Electronic Supplementary Information (ESI)†

Microgrid-patterned silicon electrode as an electroactive lithium host

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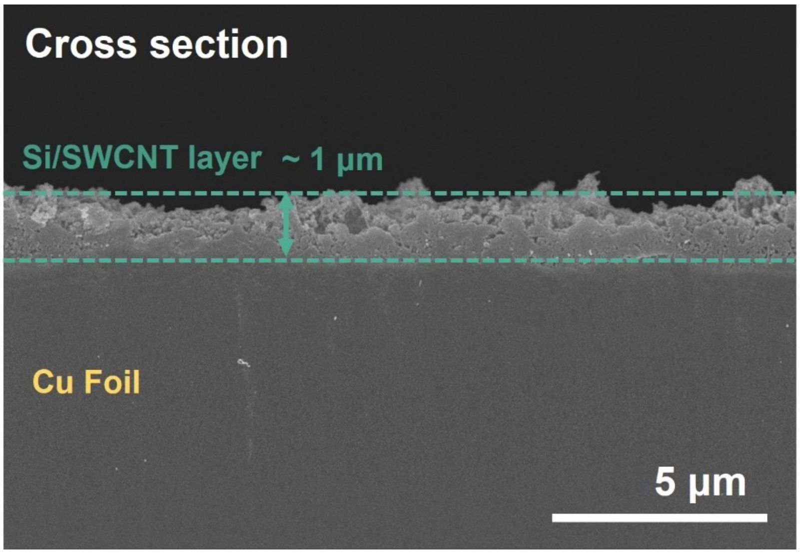

Fig. S1 Cross-sectional SEM image of the *lc*-substrate.

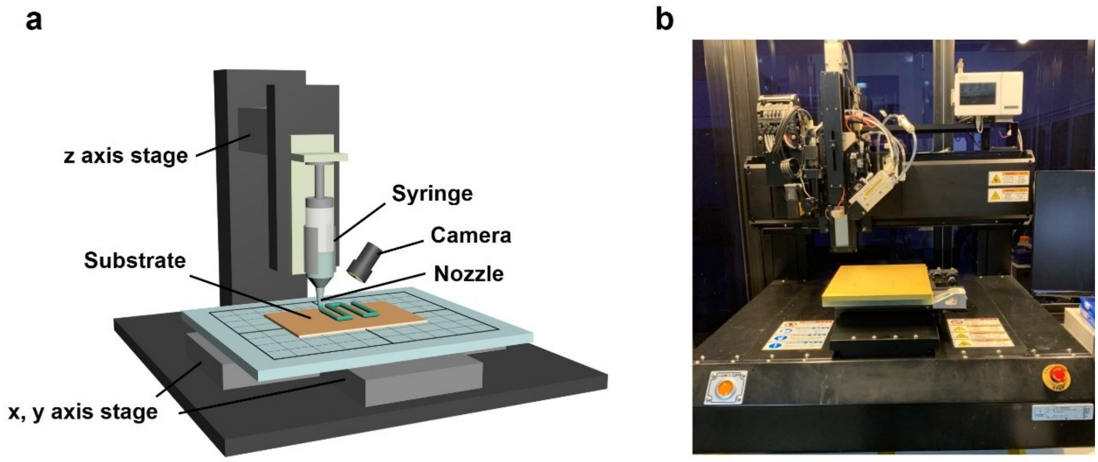

Fig. S2 (a) Schematic illustration and (b) photograph of the DIW device.

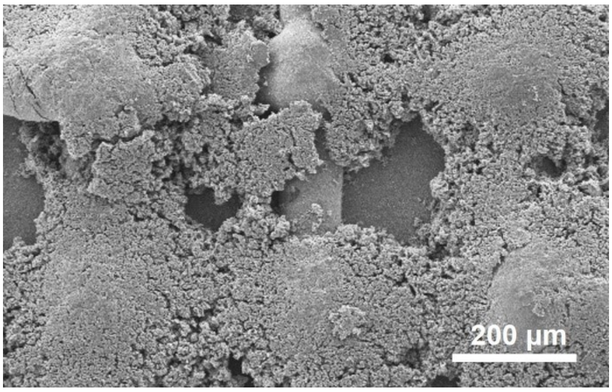

Fig. S3 Top-view SEM image of the control sample (microgrid-patterned Si electrode active layer on a slurry-cast Si electrode active layer) with a Li plating capacity of 1 mAh cm^{-2} at a current density of 0.5 mA cm^{-2}.

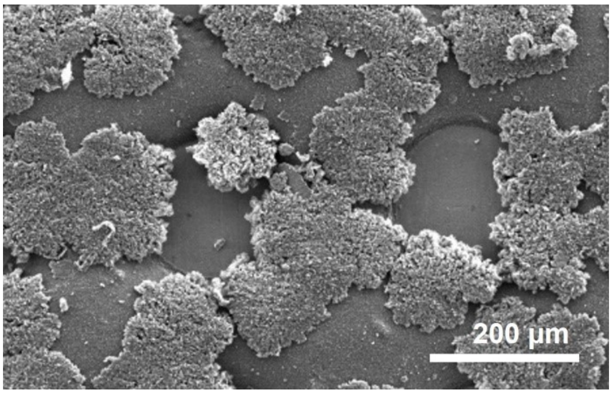

Fig. S4 Top-view SEM image of the control sample (microgrid-patterned Si electrode active layer on a pristine Cu foil) with Li plating capacity of 1 mAh cm^{-2} at a current density of 0.5 mA cm^{-2}.

