Electronic Supplementary Information for

Functional Metal-Organic Framework Boosting Lithium Metal Anode Performance via Chemical Interactions

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Experimental Details:

Preparation of MOF materials

NH_2-MIL-125(Ti) was prepared using a solvothermal method adopted with modification from the literature.[1] 2-amino-1,4-benzenedicarboxylic acid (15 mmol) and titanium isoproxide (9 mmol) were added to a solution containing 45 ml of *N,N*-dimethylformamide (DMF) and 5 mL of methanol. The mixture was stirred to form a homogeneous solution, which was then transferred to a 50 mL Teflon-lined stainless steel autoclave and heated at 453 K for 16 h. After the reaction, a yellow precipitate was collected by centrifugation and washed with DMF and methanol. The product was then dispersed in DMF and refluxed for 5 h. Centrifugation and methanol washing followed by vacuum drying at 323 K were used to recover the product. After that, the material was treated in Ar atmosphere at 473 K for 5 h in a tube furnace. The same procedure was adopted to synthesize MIL-125(Ti) except that 1,4-benzenedicarboxylic acid was used as the linker.

Fabrication of MOF-coated separators

MOF material and Nafion binder (5 wt% solution, Sigma-Aldrich) with a mass ratio of 80:20 were dispersed in ethanol to make a slurry. The slurry was then coated onto both sides of a commercial PP separator (Celgard, 3501) with the doctor blading method, followed by vacuum drying at 323 K overnight. After that, the MOF-coated separator was punched into disks with a diameter of 20 mm. The MOF-coated separator was immersed into a 1 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 volumetric ratio) solution for Li ion exchange, and then dried in vacuum before use. Control experiments were performed to exclude the contribution of Nafion to the observed cycling stability of Li metal electrodes with MOF-coated separators (Figure S11).

Characterization

XRD patterns were recorded using a Rigaku Smart Lab diffractometer with Cu K_α radiation. TEM images were obtained using a JOEL 1400 plus electron microscope operated at 80 kV. Scanning electron microscopy (SEM) observation was obtained on the Hitachi SU8230.

Electrochemical measurement

For the Li | Cu cell measurements, 2032-type coin cells were assembled with a 16 mm-diameter Li foil disk, a 14 mm-diameter Cu foil disk and a separator. 80 µL of 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) in 1, 3-dioxolane (DOL)/1, 2-dimethoxyethane (DME) (1:1 volumetric ratio) solution with 2 wt% $LiNO_3$ additive was used as electrolyte. The cells were measured by a BT2143 battery analyzer (Arbin Instrument). The assembled cell was firstly cycled between 0.005 and 1 V at 100 µA for 10 conditioning cycles. After that, electrochemical Li plating at a certain current density was performed until a certain capacity was reached, followed by Li stripping at the same current density with a cut-off voltage of 0.5 V.

For the Li | Li cell measurements, symmetric cells were assembled with Li disks as both the working and counter electrodes. 80 µL of 1 M LiTFSI in DOL/DME (1:1 volumetric ratio) solution with 2% $LiNO_3$ was used as electrolyte. The cell was firstly cycled at 0.25 and 0.5 mA cm^{-2} for 20 cycles each, with the charging and discharging time controlled to be 1 h each. Long-term cycling was then performed at 1.0 mA cm^{-2} with a cut-off capacity of 1 mAh cm^{-2}. The Li ion transference numbers were obtained from alternating-current (AC) impedance and direct-current (DC) polarization measurements performed on a symmetric Li | Li cell. AC impedance test was used to obtain the cell total resistance R_{cell}.[2] It was conducted on a Biologic VMP3 potentiostat in a scanning frequency range from 200 kHz to 0.01 Hz at open circuit potential with an amplitude of 10 mV. DC polarization measurements were also carried out on VMP3 with different voltage bias (10 mV, 30 mV and 50 mV) to obtain stable I_{DC} and derive R_{DC} ($R_{DC}=V_{DC}/I_{DC}$). The Li ion transference number was calculated by the equation $t_{Li+}=R_{cell}/R_{DC}$.[2]

Supplementary Figures:

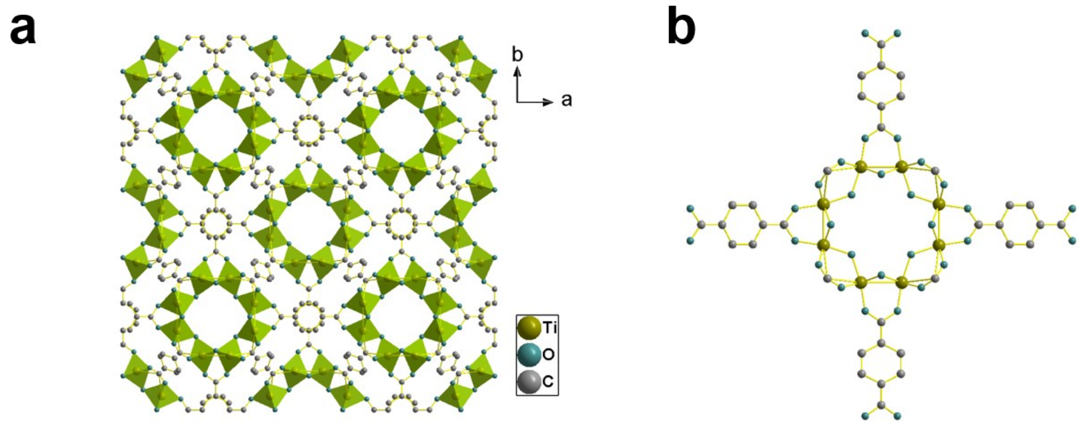

Figure S1. (a) Illustration of the structure of MIL-125(Ti). (b) One node of the MIL-125(Ti) structure.

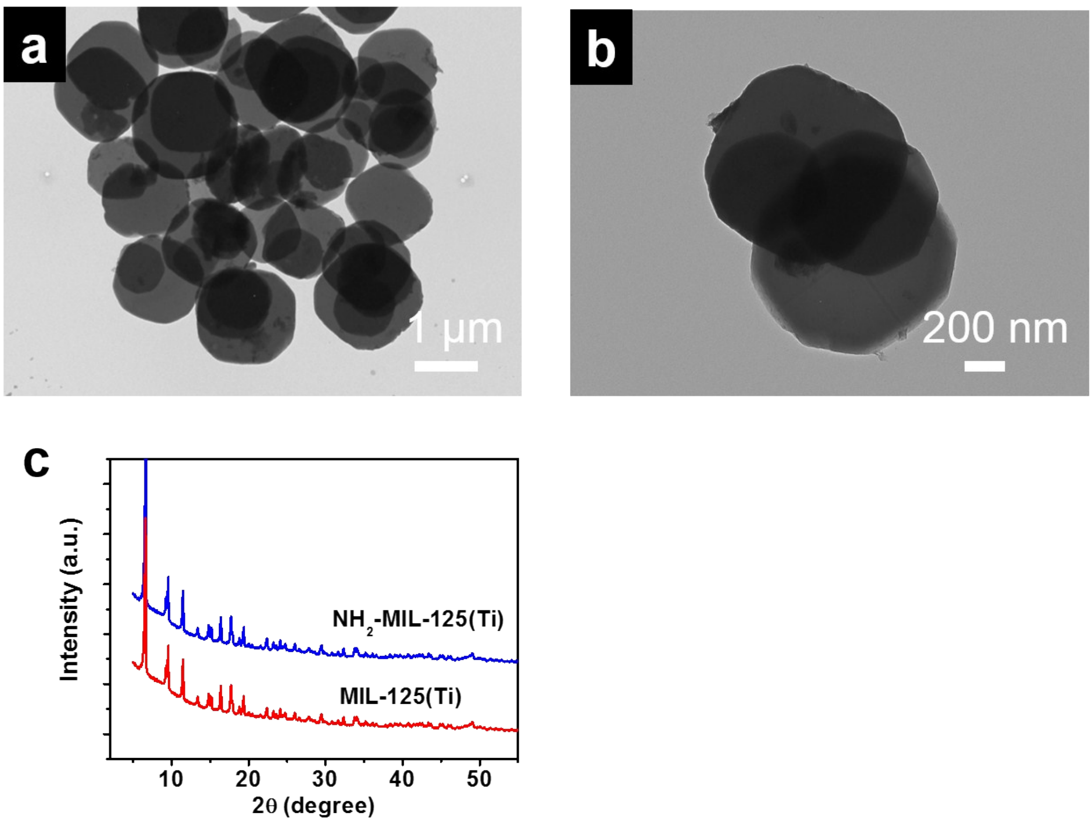

Figure S2. (a, b) TEM images of synthesized NH_2-MIL-125(Ti). (c) XRD patterns of MIL-125(Ti) and NH_2-MIL-125(Ti).

