

Supplementary Information

Silicon-based all-solid-state batteries operating free from external pressure

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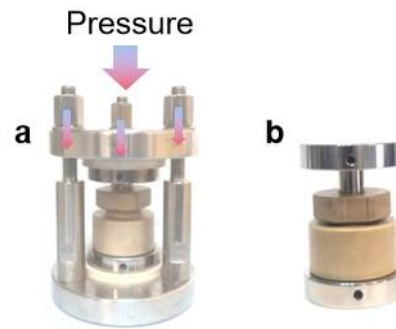
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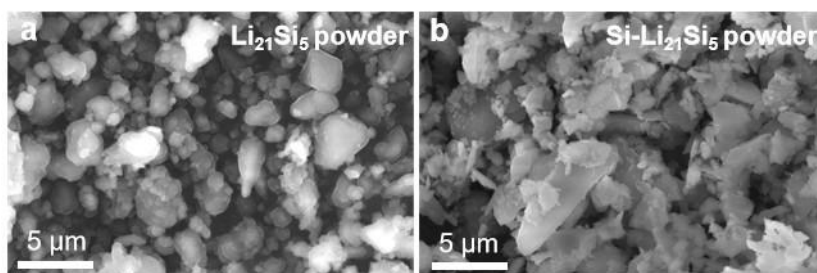
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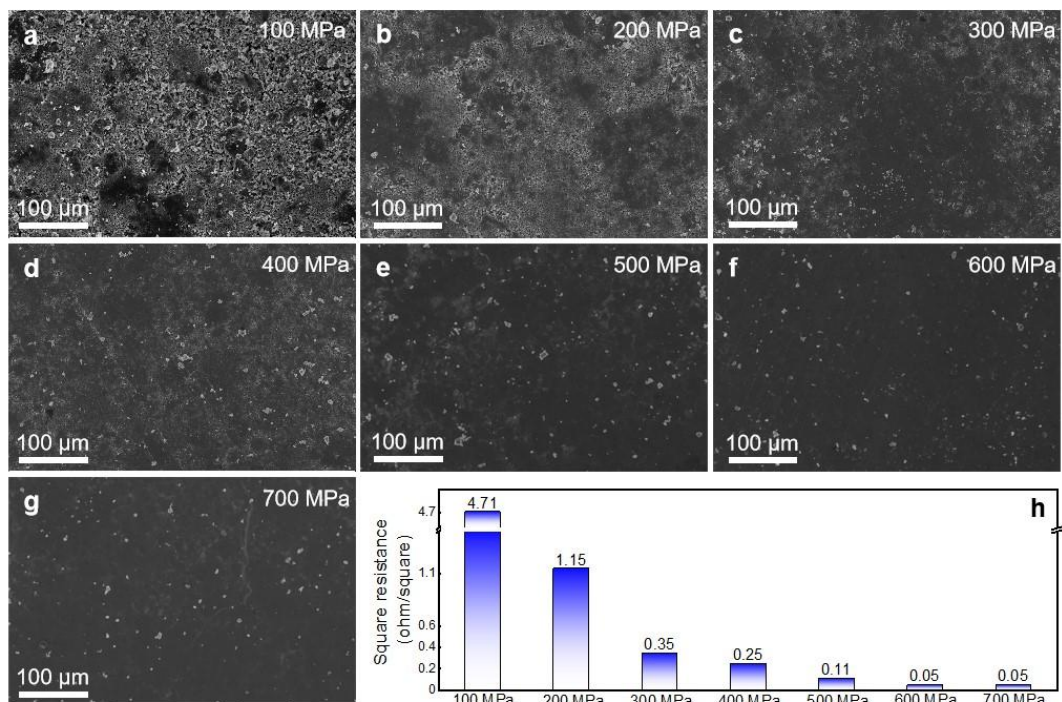
Keywords: all solid-state batteries, Li₂Si₅ alloy, silicon anode, pressure-free, ultra-high ICE