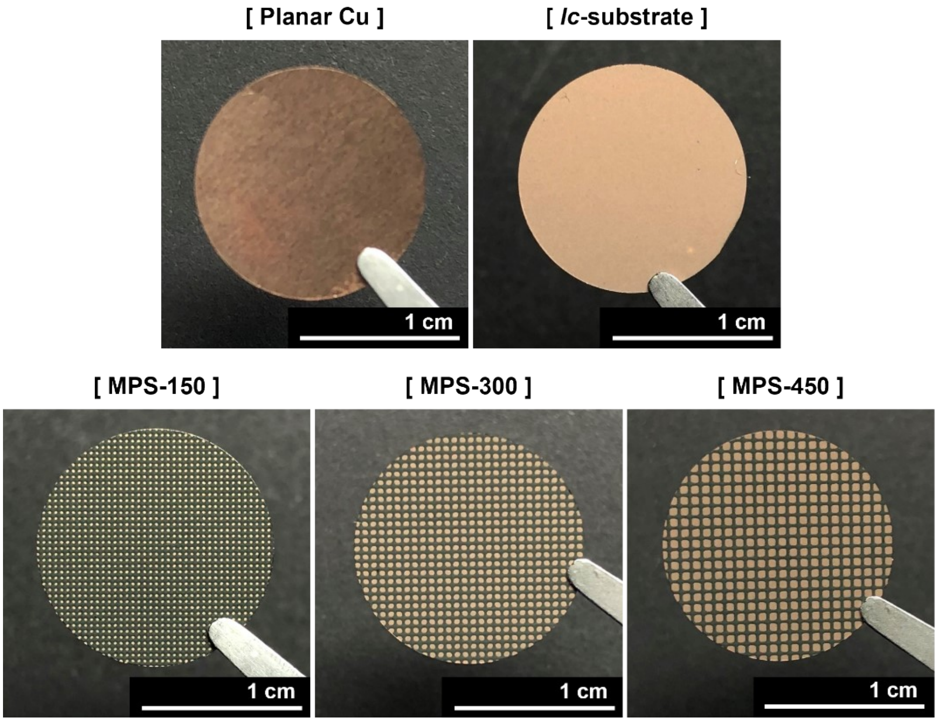

Fig. S5 Photographs of the planar Cu, *lc*-substrate and MPS hosts having different pore sizes.

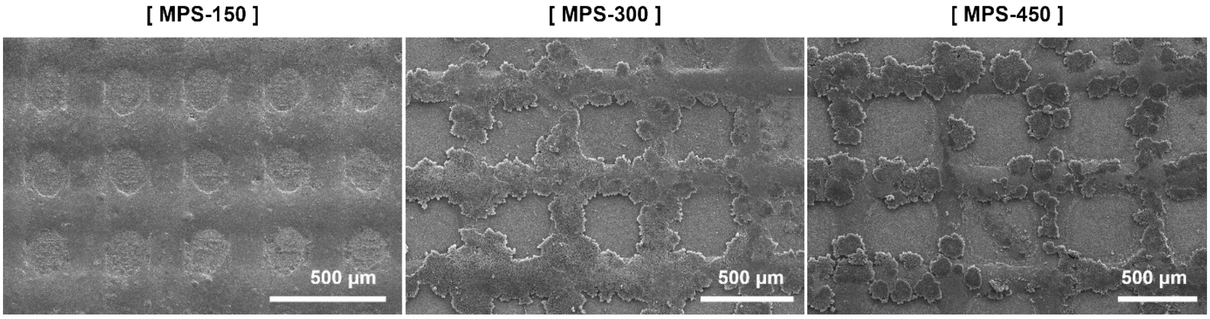

Fig. S6 Low magnification SEM images of the MPS hosts with different pore sizes after the Li deposition at a current density of 0.5 mA cm^{-2} and Li plating capacity of 1 mAh cm^{-2}: MPS-150 (left), MPS-300 (center), and MPS-450 (right).