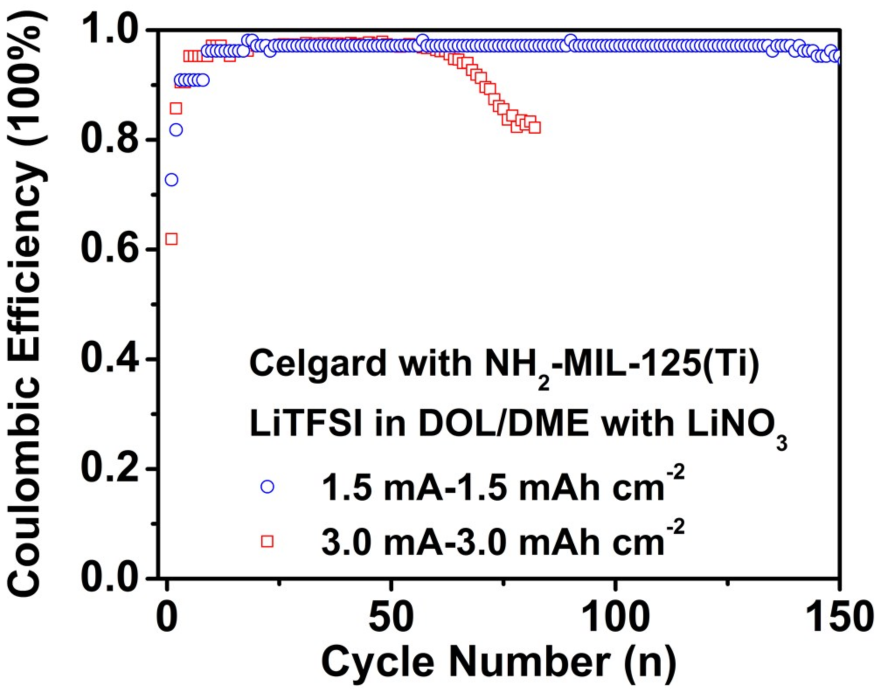

Figure S3. CE of Li plating/stripping under 1.5 mA cm^{-2}-1.5 mAh cm^{-2} and 3 mA cm^{-2}-3 mAh cm^{-2} conditions for Li | Cu cells with the NH_2-MIL-125(Ti)-coated separator.

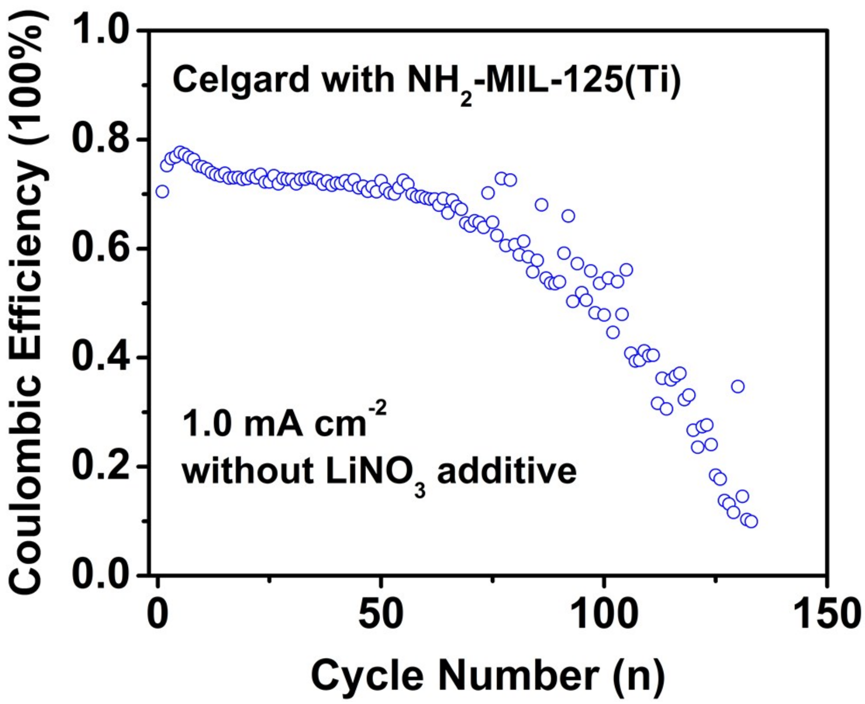

Figure S4. CE of Li plating/stripping under 1 mA cm^{-2}-1 mAh cm^{-2} conditions for a Li | Cu cell with the NH_2-MIL-125(Ti)-coated separator but without $LiNO_3$ additive in the electrolyte.