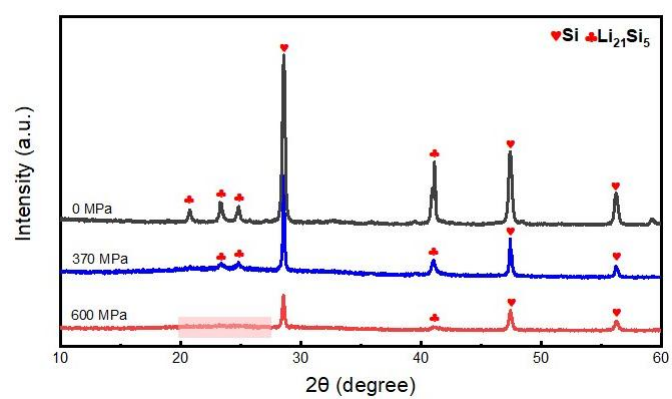
Supplementary Figure 1. (a) ASSBs operating high external pressure. (b) ASSBs operating free from external pressure.



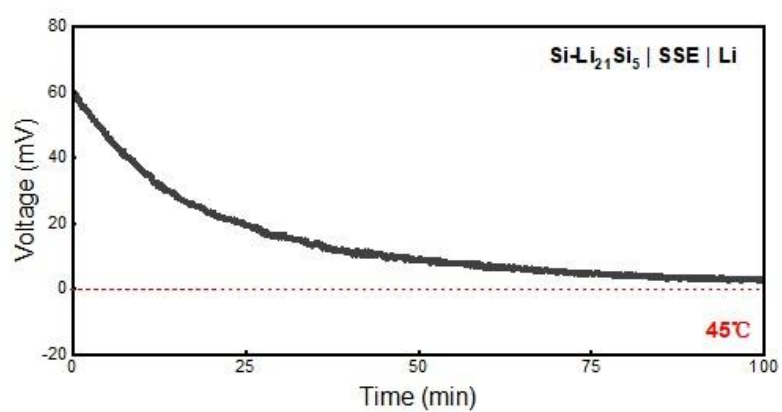
Supplementary Figure 2. SEM images of Li₂₁Si₅ and Si-Li₂₁Si₅ powder.



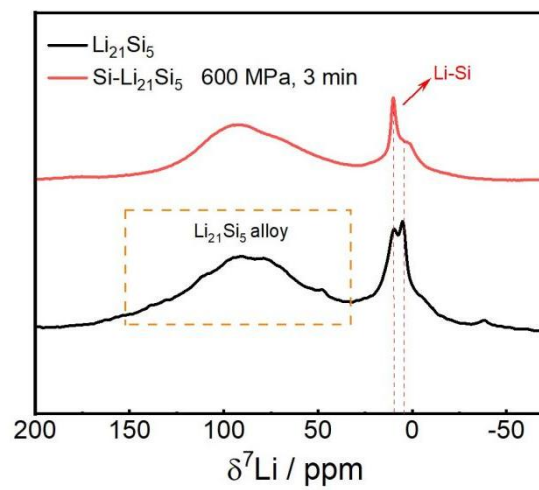
Supplementary Figure 3. SEM images of $\text{Li}_{21}\text{Si}_5$ powders cold-pressed at different stack pressure: (a) 100 Mpa, (b) 200 MPa, (c) 300 MPa, (d) 400 MPa, (e) 500 MPa, (f) 600 MPa, (g) 700 MPa. (h) Sheet resistance of cold-pressed $\text{Li}_{21}\text{Si}_5$ powders via different pressure.