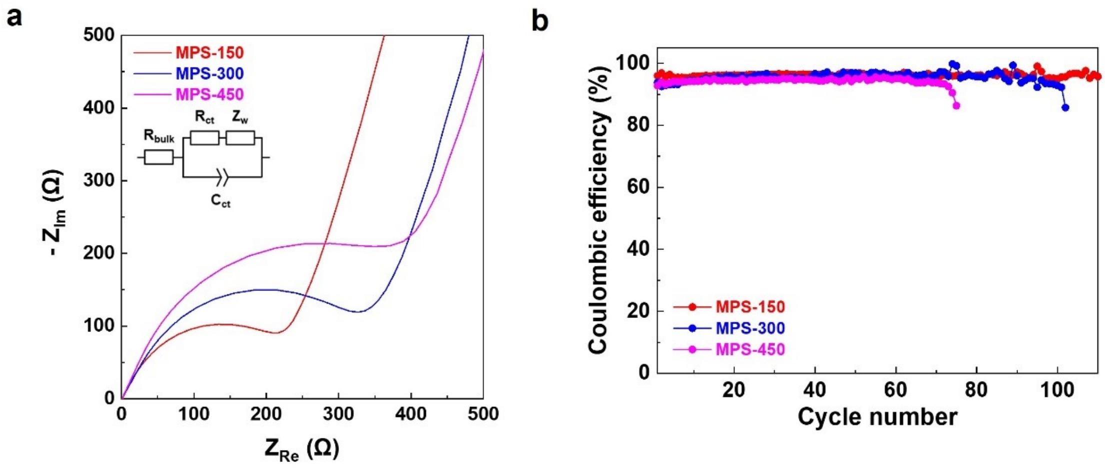

Fig. S7 (a) EIS profiles of the asymmetric cell (MPS host||Li metal) before the cycling test. (b) Coulombic efficiencies (CE) of the MPS hosts with different pore sizes (MPS-150, MPS-300 and MPS-450) during the Li plating/stripping cycling (at a current density of 3 mA cm^{-2} and an areal capacity of 3 mAh cm^{-2}).

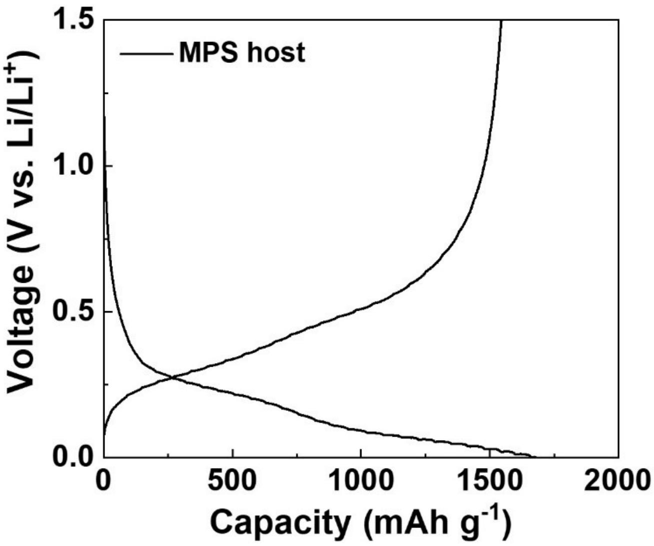

Fig. S8 Galvanostatic charge/discharge profile of the MPS host at a current density of 0.5 mA cm^{-2} and a voltage range of 0.001–1.5 V.

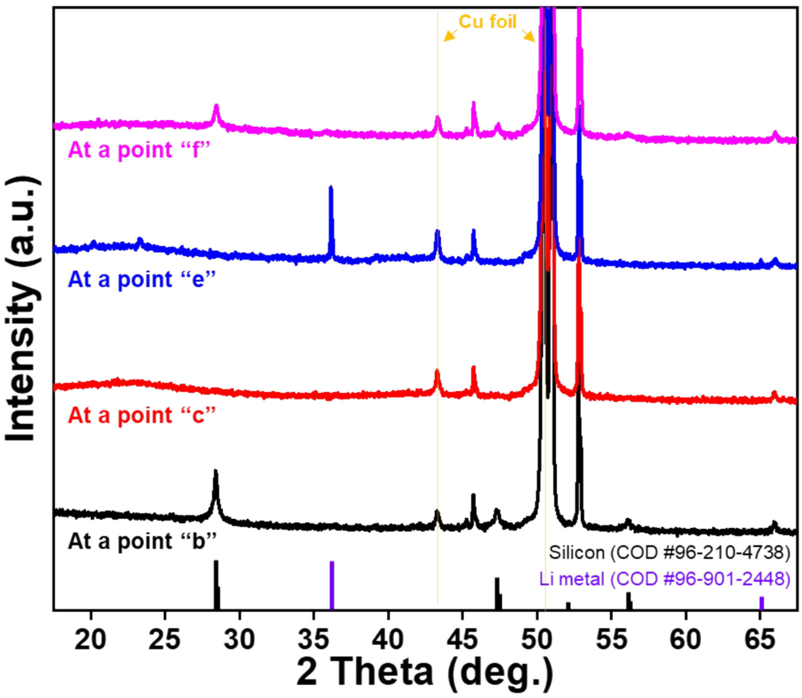

Fig. S9 Ex-situ XRD patterns of the MPS host as a function of the areal capacity shown in the voltage-capacity profile of Fig. 3a: pristine MPS host at a point "b", Si lithiation at a point "c", Li plating at a point "e", and Li stripping followed by Si delithiation at a point "f".