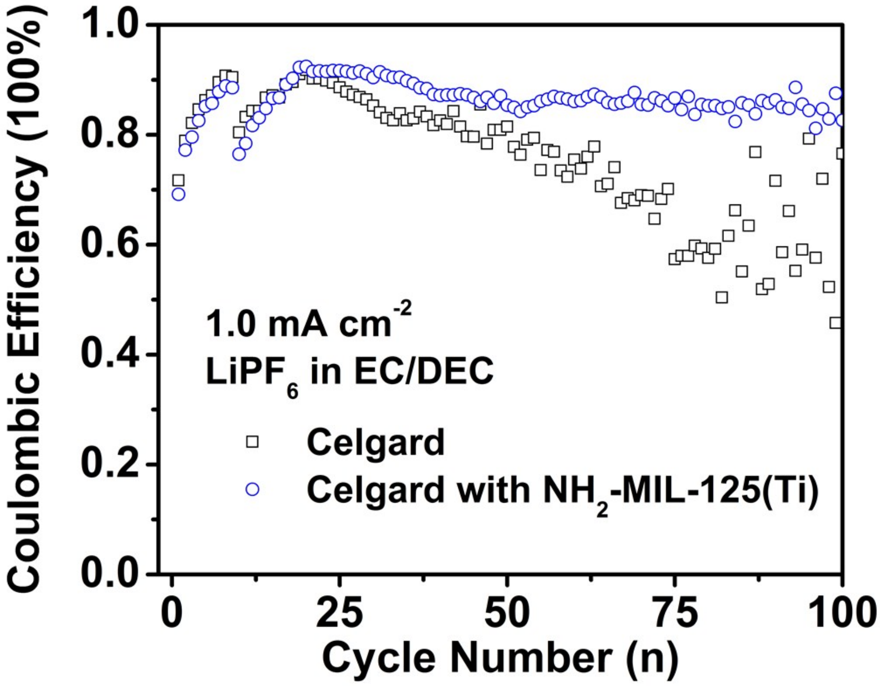

Figure S5. CE of Li plating/stripping under 1 mA cm^{-2}-1 mAh cm^{-2} conditions for Li | Cu cells with the pristine and NH_2-MIL-125(Ti)-coated separators. The electrolyte is 1.0 M $LiPF_6$ in mixed EC/DEC (1:1 V/V). The cells were first conditioned at 0.25 mA cm^{-2}-0.25 mAh cm^{-2} for 10 cycles before entering 1 mA cm^{-2}-1 mAh cm^{-2} cycling.

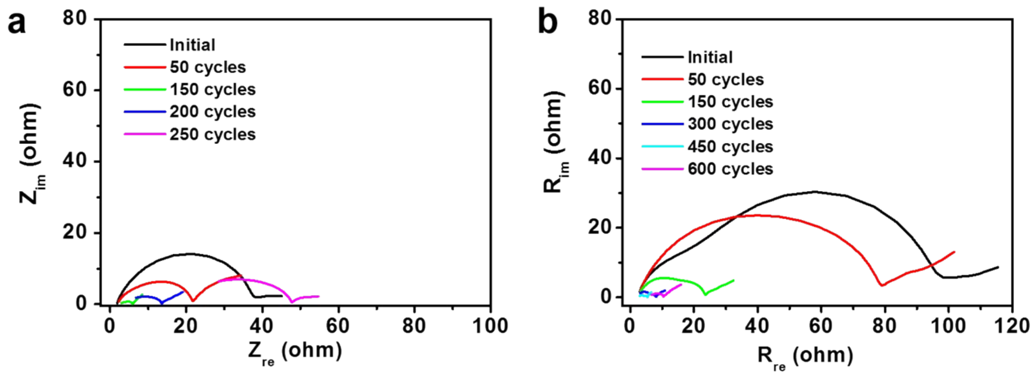

Figure S6. Evolution of EIS spectra of Li | Li cells with the (a) pristine and (b) NH_2-MIL-125(Ti)-coated separators over cycling. The cells were firstly cycled at 0.25 and 0.5 mA cm^{-2} for 25 cycles each, with the charging and discharging time controlled to be 1 h each. Long-term cycling was then performed at 1.0 mA cm^{-2} with a cut-off capacity of 1 mAh cm^{-2}. EIS spectra were collected before cycling and after every 50 cycles.