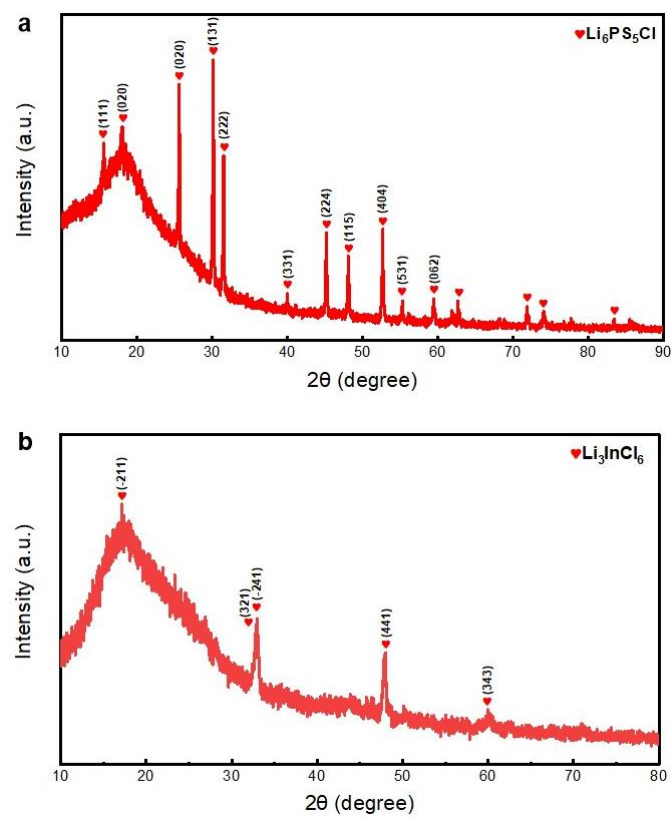
Supplementary Figure 4. XRD patterns of the Si-Li₂₁Si₅ powders sintered at a stack pressure of 600 MPa.



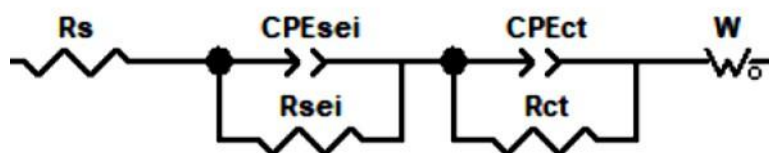
Supplementary Figure 5. Voltage profile during self-discharge. The test was performed without external pressure.



Supplementary Figure 6. NMR spectra of $\text{Li}_{21}\text{Si}_5$ powder and $\text{Si-Li}_{21}\text{Si}_5$ powders.

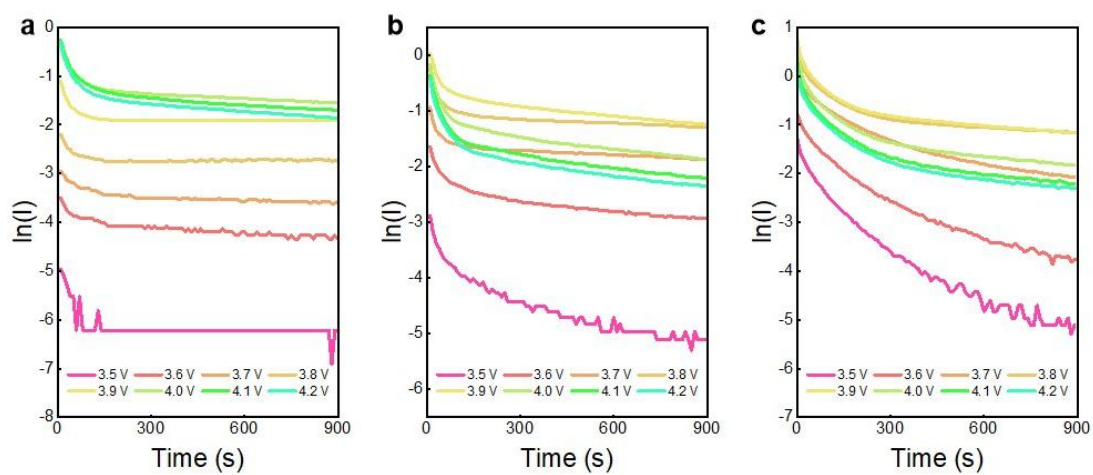


Supplementary Figure 7. XRD patterns of the $\text{Li}_6\text{PS}_5\text{Cl}$ (a) and Li_3InCl_6 (b) powders.



