Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Self-Healable Dynamic Poly(Urea-Urethane) Gel Electrolyte for Lithium Batteries

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Supporting Information

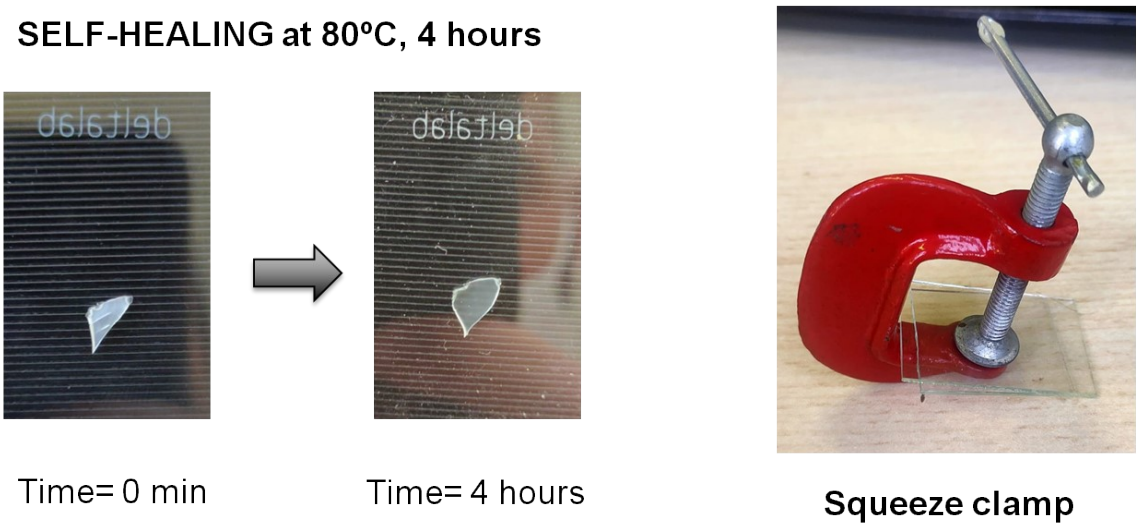


Figure S1. Representative image of self-healing process at 80 °C applying pressure with a squeeze clamp for 4 h.