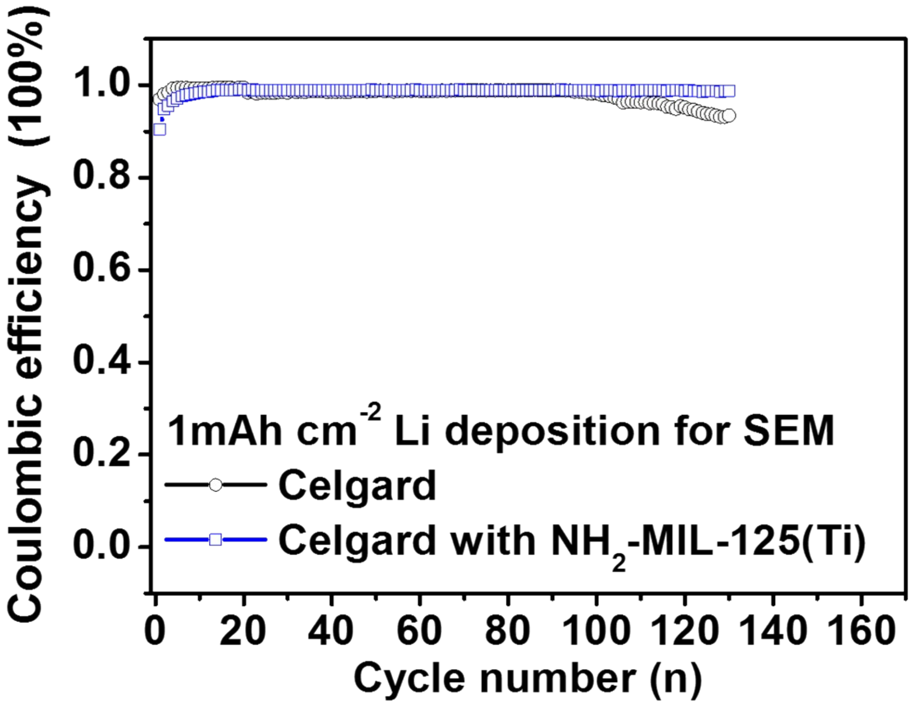

Figure S7. CE of consecutive Li plating/stripping cycles under 0.5 mA cm^{-2}-1 mAh cm^{-2} conditions for Li | Cu cells with the pristine and NH_2-MIL-125(Ti)-coated separators. The electrodes after cycling were imaged with SEM to generate the results shown in Figure 4. The separator after cycling was analyzed with XRD to get the diffraction pattern in Figure S8.

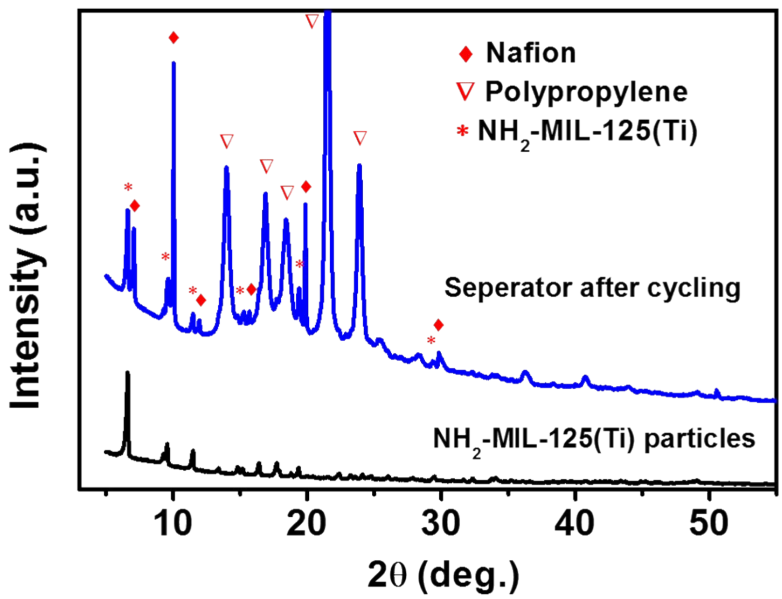

Figure S8. XRD pattern of the NH_2-MIL-125(Ti)-coated separator after repeated lithium deposition/stripping, compared to that of the as-synthesized NH_2-MIL-125(Ti) material.