	Rs (ohm)	error% (Rs)	Rsei (ohm)	error% (Rsei)	Rct (ohm)	error% (Rct)
Si SSE LCO cell	55.3	0.58%	29.7	2.04%	201.8	0.69%
Si-Li ₂₁ Si ₅ SSE LCO cell	35.6	0.54%	12.6	5.96%	74.1	3.06%
Li ₂₁ Si ₅ /Si-Li ₂₁ Si ₅ SSE LCO cell	12.9	0.15%	5.3	0.70%	13.3	0.39%

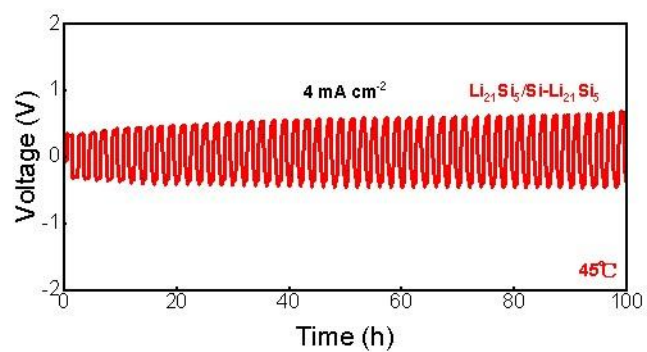
Supplementary Figure 8. Corresponding equivalent circuit of EIS.



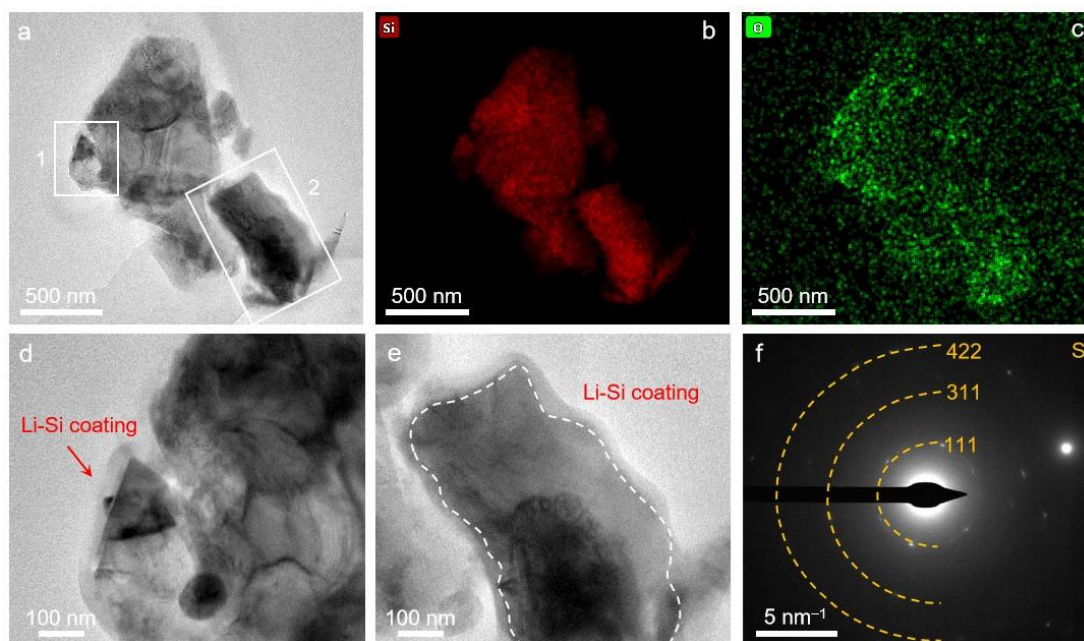
Supplementary Figure 9. PITT curves of Si|SSE|LCO (a), Si-Li₂₁Si₅|SSE|LCO (b), and Li₂₁Si₅/Si-Li₂₁Si₅|SSE|LCO (c). The PITT tests were operated at 45 °C.

Supplementary Table 1 | Comparison of diffusion coefficient in this work and different anode in published literature.

