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

Supporting Information

Self-healable, super Li-ion conductive, and flexible quasi-solid electrolyte for long-term safe lithium sulfur battery

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Experimental procedure

Preparation of ionic liquid (IL): PYR−TFSI was prepared from PYR and IB, as described in **Fig. S1A**. A solution of IB (19 g)/ THF (10 mL) was slowly dropped in a reactor containing PYR (10 g) and acetylacetate (25 mL). The reactor was heated at 50 °C for 6 h to obtain white solids. The filtered solids were washed three-times with acetylacetate, and dried under vacuum at room temperature for 24 h to produce PYR−I solids. The PYR−TFSI IL was obtained via ionic exchange from PYR−I (9.5 g), LiTFSI (10 g), and deionized water (9 g). The phase separation appears from an initial mixture after 6 h. The bottom phase was filtered and washed with cold water to remove excess salts. PYR−TFSI IL was obtained after freeze drying for 48 h.

Results and Discussion

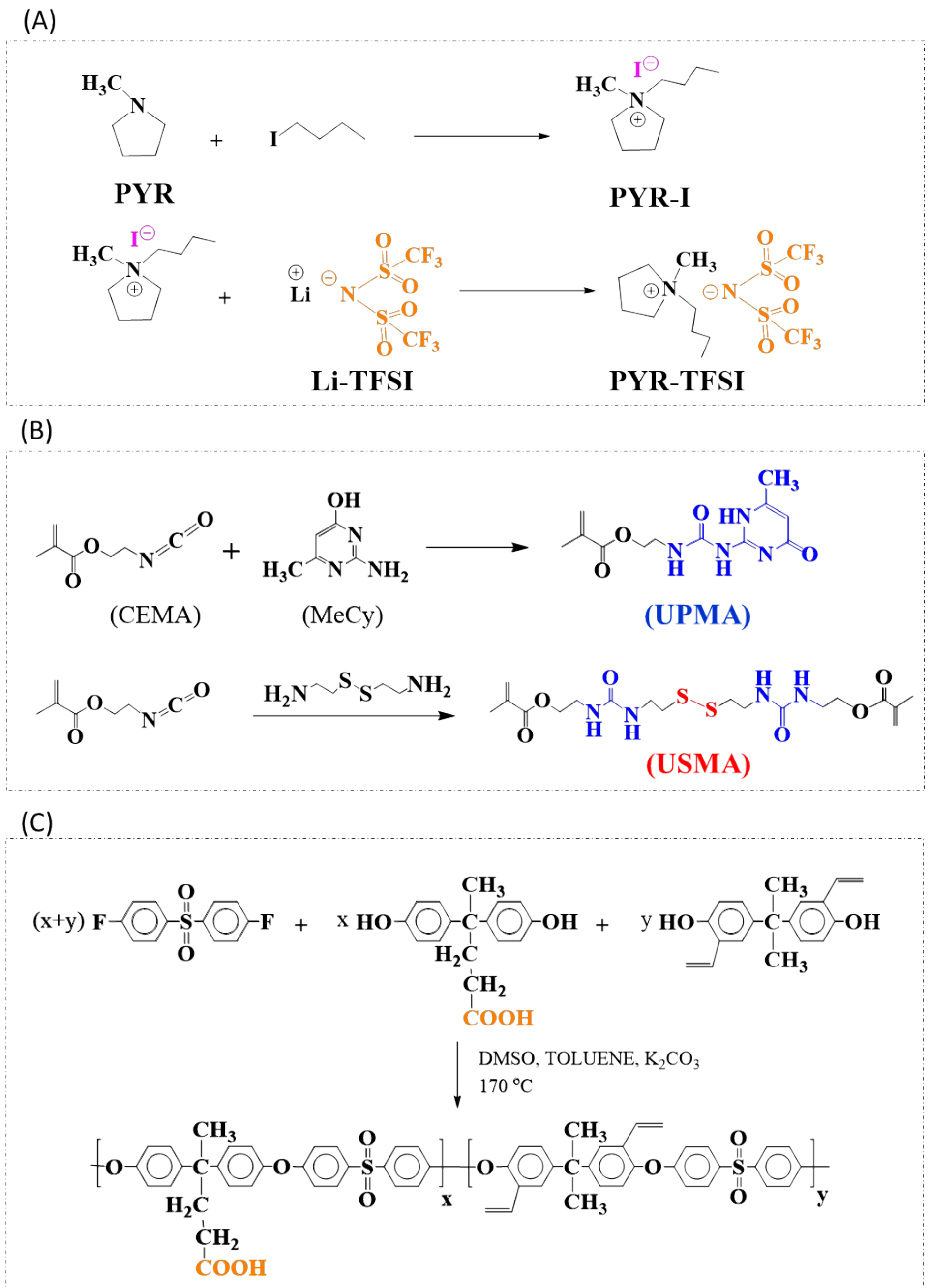


Figure S1. Synthetic scheme of (A) ionic liquid; (B) self-healing monomer (UPMA and SSMA); and (C) PAES backbone.