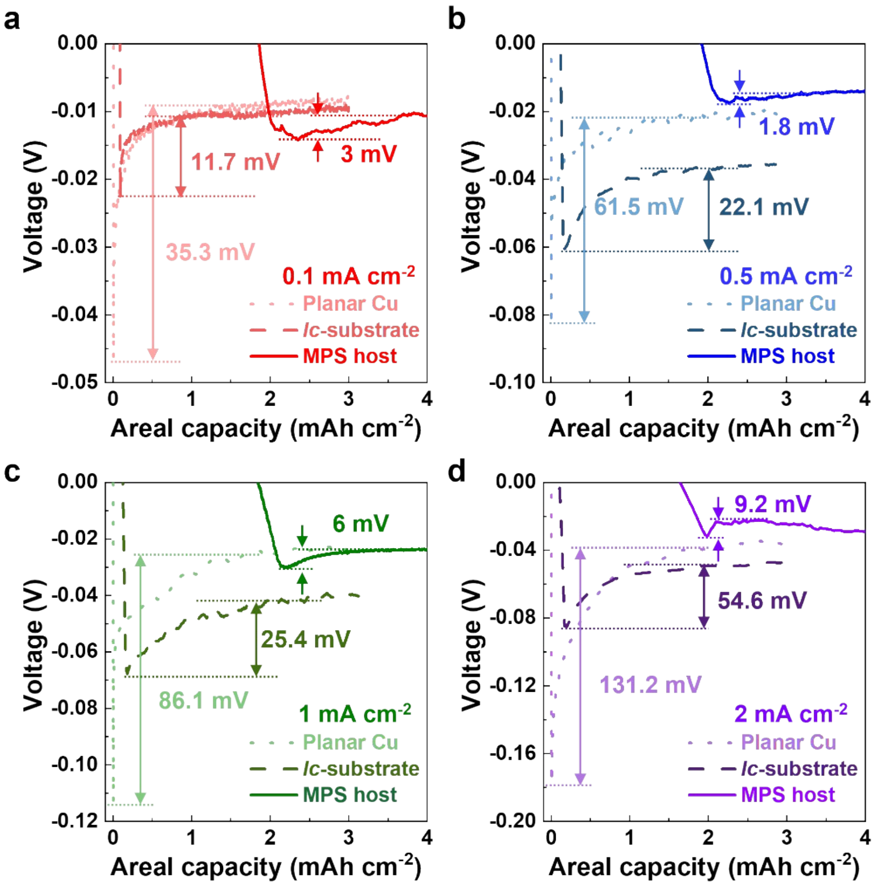

Fig. S10 Voltage profiles of the Li deposition on the planar Cu, *lc*-substrate, and MPS host at various current densities of (a) 0.1, (b) 0.5, (c) 1, and (d) 2 mA cm^{-2}.

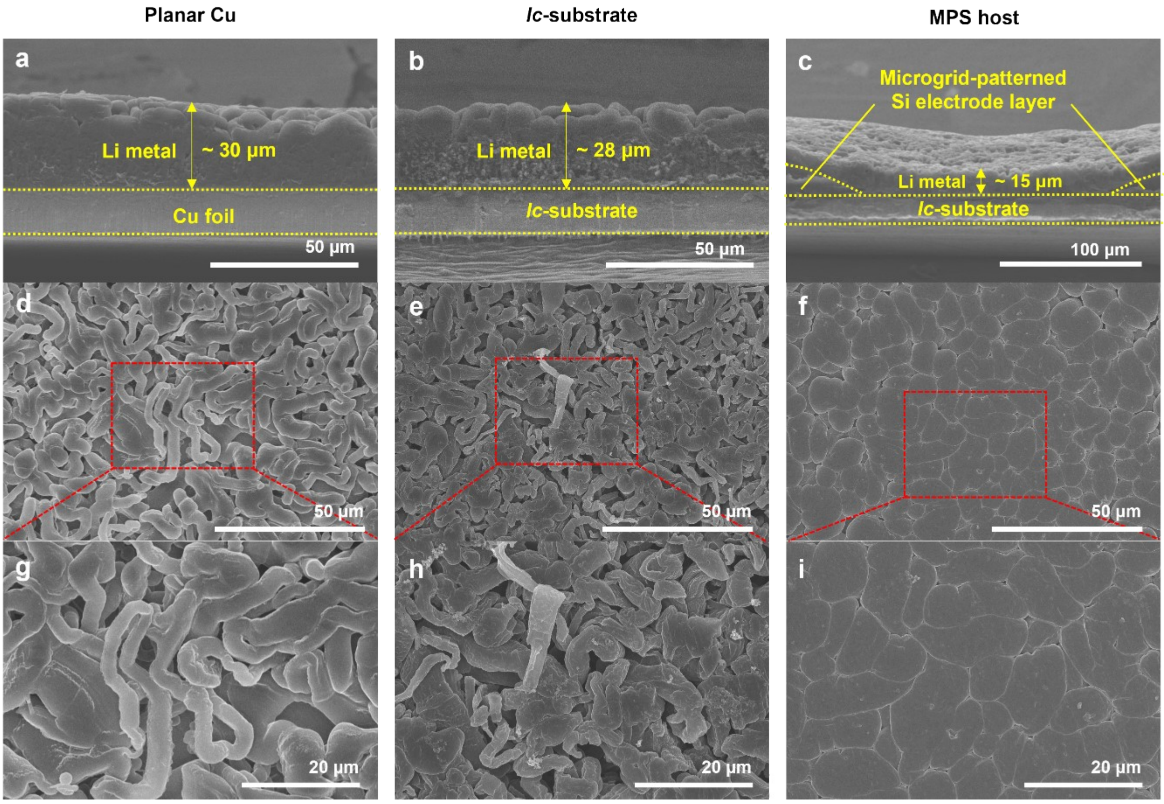

Fig. S11 Cross-sectional (a-c) and top-view (d-i) SEM images. (a, d, g) Planar Cu foil, (b, e, h) *lc*-substrate, and (c, f, i) MPS host after the Li deposition at a current density of 0.5 mA cm^{-2} and an areal capacity of 3 mAh cm^{-2}.