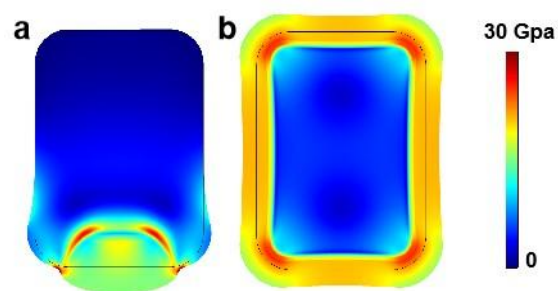
References	Anode	Diffusion coefficients (cm ² s ⁻¹)	Years
1	RGR	2.0×10^{-13}	2024
2	Cr _{0.5} Nb _{24.5} O ₆₂	2.19×10^{-13}	2017
3	W ₃ Nb ₁₄ O ₄₄	8.02×10^{-13}	2019
4	Li _{0.38} Pr _{0.54} TiO ₃	1.80×10^{-12}	2024
5	NiNb ₂ O ₆	1.20×10^{-12}	2022
6	Si@Si ₃ N ₄ @C	8.11×10^{-11}	2020
7	Li ₄ Ti ₅ O ₁₂	3.89×10^{-11}	2022
8	LiCrTiO ₄	1.54×10^{-11}	2017
9	Li _{1.2} Ni _{2.5} B ₂	10^{-10} - 10^{-11}	2024
10	LiMg	1.60×10^{-10}	2022
11	Co ₂ VO ₄	3.14×10^{-10}	2022
12	MnO ₂ @PNC	10^{-8}	2022
13	Li ₂ MSiO ₄	$10^{-6.5}$ - $10^{-7.5}$	2022
14	LiC ₆	2.0×10^{-7}	2024
This work	Li₂₁Si₅	$\geq 2.09 \times 10^{-6}$	2024



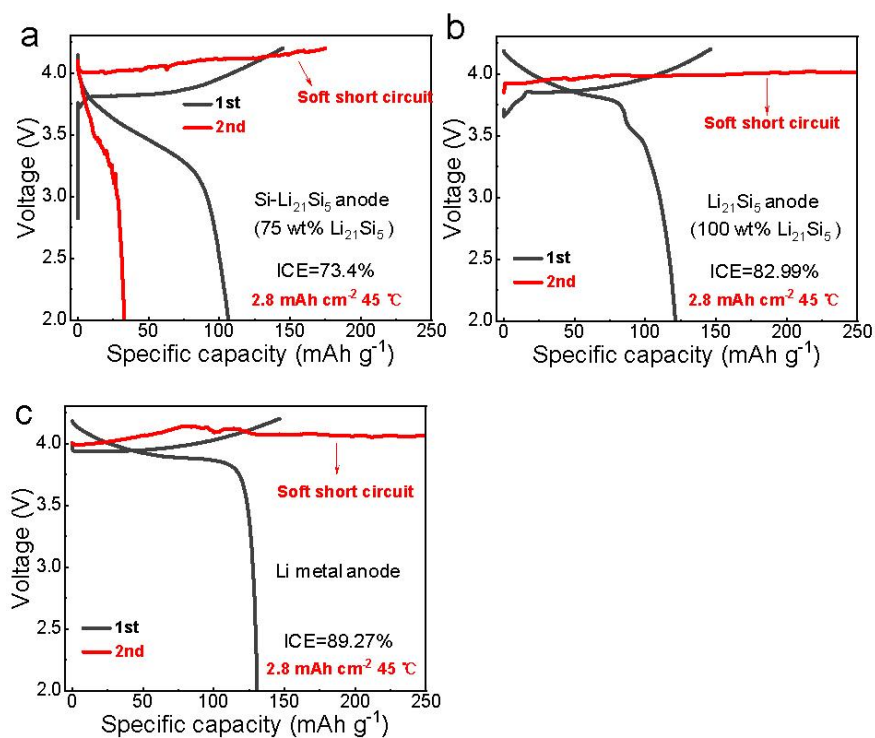
Supplementary Figure 10. Galvanostatic cycling of symmetric cell ($\text{Li}_{21}\text{Si}_5/\text{Si-Li}_{21}\text{Si}_5|\text{SSE}|\text{Li}_{21}\text{Si}_5$) at 4 mA cm^{-2} .



