mass		14.29		
Specific energy		42.00 Wh kg⁻¹		
Specific energy (excluding current collectors)		92.45 Wh kg⁻¹		

Table S4 Comparison of the electrochemical performance a of Si-based full cells.

Reference	Cell type	Mass loading	Operating temperature	Specific current (A g ⁻¹)	Cycle number	Capacity retention (%)
This work	MSi-Zn-C SPE LFP	1 mg cm ⁻²	26 °C	0.56	2000	71
This work	MSi-Zn-C SPE LFP	1 mg cm ⁻²	30 °C	0.14	1000	80
This work	MSi-Zn-C SPE NC M811	1 mg cm ⁻²	30 °C	0.24	800	80
[2]	μm-Si elastic electrolyte LFP	6 mg cm ⁻²	25 °C	0.0875	145	80

[7]	Si@SiO ₂ -C ₂ Liquid electrolyte LFP	3-3.5 mg cm ⁻²	Not specified	0.68	500	80
[8]	Si Liquid electrolyte NCM811	13 mg cm ⁻²	25 °C	0.036	150	83.7
[11]	μSi Li ₆ PS ₅ Cl NCM811	25 mg cm ⁻²	Room temperature	5 mA cm ⁻²	500	80
[36]	Si MgF ₂ -1 Liquid electrolyte NCM811	12 mg cm ⁻²	Not specified	0.44	200	75.3
[37]	Si@LaF ₃ Liquid electrolyte LFP	Not specified	Room temperature	0.35 C	200	84.7
[55]	Si-CPBOD Liquid electrolyte NCM811	~ 17 mg cm ⁻²	25 °C	0.04	300	75.6
[56]	Si Liquid electrolyte NCM811	11 mg cm ⁻²	25 °C	0.036	160	82.8%

Chemo-mechanical simulation details

Chemo-mechanical simulations were conducted to reveal the stress adaptive

characteristics of MSi-Zn-C compared to the particles without Zn nanoparticles and empty space (MSi-C) and with Zn nanoparticles but no empty space ^[1,2]. In the model, the mechanical equilibrium equation of the system with body force neglected is written as:

$$\nabla \cdot \boldsymbol{\sigma} = 0 \quad (1)$$

where, $\boldsymbol{\sigma} = \mathbf{C} : \boldsymbol{\varepsilon}_e$ is the Cauchy stress tensor, $\mathbf{C}$ is the elasticity tensor, and $\boldsymbol{\varepsilon}_e$ is the elastic strain tensor defined by $\boldsymbol{\varepsilon}_e = \boldsymbol{\varepsilon} - \boldsymbol{\varepsilon}_c$, in which $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}_c$ are the total strain tensor and chemical strain tensor, respectively. The chemical strain tensor can be defined as:

$$\boldsymbol{\varepsilon}_c = \boldsymbol{\beta}(c - c_0) \quad (2)$$

where, c is the current Li concentration, c_0 is the initial Li concentration, $c_{\max}$ is the maximal Li concentration, and $\boldsymbol{\beta}$ is the dilatational tensor given by $\boldsymbol{\beta} = \beta \mathbf{I}$, with β and $\mathbf{I}$ represent the lithiation expansion coefficient and the identity tensor, respectively.

For the chemical part, the governing equation of Li diffusion is expressed as:

$$\frac{\partial c}{\partial t} - \nabla \cdot \left\{ \mathbf{D} [1 - 2\chi \tilde{c}(1 - \tilde{c})] \nabla c - \frac{c(1-\tilde{c})}{R_g T} \mathbf{D} \nabla (\boldsymbol{\sigma} : \boldsymbol{\beta}) \right\} = 0 \quad (3)$$

where, t is time, R_g is the gas constant, T is the temperature, and $\mathbf{D}$ is the diffusivity. $\tilde{c} = c/c_{\max}$ signifies the normalized lithium-ion concentration, with $c_{\max}$ the saturation concentration of the host. χ is the Flory-Huggins binary interaction parameter which controls the phase separation phenomenon.

Considering the lithiation/delithiation induced damage in the C shell and Si core during cycling, the governing equation of damage evolution is given by:

$$\frac{\partial d}{\partial t} = M_d \left[2(1-d)H - f(\bar{\alpha}) \frac{G_c}{l_0} (d - l_0^2 \nabla^2 d) \right] \quad (4)$$

where, $d = d(\mathbf{x}, t)$ is the damage phase-field parameter, with $d = 0$ represents an intact phase while $d = 1$ indicates the completely damaged region, $\mathbf{x}$ is the spatial

coordinate vector, M_d is the mobility for the evolution of d . $H = \max(\psi_e^+)$ is the history variable introduced to satisfy the irreversibility of the propagation of crack, with ψ_e^+ the positive part of the decomposed elastic energy density $\psi_e = \psi_e(\epsilon_e, c, d)$. G_c is the critical energy release rate for the fracture and l_0 is the characteristic length defined that regulates the width of the diffused interface between damaged and undamaged regimes. $\bar{\alpha} = \int_0^t H(\alpha \dot{\alpha}) |\dot{\alpha}| d\tau$ is a variable describing the accumulated state of fatigue history, $H(g)$ is the Heaviside function, α is a history variable, τ refers to the pseudo time for integration, and the fatigue degradation function $f(\bar{\alpha})$ is defined as follows:

$$f(\bar{\alpha}) = \begin{cases} 1 & \text{if } \bar{\alpha} \leq \alpha_T \\ [1 - \kappa \log(\bar{\alpha}/\alpha_T)]^2 & \text{if } \alpha_T < \bar{\alpha} < \alpha_T 10^{1/\kappa} \\ 0 & \text{if } \bar{\alpha} \geq \alpha_T 10^{1/\kappa} \end{cases} \quad (5)$$

with $\alpha_T = G_c/6l_0$ the fatigue crack threshold and κ is a material parameter.

By solving the Eqs (1-3) with proper initial and boundary conditions, the evolutions of normalized Li concentration, maximum principal stress, and damage of the MSi-C, MSi-Zn-C without void space, and MSi-Zn-C particles induced by Li insertion/extraction during the first cycle were simulated in COMSOL Multiphysics software.

Supplementary References

- [1] Ai W, Wu B, Martínez-Pañeda E. A coupled phase field formulation for modelling fatigue cracking in lithium-ion battery electrode particles. *Journal of Power Sources*, 2022, 544: 231805.
- [2] Singh A, Pal S. Chemo-mechanical modeling of inter-and intra-granular fracture in heterogeneous cathode with polycrystalline particles for lithium-ion battery. *Journal of the Mechanics and Physics of Solids*, 2022, 163: 104839.