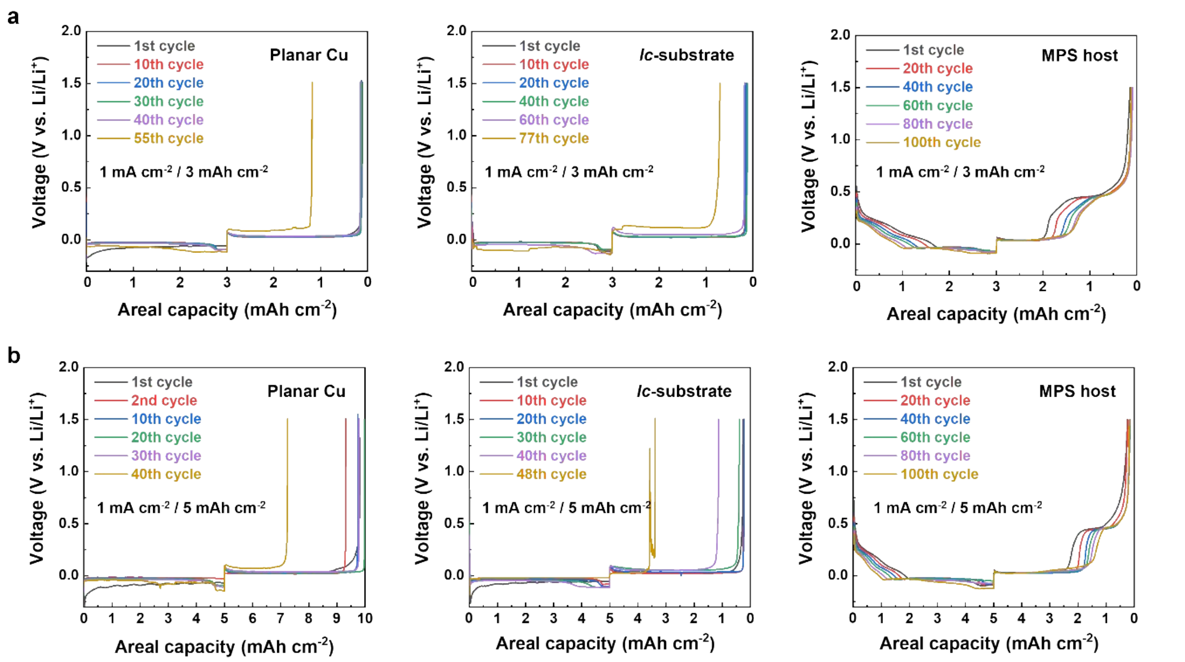

Fig. S12 Charge/discharge profiles of the planar Cu, *lc*-substrate, and MPS host during the CE test at a current density of 1 mA cm^{-2} with areal capacities of (a) 3 mAh cm^{-2} and (b) 5 mAh cm^{-2}.

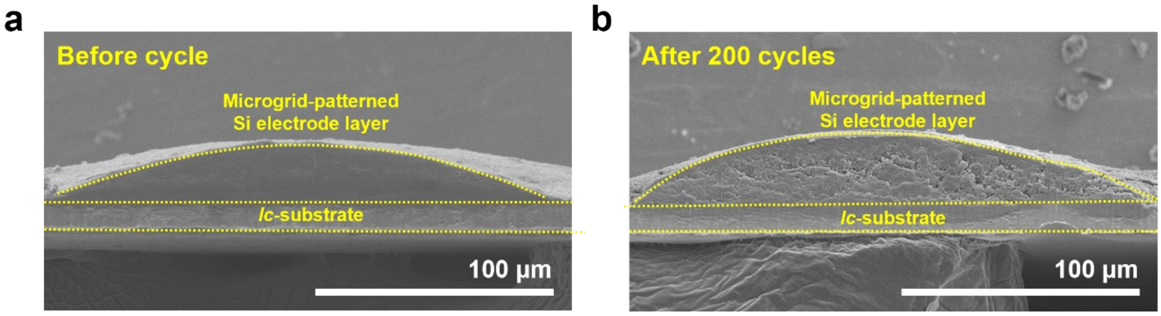

Fig. S13 Cross-sectional SEM images of the MPS host (a) before cycle and (b) after 200 cycles of CE test (current density = 1 mA cm^{-2} and areal capacity = 3 mAh cm^{-2}).