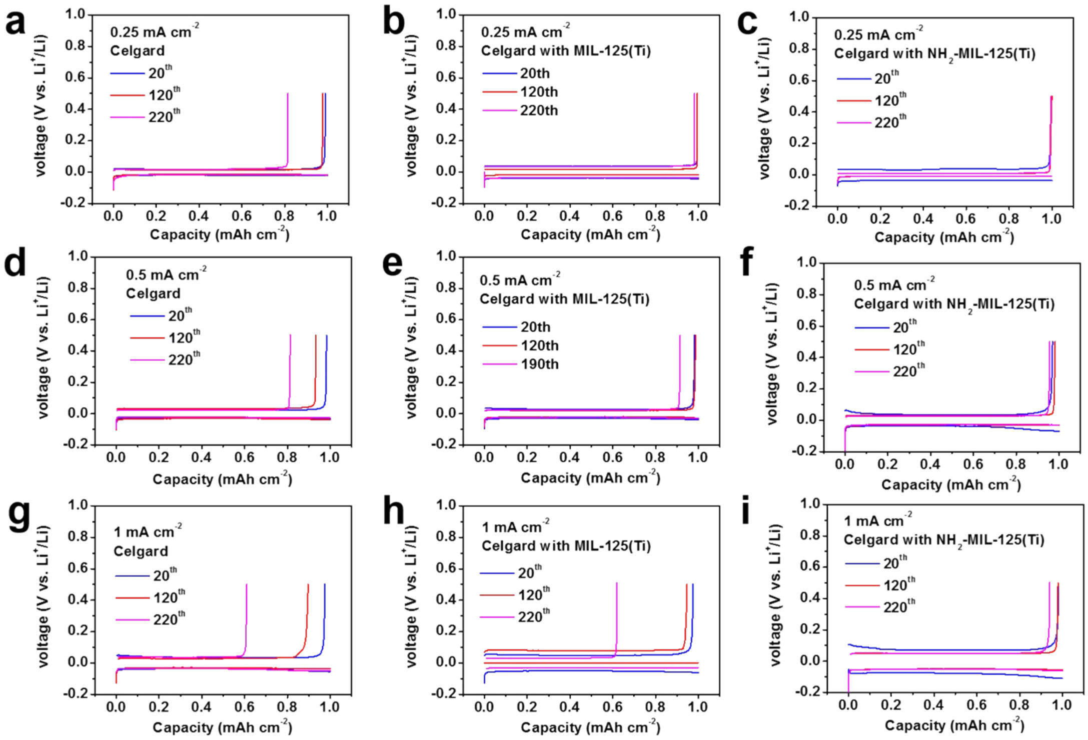

Figure S9. Discharging and charging voltage profiles of Li | Cu cells with the pristine (a, d and g), MIL-125 (Ti)-coated (b, e and h) and NH_2-MIL-125 (Ti)-coated (c, f and i) separators at various current densities of 0.25, 0.5 and 1 mA cm^{-2}.

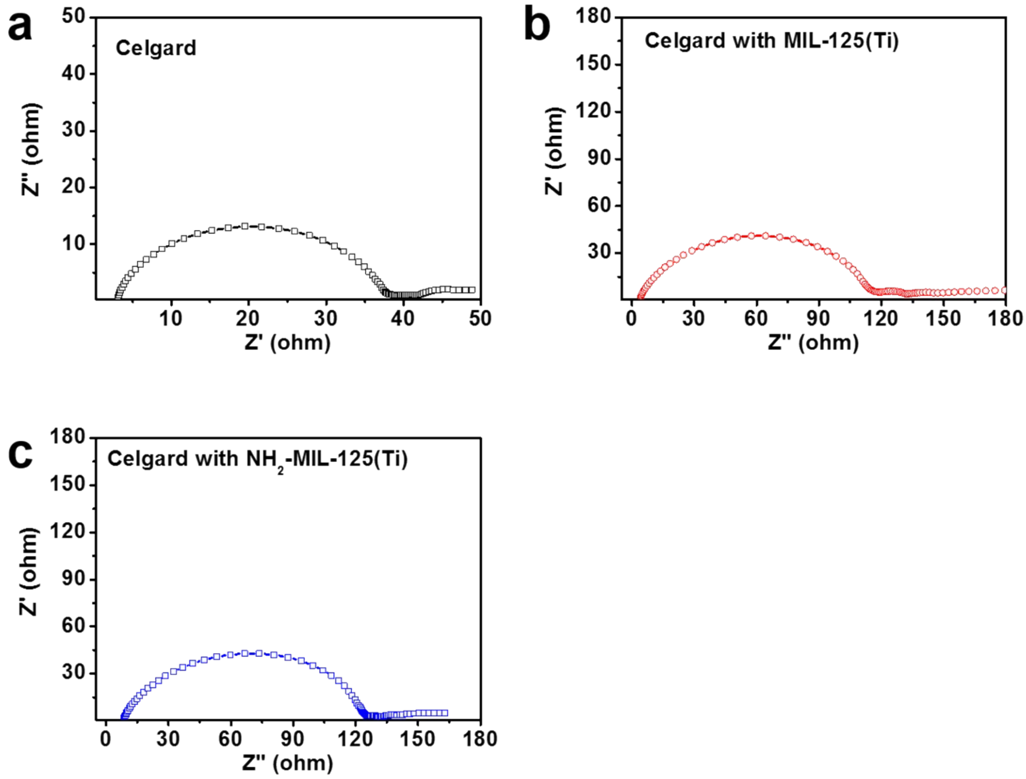

Figure S10. EIS spectra of Li | Li cells with the (a) pristine, (b) MIL-125 (Ti)-coated and (c) NH_2-MIL-125 (Ti)-coated separators.