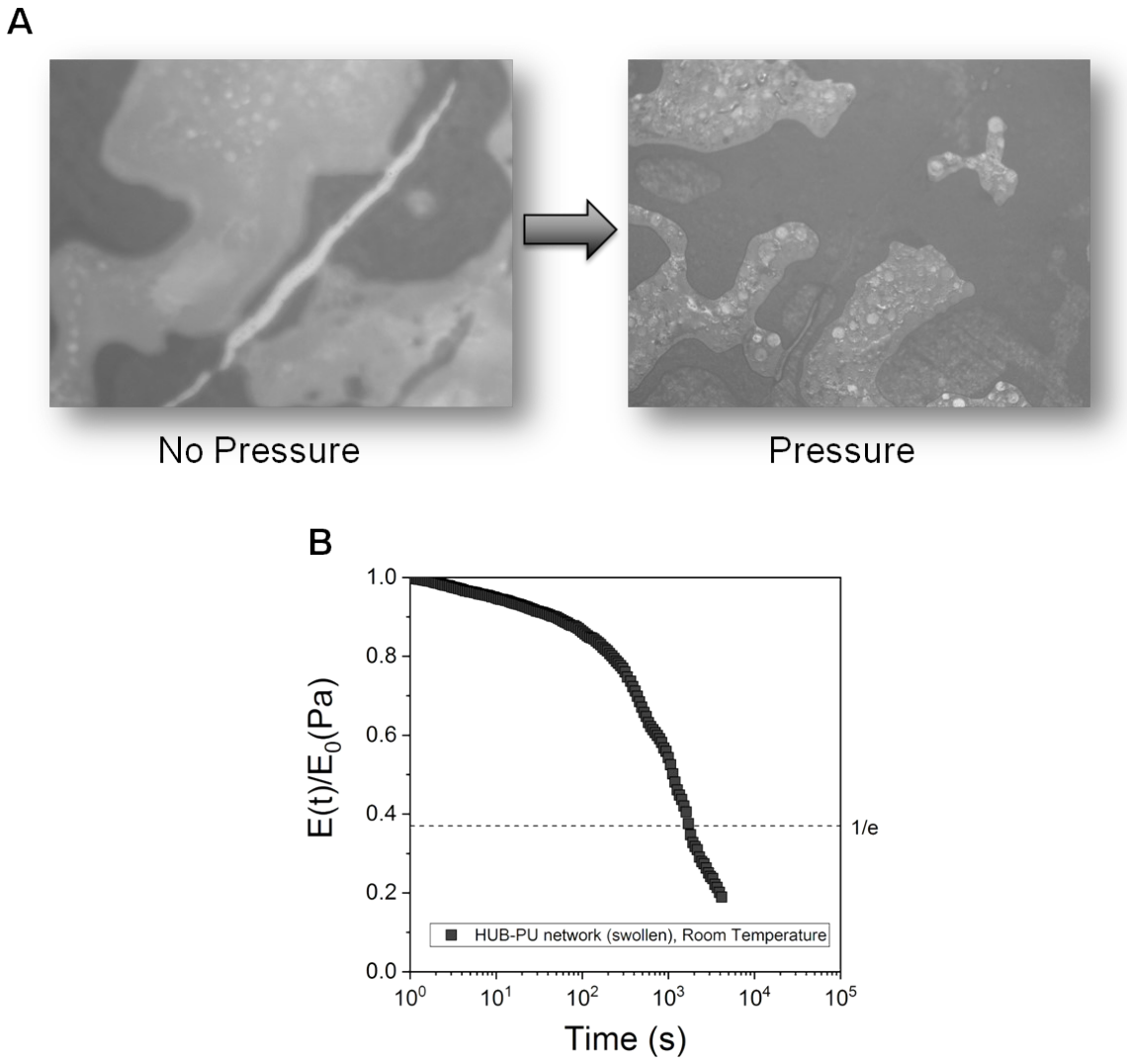


Figure S2. A) Microscopic image of scratch disappearance and **B)** Stress-relaxation measurement at room temperature of swollen HUB-PU network.