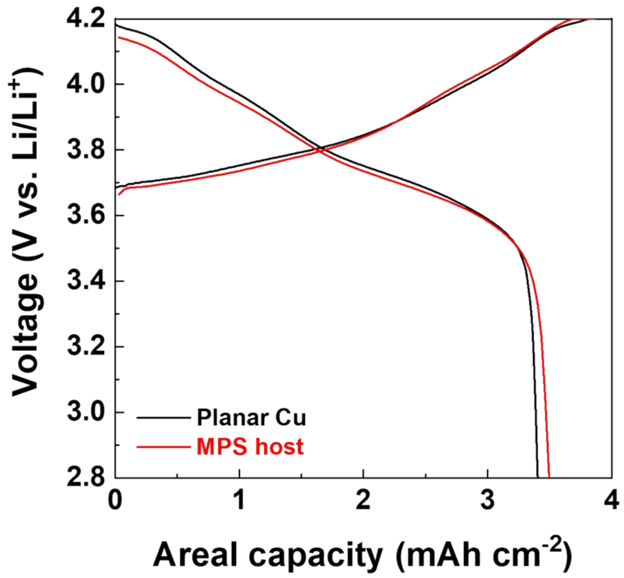

Fig. S14 The 1st charge/discharge profile of the Li-metal full cells (planar Cu foil vs. MPS host) at charge/discharge current densities of 0.1 C/0.1 C and a voltage range of 2.8–4.2 V.

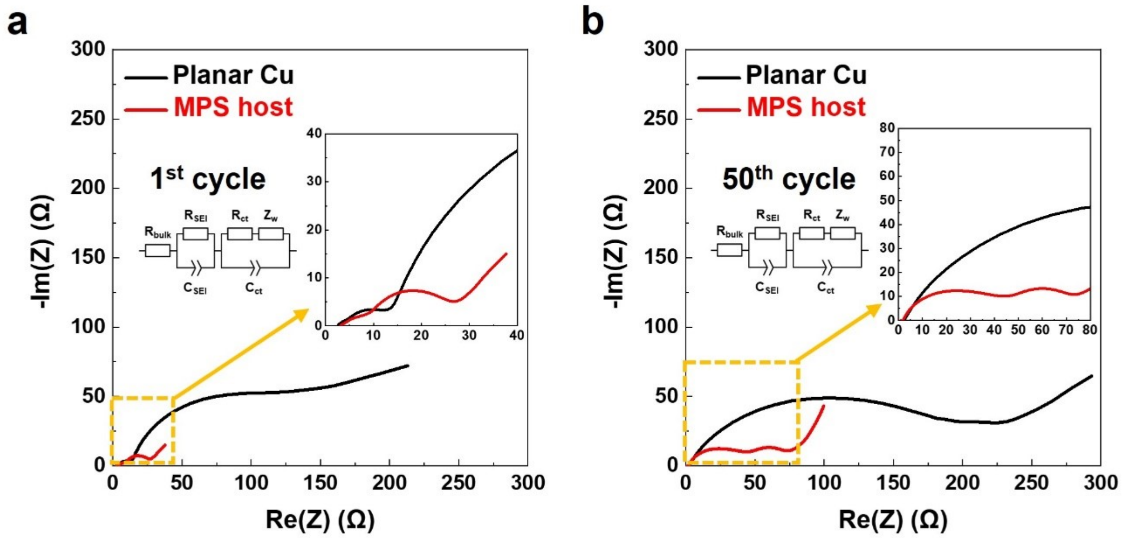

Fig. S15 EIS profiles of the Li-metal full cells with planar Cu and MPS host, in which the cells were cycled at charge/discharge current densities of 0.5 C/0.5 C and a voltage range of 2.8–4.2 V after the (a) 1st and (b) 50th cycles.

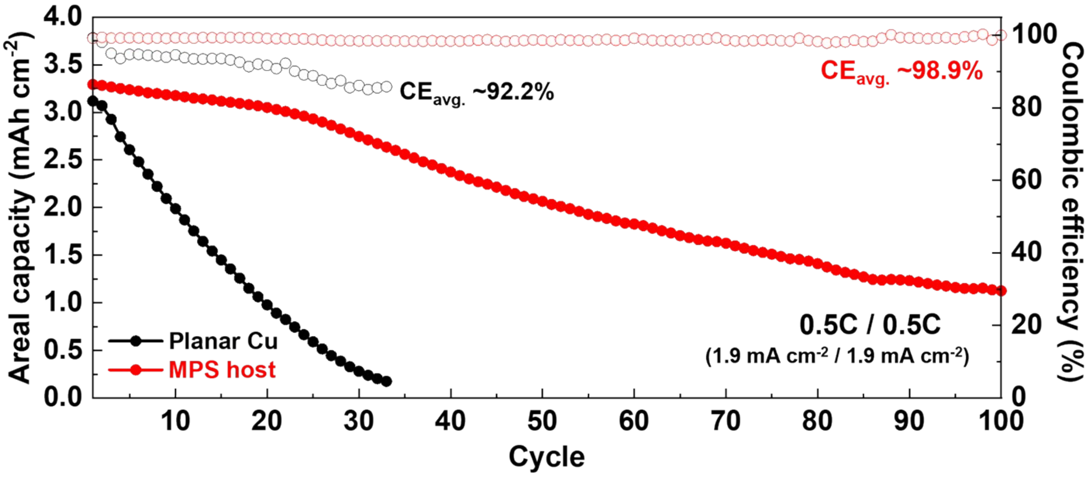

Fig. S16 Cycling performance of the Li-free full cells at charge/discharge current densities of 0.5 C/0.5 C (= 1.9 mA cm^{-2}), in which the NCM811 cathodes (areal capacity = 3.8 mAh cm^{-2}) were coupled with the pristine MPS host (vs. planar Cu foil).