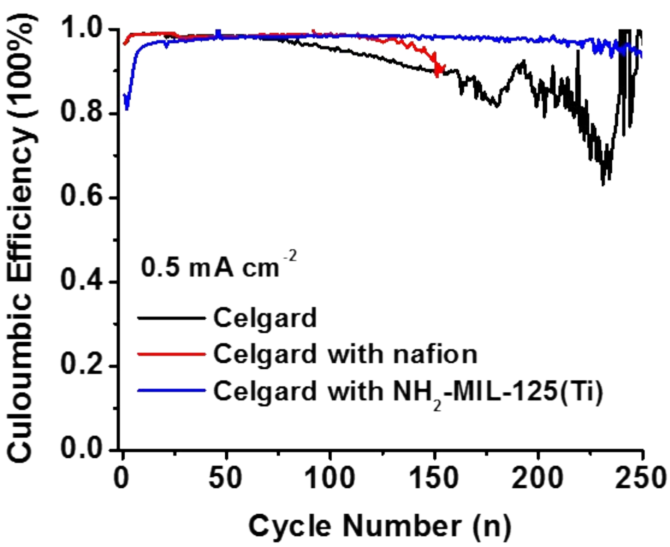

Figure S11. CE of consecutive Li plating/stripping cycles under 0.5 mA cm^{-2}-1.0 mAh cm^{-2} conditions for Li | Cu cells with the pristine separator, a Nafion-coated separator, and the NH_2-MIL-125(Ti)-coated separator.

Table S1：Performance comparison with the state-of-the-art Li metal anodes stabilized by various strategies.

	Material	**Electrolyte**	**Coulombic efficiency for Li | Cu cell**	**Cycle number for Li | Li cell**	**Refer**
1	NH_2-MIL-125(Ti) coated separator	1 M LiTFSI in DOL/DME with 2% $LiNO_3$	99%@0.25 mA cm^{-2}-1 mAh cm^{-2} for 350 cycles; 98.2%@ 0.5 mA cm^{-2}-1 mAh cm^{-2} for 250 cycles; 97.5% @1 mA cm^{-2}-1 mAh cm^{-2} for 220 cycles	500 cycles (1200 h)@1 mA cm^{-2}-1 mAh cm^{-2}	This work
			400 consecutive cycles with 99% @ 0.5 mA cm^{-2}-0.5 mAh cm^{-2} for 200 cycles and 98.5% @1 mA cm^{-2} -1 mAh cm^{-2} for 200 cycles		
2	Polyimide coating layer with nano channels	1 M LiTFSI in DOL/DME with 1% $LiNO_3$	97.6%@1 mA cm^{-2}-0.5 mAh cm^{-2} for over 240 cycles; 92.9%@2 mA cm^{-2}-0.5 mAh cm^{-2} for over 150 cycles; 88.6%@3 mA cm^{-2}-0.5 mAh cm^{-2} for over 140 cycles	N/A	[3]
3	3D ZnO-polyimide matrix	1 M LiTFSI in DOL/DME with 1 wt% $LiNO_3$	N/A	100 cycles@1/3/5 mA cm^{-2}-1 mAh cm^{-2}	[4]
4	3D rGO	1 M $LiPF_6$ in EC/DEC with VC+FEC	N/A	250 cycles@1 mA cm^{-2}-1 mAh cm^{-2}	[5]
		1 M LiTFSI in DOL/DME with 1 wt% LiNO3	N/A	450 cycles@1 mA cm^{-2}-1 mAh cm^{-2}	
5	Interconnected hollow carbon nano spheres	1 M LiTFSI in DOL/DME with 1% $LiNO_3$ and 100 mM Li_2S_8	99%@0.25 mA cm^{-2}-1 mAh cm^{-2} for 150 cycles; 98.5%@0.5 mA cm^{-2}-1 mAh cm^{-2} for 150 cycles; 97.5%@1 mA cm^{-2} -1 mAh cm^{-2} for 150 cycles	N/A	[6]
6	Adaptive polymer film	1 M LiTFSI in DOL/DME with 1% $LiNO_3$	97%@1 mA cm^{-2}-1 mAh cm^{-2} for 180 cycles; 97.7%@1 mA cm^{-2}-3 mAh cm^{-2} for 80 cycles	N/A	[7]