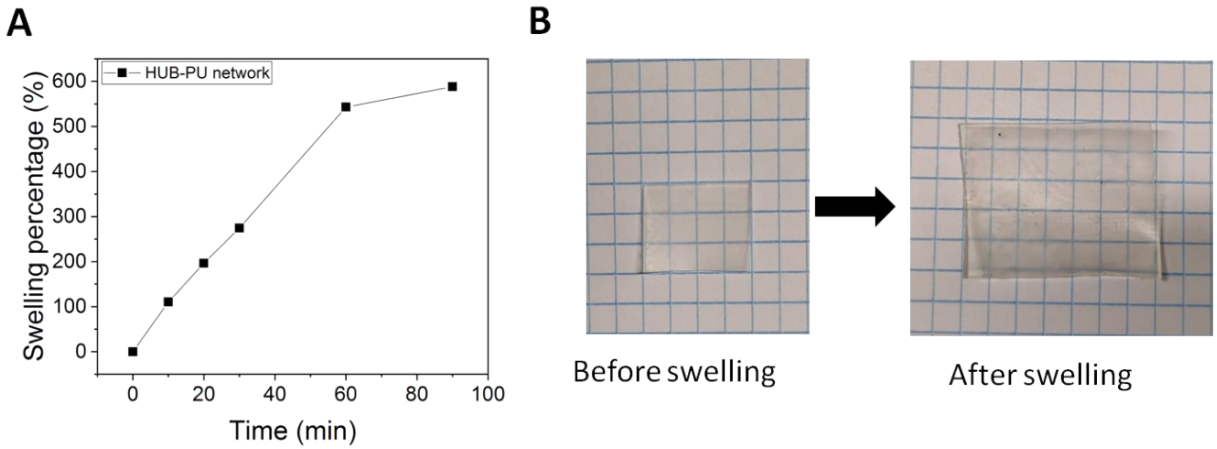
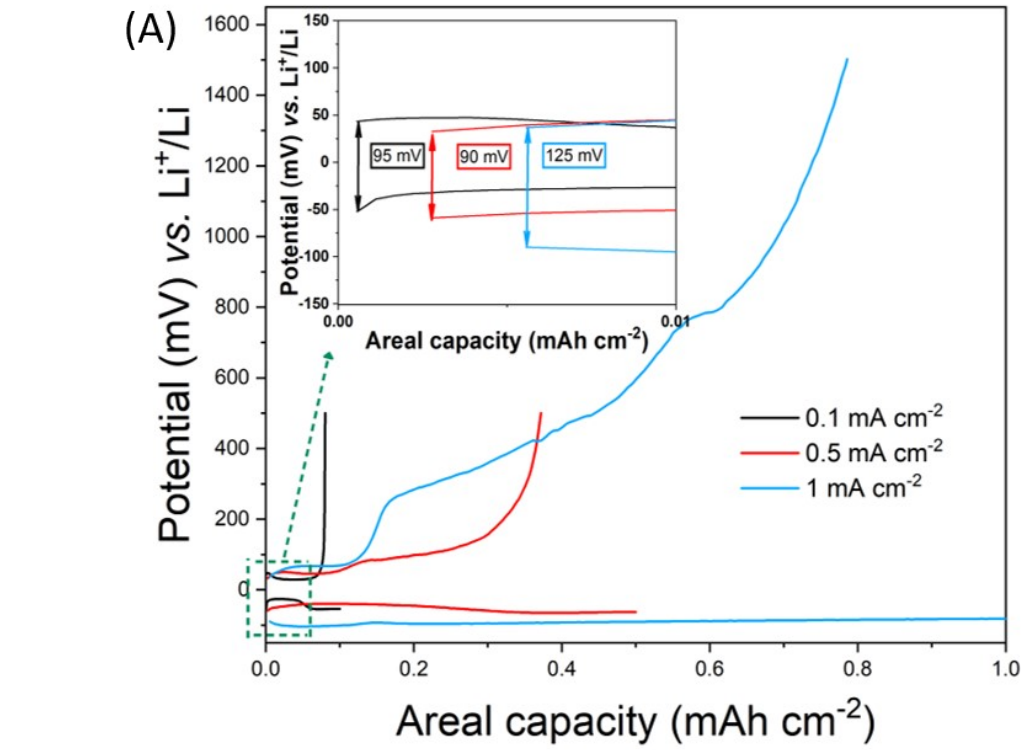
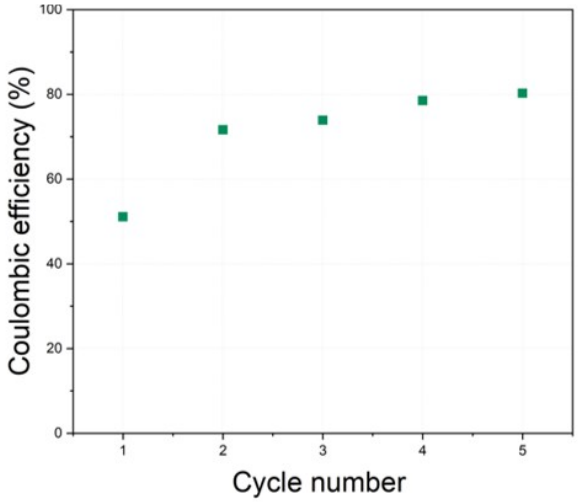


Figure S3. A) Swelling percentage (%) upon time (min) of HUB-PU network. **B)** Representative image before and after swelling of HUB-PU network in $LiPF_6$ EC:DEC (1:1 v:v).



(B)



(C)

Cycle number	CE (%)	Current density (mA cm-2)
1	51	0.1
2	71	0.1
3	74	0.1
4	78	0.1
5	80	0.1
6	73	0.5
7	61	0.5
8	68	0.5
9	74	0.5
10	74	0.5
11	61	1
12	78	1
13	90	1
14	47	1
15	51	1

Figure S4 A) Li plating and stripping potential profiles *vs.* areal capacity, measured at different current density values (0.1, 0.5 and 1 mA cm^{-2}) and referred to selected cycles (5^{th}, 10^{th} and 12^{th}). In the inset, the magnification of the initial voltage hysteresis with related values is shown; it remains quite similar even when the current is increased by an order of magnitude. **B)** Increasing trend of the Coulombic efficiencies of the first 5 cycles at 0.1 mA cm^{-2}. **C)** Coulombic efficiencies values at different cycles and current density values.