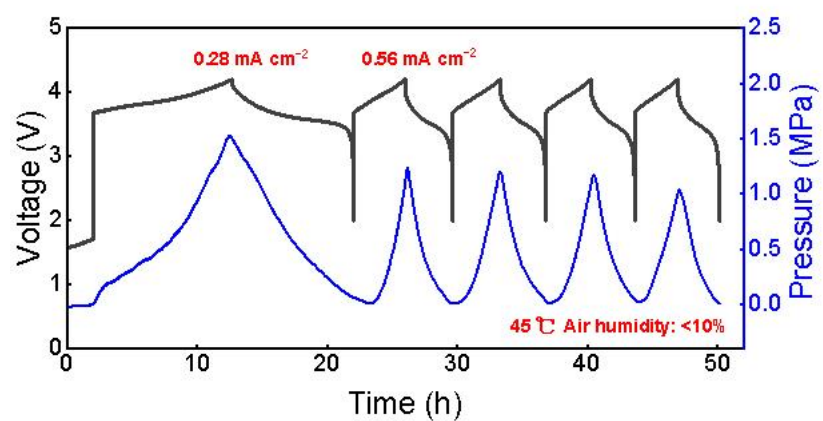
Supplementary Figure 11. (a) TEM image of Li-Si@Si particles. (b-c) Elemental mapping of Li-Si@Si particles. (d-e) HRTEM images of regions 1 and 2 in Supplementary Fig. 11a. (f) Selected area electron diffraction patterns of Li-Si@Si particles.



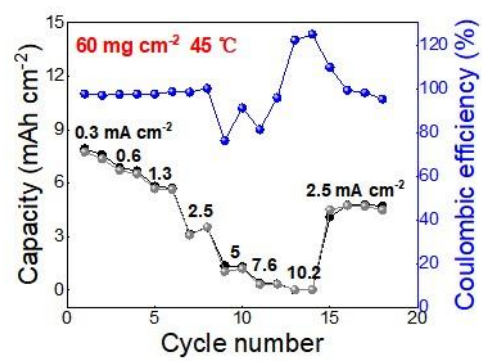
Supplementary Figure 12. Simulated volume expansion of Si particle (a) and Li-Si@Si particle (b) during lithiation.



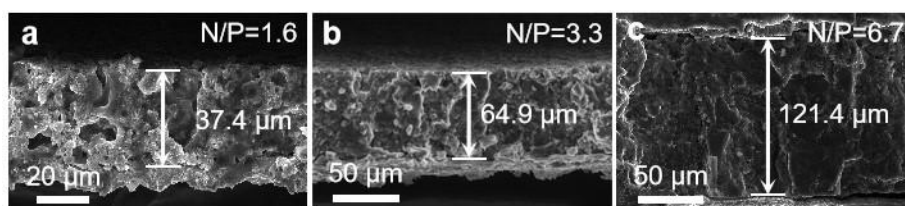
Supplementary Figure 13. Charge-discharge profiles of ASSBs at 2.3 mA cm⁻² with Si-Li₂₁Si₅ anode (Li₂₁Si₅ mass ratio of 75%) (a), pure Li₂₁Si₅ anode (b), and Li metal anode (c).