Table S1. Comparison of the CE (MPS host vs. previously reported hybrid Li-ion/Li-metal anodes) with particular attention to current density and areal capacity.

Concept	Electrolyte	Current density [mA cm^{-2}]	Areal capacity [mAh cm^{-2}]	$CE_{avg.}$[a] [%] (at cycle #)	Reference
MPS host	1M $LiPF_6$ in EC/DEC = 1:1 (v/v) + 10 wt% FEC + 1 wt% VC	1	3	97.7 (200)	This work
			5	95.8 (100)	
		3	3	95 (100)	
Hybrid graphite /lithium metal	1M LiDFOB + 0.4M $LiBF_4$ in FEC:DEC = 1:2 (v/v)	-	-	-	S1
Porous lithiated graphite lamina	1M $LiPF_6$ in EC/DEC = 1:1 (v/v) + 10 wt% FEC	2	2	98.5 (140)	S3
Surface fluorinated MCMBs	1M LiFSI/LIDFOB = 8:2 (mol/mol) in FEC	0.5	2.4	99.2 (200)	S4
Prelithiated Li_xSi	1M $LiPF_6$ in FEC/FDEC/HFE = 2:6:2 (v/v/v)	-	-	-	S5
Graphite-encapsulated lithium metal	1M $LiPF_6$ in EC/DEC = 1:1 (w/w)	0.15	1.488	95 (80)	S6

a) $CE_{avg.}$ = Average coulombic efficiency = $\sum(CE)/(\text{cycle }\#)$

Table S2. Calculation details for the gravimetric and volumetric energy densities of the Li-metal full cell (NCM811||MPS host).

The gravimetric energy density of the full cell was calculated based on the weight of the cathode and anode materials. The equation was provided below:

$$Gravimetric\ energy\ density\ (Wh\ kg_{cell}^{-1}) = \frac{\text{Energy}}{\text{Mass of cell}} = \frac{\frac{\text{Energy}}{\text{Area}}}{\frac{\text{Mass of cell}}{\text{Area}}} = \frac{\text{Nominal Volatge} \times \text{C/A}}{\text{M}_{\text{cathode}}/\text{A} + \text{M}_{\text{anode}}/\text{A}}$$

, where $M_{cathode}$ and M_{anode} are the mass of cathode and anode (consisting of MPS host (2 mAh cm^{-2}) and pre-deposited Li metal (2 mAh cm^{-2}) corresponding to an areal capacity of 4 mAh cm^{-2}). C and A represent discharge capacity and area, respectively. The nominal voltage of the cell was estimated based on the integral of discharge profile divided by the discharge capacity, leading to 3.51 V. For more details, the information used to calculate the gravimetric energy density is shown below:

C/A [mAh cm^{-2}]	Nominal voltage [V]	$M_{cathode}$/A [mg cm^{-2}]	M_{anode}/A [mg cm^{-2}]	M_{total}/A [mg cm^{-2}]	Gravimetric energy density [Wh kg_{cell}^{-1}]
3.55	3.51	16.66	2.68	19.34	644

The volumetric energy density of the full cell was calculated based on the thickness of the cathode and anode materials. The equation was provided below:

$$Volumetric\ energy\ density\ (Wh\ L_{cell}^{-1}) = \frac{\text{Energy}}{\text{Thickness of cell}} = \frac{\text{Nominal Volatge} \times \text{C/A}}{\text{T}_{\text{cathode}} + \text{T}_{\text{anode}}}$$

, where $T_{cathode}$ and T_{anode} are the thickness of cathode and anode (consisting of MPS host (21 μm) and pre-deposited Li metal (1mAh cm^{-2} of Li metal is deposited inside the pore and 1mAh cm^{-2} of Li metal is densely deposited on over the whole region of the MPS host, corresponding to 5 μm of thickness). C and A represent discharge capacity and area, respectively. For more details, the information used to calculate the volumetric energy density is shown below:

C/A [mAh cm^{-2}]	Nominal voltage [V]	$T_{cathode}$ [μm]	T_{anode} [μm]	T_{total} [μm]	Volumetric energy density [Wh L_{cell}^{-1}]
3.55	3.51	55	26	81	1538

Table S3. Calculation details for the gravimetric and volumetric energy densities of the Li-ion full cell (NCM811||graphite).

To make a fair comparison, we assumed that the same areal capacity of NCM811 cathode and the N/P ratio used in the Li-metal full cell (NCM811||MPS host) were applied to the Li-ion full cell.