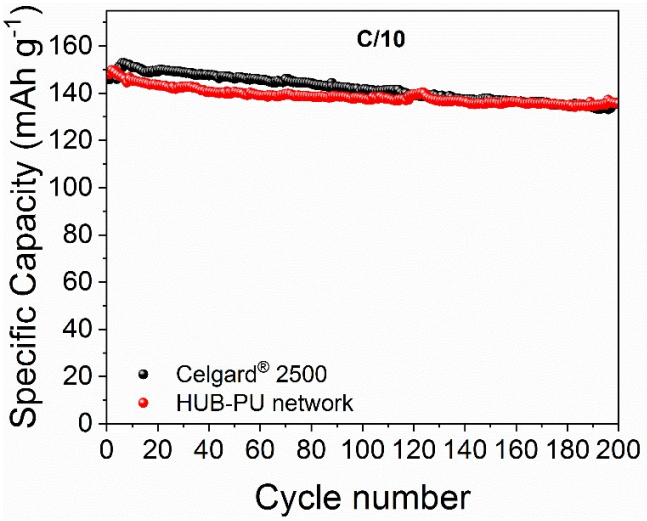


Figure S5. Comparison of specific capacities vs. cycle number of Celgard® 2500 and HUB-PU network at C/10 for 200 cycles.

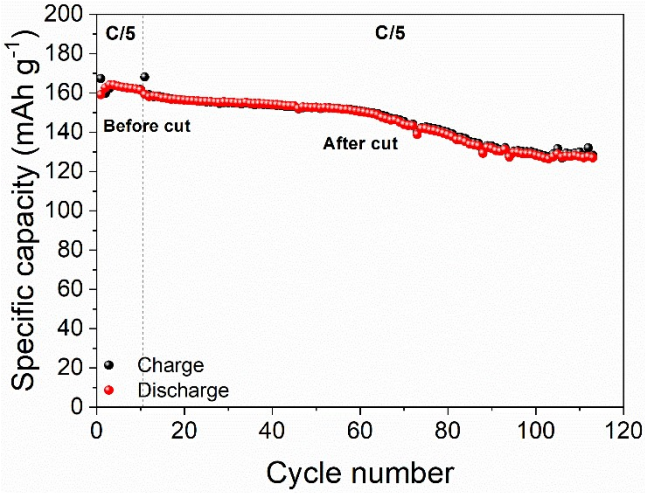


Figure S6. Cycling performances for 116 cycles of HUB-PU network mechanically damaged after 10 cycles.

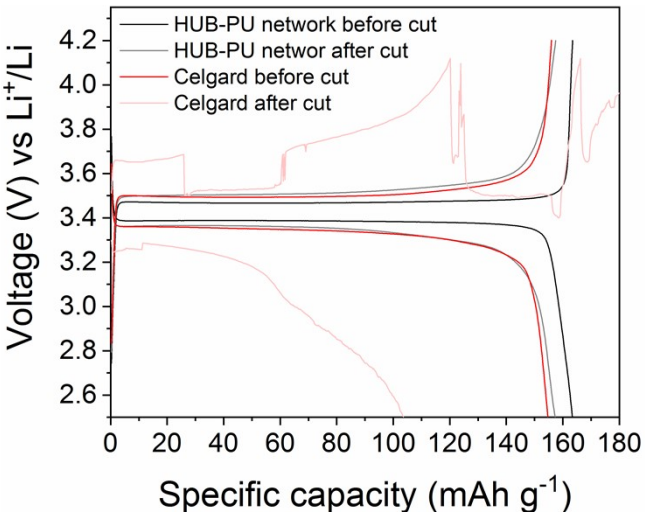


Figure S7. Comparison of voltage profiles before and after cut of commercial Celgard® 2500 and HUP-PU network.