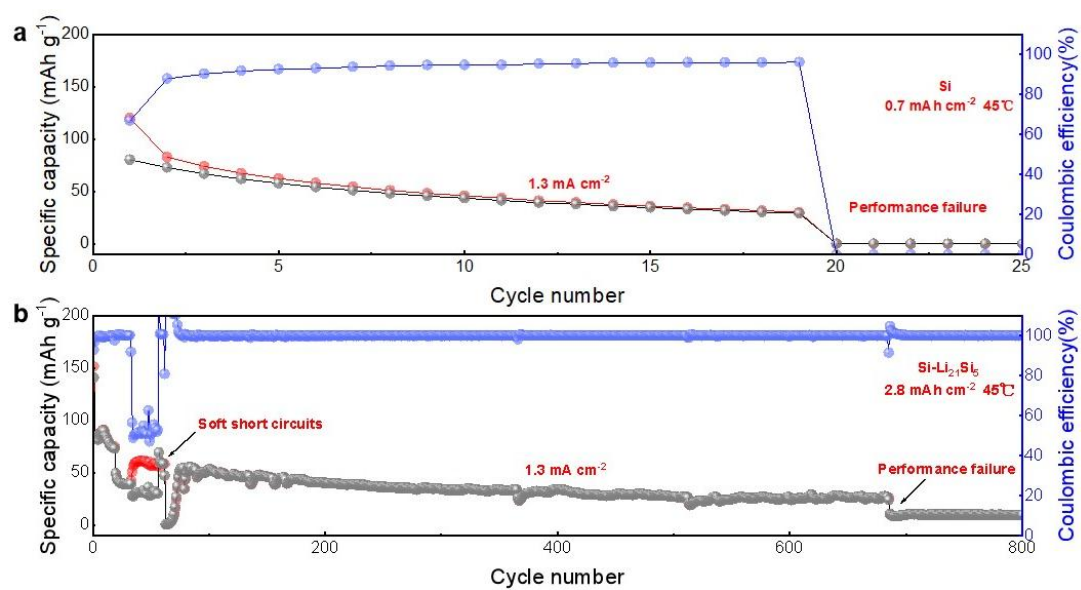
Supplementary Figure 14. Real-time pressure monitoring for Li₂₁Si₅/Si-Li₂₁Si₅-ASSB. Testing conditions: 45 °C, air atmosphere, air humidity: <10%.



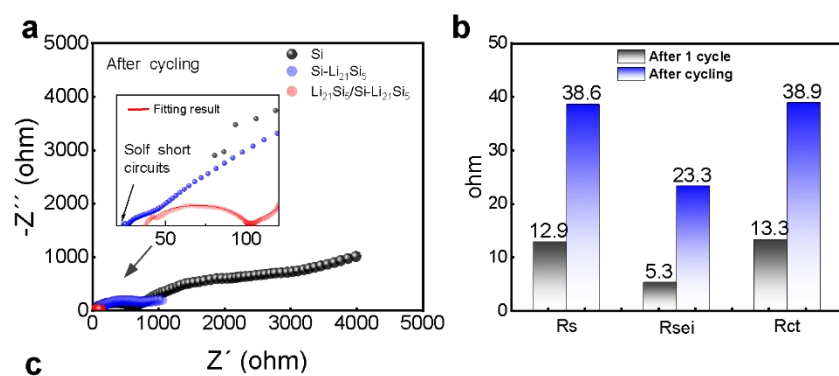
Supplementary Figure 15. Rate capability of Li₂₁Si₅/Si-Li₂₁Si₅-ASSBs with cathode mass loadings of 60 mg cm⁻².



Supplementary Figure 16. Cross-section SEM images of $\text{Li}_{21}\text{Si}_5/\text{Si-Li}_{21}\text{Si}_5$ anode with N/P ratios of 1.6 (a), 3.3 (b), 6.7 (c) after cycling.

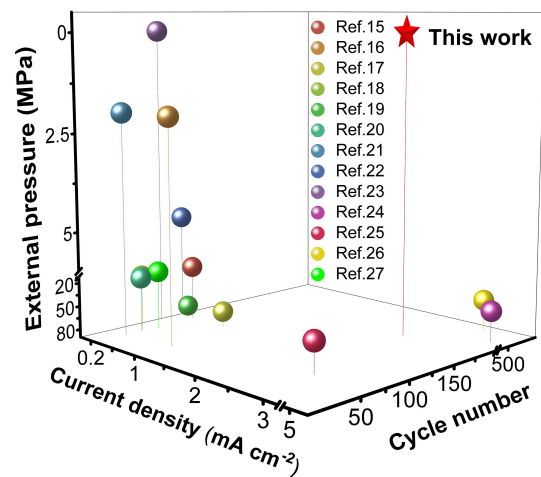


Supplementary Figure 17. Cycling performance of Si-ASSB and Si-Li₂₁Si₅-ASSB.