The gravimetric energy density of the full cell was calculated based on the weight of the cathode and anode materials. The equation was provided below:

$$Gravimetric\ energy\ density\ (Wh\ kg_{cell}^{-1}) = \frac{\text{Energy}}{\text{Mass of cell}} = \frac{\frac{\text{Energy}}{\text{Area}}}{\frac{\text{Mass of cell}}{\text{Area}}} = \frac{\text{Nominal Volatge } \times \text{ C/A}}{\text{M}_{\text{cathode}}/\text{A} + \text{M}_{\text{anode}}/\text{A}}$$

, where $M_{cathode}$ and M_{anode} are the mass of cathode and anode, respectively. The graphite anode was assumed to entirely deliver its theoretical capacity (= 372 mAh g^{-1}). Using this assumption, the mass loading of the graphite anode was estimated to be 10.75 mg cm^{-2}. C and A represent discharge capacity and area, respectively. The nominal voltage of the cell was 3.7 V.[S1] For more details, the information used to calculate the gravimetric energy density of the NCM811||graphite full cell is shown below:

C/A [mAh cm^{-2}]	Nominal voltage [V]	$M_{cathode}$/A [mg cm^{-2}]	M_{anode}/A [mg cm^{-2}]	M_{total}/A [mg cm^{-2}]	Gravimetric energy density [Wh kg_{cell}^{-1}]
3.8	3.7	16.66	10.75	27.41	513

The volumetric energy density of the full cell was calculated based on the thickness of the cathode and anode materials. The equation was provided below:

$$Volumetric\ energy\ density\ (Wh\ L_{cell}^{-1}) = \frac{\text{Energy}}{\text{Thickness of cell}} = \frac{\text{Nominal Volatge } \times \text{ C/A}}{\text{T}_{\text{cathode}} + \text{T}_{\text{anode}}}$$

, where $T_{cathode}$ and T_{anode} are the thickness of cathode and anode sheets, respectively. The thickness of the graphite anode sheet was calculated based on the previous work, in which the density of graphite anode sheet was assumed to be 1.35 g cm^{-3}.[S2] C and A represent discharge capacity and area, respectively. For more details, the information used to calculate the volumetric energy density of the NCM811||graphite full cell is shown below:

C/A [mAh cm^{-2}]	Nominal voltage [V]	$T_{cathode}$ [μm]	T_{anode} [μm]	T_{total} [μm]	Volumetric energy density [Wh L_{cell}^{-1}]
3.8	3.7	55	79.63	134.63	1044

Table S4. Comparison of the major specification and gravimetric/volumetric energy densities between the Li-metal full cell of this study and those of previously reported Li-metal full cells with hybrid Li-ion/Li metal anodes.

Concept	Active materials (cathode/ anode)	C/A [mAh cm^{-2}]	Nominal voltage [V]	$M_{cathode}$/A [mg cm^{-2}]	M_{anode}/A [mg cm^{-2}]	$T_{cathode}$ [μm]	T_{anode} [μm]	Gravimetric energy density^{a} [Wh kg_{cell}^{-1}]	Volumetric energy density^{b} [Wh L_{cell}^{-1}]	Referemce
MPS host	NCM811 /Si, Li metal	3.55	3.51	16.66	2.68	55	26	644	1538	This work
Hybrid graphite/ lithium metal	NCM532 /Graphite, Li metal	-	3.76	15.7	5.07	46.25	36	363^{c}	890^{c}	S1
Silicon coated graphite	LCO /Si, Graphite, Li metal	3.35	3.74	6.06	20.41	82	55	474	915	S2
Porous lithiated graphite lamina	NCM811 /Graphite, Li metal	2.8	3.75	20	3	-	30	457	-	S3
Surface fluorinated MCMBs	LFP /Graphite, Li metal	2.4	3.4	18.5	2.66	-	-	386	-	S4
Prelithiated Li_xSi	NCM811 /Si, Li metal	2	3.6	10	2.5	-	457	576	-	S5

a) The weight of active materials, conducting materials, binders are exclusively utilized for calculating energy density.

b) The thickness of cathode and anode materials are exclusively utilized for calculating energy density.

c) For this paper, all of the cell components (ex. electrolytes, current collectors, etc.) are utilized for calculating energy density.

Movie S1. Fabrication of the microgrid-patterned Si electrode active layers on top of the *lc*-substrate using the DIW-based printing.

Supplemental References

S1 C. Martin, M. Genovese, A. J. Louli, R. Weber and J. R. Dahn, *Joule*, 2020, **4**, 1296–1310.

S2 Y. Son, T. Lee, B. Wen, J. Ma, C. Jo, Y. Cho, A. Boies, J. Cho and M. D. Volder, *Energy Environ. Sci.*, 2020, **13**, 3723–3731.

S3 Y. Liu, X. Qin, F. Liu, B. Huang, S. Zhang, F. Kang and B. Li, *ACS Nano*, 2020, **14**, 1837–1845.

S4 C. Cui, C. Yang, N. Eidson, J. Chen, F. Han, L. Chen, C. Luo, P. F. Wang, X. Fan and C. Wang, *Adv. Mater.*, 2020, **32**, 1906427.

S5 L. Chen, X. Fan, X. Ji, J. Chen, S. Hou and C. Wang, *Joule*, 2019, **3**, 732–744.

S6 Y. Sun, G. Zheng, Z. W. Seh, N. Liu, S. Wang, J. Sun, H. R. Lee and Y. Cui, *Chem*, 2016, **1**, 287–297.