Table S1. Comparison among the most authoritative publications in the field of self-healing polymer electrolytes for LIBs. Note: in the present work, the data relative to the last two columns are the following: 161 mAh g^{-1} (1st cycle), then 159 mAh g^{-1} after the cut (11th cycle) and 127 mAh g^{-1} at the 100th cycle.

Ref.	Electrolyte	Self-healing mechanism	Electrode and its theoretical capacity	Cycles	Specific capacity of first and last cycles	Self-healing electrochemical test
[1]	CSE, PolyIL, 2D BN nanosheets, EMIMTFSI, LiTFSI	Electrostatic interaction between IL cations and salt anions	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	200	152 and 132.4 mAh g^{-1} (@ 0.1C, 55 °C)	Cut and healed outside, then used in cell, cycled @ 0.1C, 55°C
[2]	Ceramic-in-polymer, SPE, SiO_2 NPs, PEG, PEO, LiTFSI	Chemical interaction of Li dendrites with silica	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	55	94 and and 156 mAh g^{-1} (@ 0.05C, 70 °C)	None
[3]	SPE, dicationic quaternary ammonium 6-armed, EMIMTFSI	Electrostatic interaction between IL cations and salt anions	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	50	147 and 138 mAh g^{-1} (@ 0.1C, 60 °C)	None
[4]	IGPE, NH_2-PEG-NH_2, TPB, BMImTFSI	Dynamic covalent imine bonds	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	50	154 and 132 mAh g^{-1} (@ 0.1C, RT)	None
[5]	GPE, NH_2-PEG-NH_2, BTA, LiFSI, LiDFOB, $LiPF_6$	Dynamic covalent imine bonds	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	125	142 and 139 mAh g^{-1} (@ 1C, 30 °C)	Cut and healed outside, then used in cell, cycled @ 0.1C, 55 °C
[6]	GPE, NH_2-PEG-NH_2, TFB, $LiPF_6$	Dynamic covalent imine bonds	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	300	150 and 126 mAh g^{-1} (@ 0.1C, RT)	None
[7]	SPE, SBMA, HFBM, EMITFSI, LiTFSI	Ion-dipole interaction	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	100	144 and 118 mAh g^{-1} (@ 0.2C, 60 °C)	None
[8]	SIGPE, PEGMA, UPy-MA, SSPSILi	Hydrogen bonding	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	60	129 and 129 mAh g^{-1} (@ 0.1C, 60 °C)	None
[9]	SPE, PVT, EMIMTFSI, LiTFSI	Electrostatic interaction between IL cations and salt anions	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	40	145 and 144 mAh g^{-1} (@ 0.1C, RT)	None

[10]	SPE, UPy-MA, PEGMA, LiTFSI	Quadruple hydrogen bonding	LFP 0.8, CB 0.1, PVDF 0.1, 170 mAh g^{-1}, *vs.* Li-metal	100	157 and 143 mAh g^{-1} (@ 0.1C, 60 °C)	Cut and healed outside, then used in a cell, cycled @ 0.1C, 60 °C

BMIm *= bis-trifluoromethanesulphonimide;* ***BN*** *= boron nitride;* ***BTA*** *= benzene-1,3,5-tricarbaldehyde;* ***CSE*** *= composite solid electrolyte;* ***DFOB*** *= difluoro(oxalato)borate;* ***EMIMTFSI*** *= 1-ethyl-3-methylimidazoliumbis (trifluoromethylsulfonyl) imide;* ***HFBM*** *= hexafuorobutyl methacrylate;* ***IGPE*** *= ionic gel polymer electrolyte;* ***IL*** *= ionic liquid;* ***NPs*** *= nanoparticles;* ***PolyIL*** *= poly(N,N,N-trimethyl-N-(1-vinlyimidazolium-3-ethyl)-ammonium bis(trifluorome thanesulfonyl)imide);* ***PVT*** *= poly(4-vinylpyridine)(propyl-trimethylammonium);* ***SBMA*** *= sulfobetaine methacrylate;* ***SIPE*** *= single-ion conducting gel polymer electrolyte;* ***SPE*** *= solid-state polymer electrolyte;* ***TPB*** *= 1,3,5-benzenetricarboxaldehyde;* ***TFB*** *= 1,3,5-triformylbenzene.*

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