	Rs (ohm)	error% (Rs)	Rsei (ohm)	error% (Rsei)	Rct (ohm)	error% (Rct)
After 1 cycle	12.9	0.15%	5.3	0.70%	13.3	0.39%
After cycling	38.6	0.39%	23.3	1.67%	38.9	0.50%

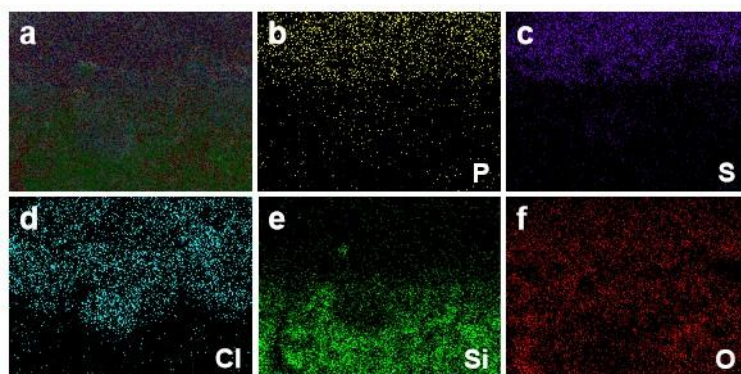
Supplementary Figure 18. (a), EIS test of ASSBs using Si, Si-Li₂₁Si₅, and Li₂₁Si₅/Si-Li₂₁Si₅ anode after cycling. (b-c), Corresponding equivalent circuit of Li₂₁Si₅/Si-Li₂₁Si₅-ASSB after 1 cycle and 1000 cycles.



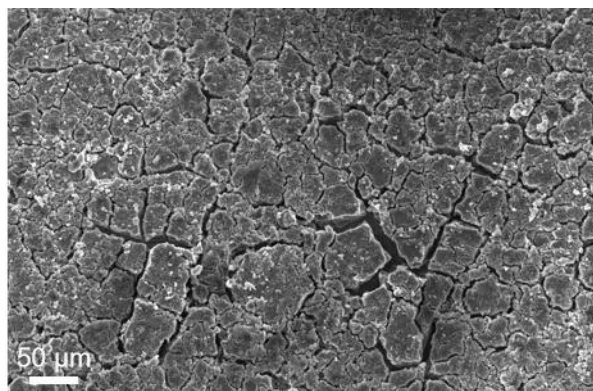
Supplementary Figure 19. Cycling performance of Si-ASSB and Si-Li₂₁Si₅-ASSB.

Supplementary Table 2 | Comparison of key parameters in this work and published literature.

Ref.	External pressure (Mpa)	Cycle number	Current density (mA cm ⁻²)	Areal capacity (mAh cm ⁻²)	Temperature (°C)	Anode	Cathode
15	20	100	0.24	1	25	Si	NCM-111
16	2	35	1	3	80	Li	NMC
17	70	100	0.785	2	60	Si	NCA
18	20	50	0.2	2.7	25	Si	NCM
19	75	100	0.15	0.15	30	Li-In	NCM
20	20	45	0.28	1	30	Si	LCO
21	2	30	0.27	2.7	25	MXene/Mg	NCM-811
22	5	100	0.05	0.5	25	Li	NCA
23	0	80	0.008	0.05	25	Si	LFP
24	50	500	5	2	25	Si	NCM-811
25	50	62	2.8	0.5	25	Si	NCM
26	50	600	3	3.2	55	Si	LCO
27	15	60	0.32	1.6	30	Si	NCM
This work	0	183	2.5	2.8	45	Si	LCO



Supplementary Figure 20. EDS mappings of $\text{Li}_{21}\text{Si}_5/\text{Si-Li}_{21}\text{Si}_5$ anodes. The corresponding secondary electron SEM image is shown in Fig. 6e.



Supplementary Figure 21. SEM image of the surface of Li₂₁Si₅-ASSB after cycling.

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