7	3D porous Cu	1 M LiTFSI in DOL/DME with 1% $LiNO_3$	97%@0.5 mA cm^{-2}-1 mAh cm^{-2} for 250 cycles; 97%@1.0 mA cm^{-2}-1.0 mAh cm^{-2} for 150 cycles	100 cycles (1000 h)@0.2 mA cm^{-2}-1 mAh cm^{-2}	[8]
8	3D oxidized polyacrylonitrile nanofiber network	1 M LiTFSI in DOL/DME with 2% $LiNO_3$	97.9%@1 mA cm^{-2}-1 mAh cm^{-2} for over 120 cycles; 97.4%@3.0 mA cm^{-2}-1.0 mAh cm^{-2} for over 120 cycles	120 cycles (80 h)@3 mA cm^{-2}-1 mAh cm^{-2}	[9]
9	3D glass fiber cloth	1 M LiTFSI in DOL/DME with 2% $LiNO_3$	98%@0.5 mA cm^{-2}-0.5 mAh cm^{-2} for 90 cycles; 97%@1.0 mA cm^{-2}-0.5 mAh cm^{-2} for 70 cycles; 96%@2.0 mA cm^{-2}-0.5 mAh cm^{-2} for 63 cycles	500 cycles (160 h)@1 mA cm^{-2}-0.16 mAh cm^{-2}	[10]
10	PDMS film with nano-pores	1 M $LiPF_6$ in EC/DEC	94.5%@0.5 mA cm^{-2}-1 mAh cm^{-2} for 200 cycles	N/A	[11]
		1 M LiTFSI in DOL/DME with 1% $LiNO_3$	98.2%@1 mA cm^{-2}-1 mAh cm^{-2} for 100 cycles	N/A	
11	Cu nanowire membrane	1 M LiTFSI in DOL/DME with 1% $LiNO_3$ and 5mM Li_2S_8	98.6%@1 mA cm^{-2}-1 mAh cm^{-2} for 200 cycles;	225 cycles (550 h)@1 mA cm^{-2}-1 mAh cm^{-2}	[12]
12	Py13TSI	2 M LiTFSI/PY13TFSI in DOL/DME	99.1%@1 mAh cm^{-2} for 360 cycles;	90 cycles@0.5 mA cm^{-2}-1 mAh cm^{-2}	[13]
13	lithium polysulfide additive	1M LiTFSI in DOL/DME with 5% $LiNO_3$ and 180 mM Li_2S_8	99.1%@2 mA cm^{-2}-1 mAh cm^{-2} for over 400 cycles; 98.5%@2 mA cm^{-2}-2 mAh cm^{-2} for over 200 cycles	N/A	[14]
14	LiF additive	1 M $LiPF_6$ in EC/EMC with VC additive	82-85%@1 mA cm^{-2}-1 mAh cm^{-2} for 50 cycles	N/A	[15]
		1 M LiTFSI in PC	N/A	300 cycles@0.38 mA cm^{-2}-1.14 mAh cm^{-2}	
15	Nanoporous polymer-ceramic composite electrolyte	1 M LiTFSI in PC	N/A	160 cycles (1000 h)@0.2 mA cm^{-2}-0.6 mAh cm^{-2}	[16]
16	High concentration electrolyte	4 M LiFSI in DME	98.4%@4.0 mA cm^{-2}-1 mAh cm^{-2} for over 1000 cycles	6000 cycles@10 mA cm^{-2}-0.5 mAh cm^{-2}	[17]

17	Hollow carbon shells with Au particle	1 M $LiPF_6$-EC/DEC with 1%VC+10%FEC	98%@0.5 mA cm^{-2}-1 mAh cm^{-2} for over 300 cycles	N/A	[18]
18	3D conducting scaffold	1 M $LiPF_6$ in EC/DEC	N/A	80 cycles@3 mA cm^{-2}-1 mAh cm^{-2}	[19]
19	h-BN layer	1 M $LiPF_6$ in EC/DEC (BASF LP40)	97%@0.5 mA cm^{-2}-1.0 mAh cm^{-2} for over 50 cycles; 95%@1.0 mA cm^{-2}-1.0 mAh cm^{-2} for over 50 cycles	N/A	[20]
	Graphene layer	1 M $LiPF_6$ in EC/DEC (BASF LP40)	95%@0.5 mA cm^{-2}-1.0mAh cm^{-2} for over 50 cycles; 93%@1.0 mA cm^{-2}-1.0 mAh cm^{-2} for over 50 cycles	N/A	
20	h-BN coated separator	1 M $LiPF_6$ in EC/DEC	92%@0.5 mA cm^{-2}-1.0 mAh cm^{-2} for 100 cycles; 88% @1.0 mA cm^{-2}-1.0 mAh cm^{-2} for 100 cycles	N/A	[21]
21	Nafion polymer electrolyte membrane	1 M $LiPF_6$ in EC/DEC	N/A	100 cycle (2000 h)@0.75 mA cm^{-2}-7.5 mAh cm^{-2}; 250 cycles (2000 h)@10mA cm^{-2}-40 mAh cm^{-2}	[22]
22	Polyoxyzole nanofiber membrane	1 M $LiPF_6$ in EC/DEC/EMC	N/A	116 cycles (700 h)@0.38 mA cm^{-2}-1.16 mAh cm^{-2}	[23]
23	Al_2O_3 coating layer	1 M $LiPF_6$ in EC/DMC	N/A	1259 cycles@1 mA cm^{-2}-0.25 mAh cm^{-2}	[24]

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