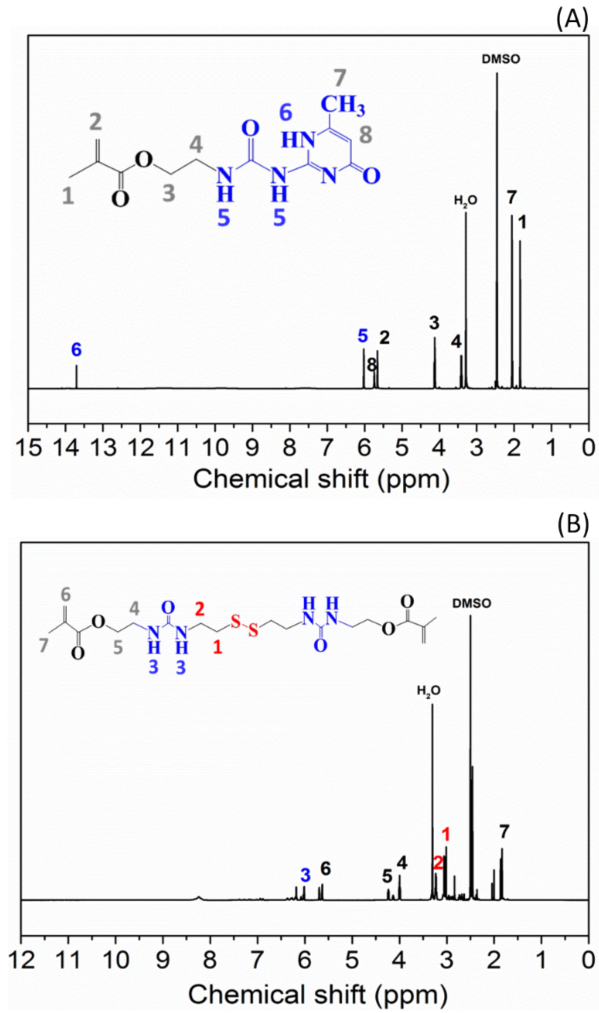


Figure S2. NMR spectra of (A) UPMA and (B) USMA monomers.

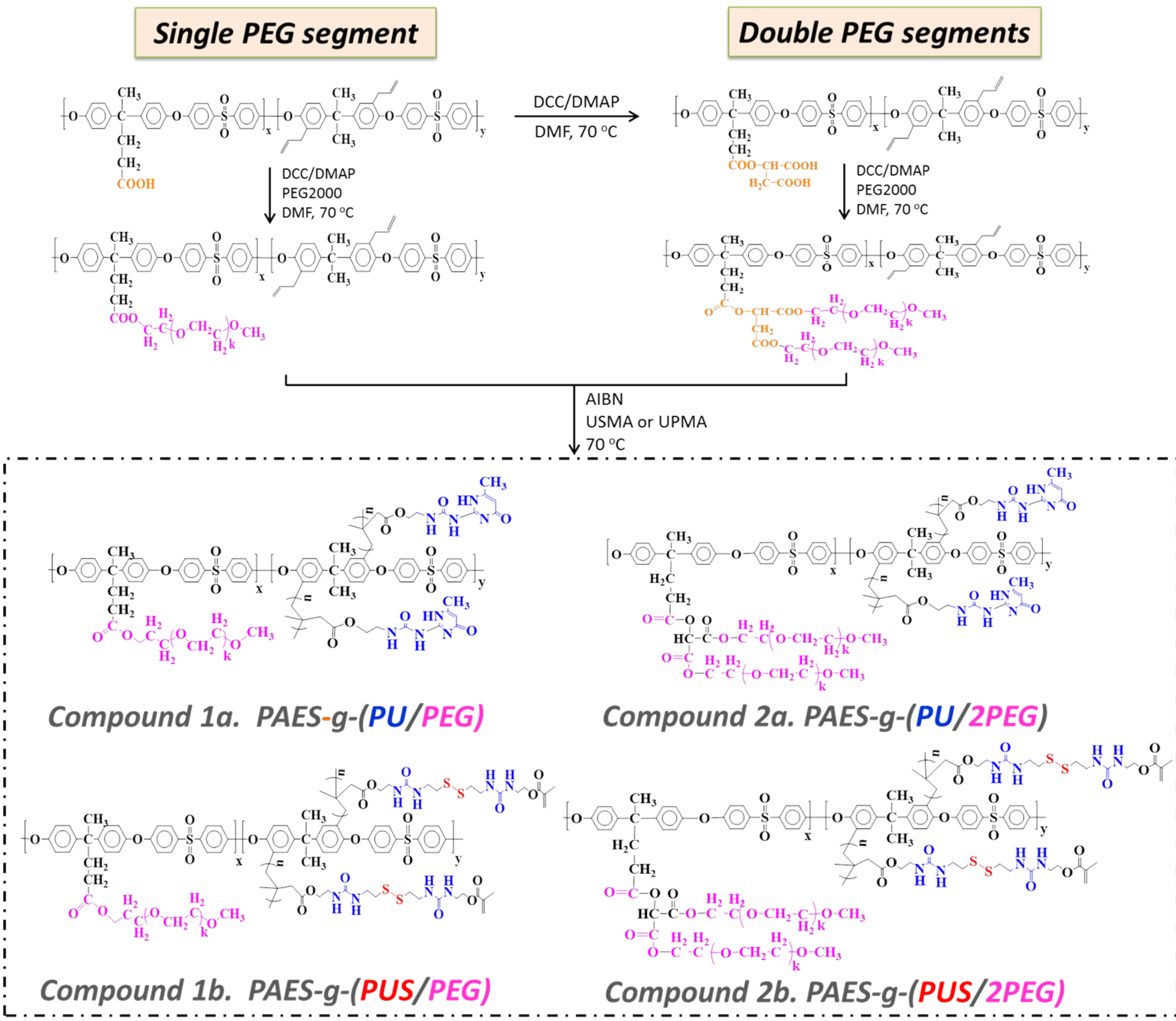


Figure S3. Synthetic scheme of PAES-g-(PU/PEG), PAES-g-(PU/2PEG), PAES-g-(PUS/PEG), and PAES-g-(PUS/2PEG).

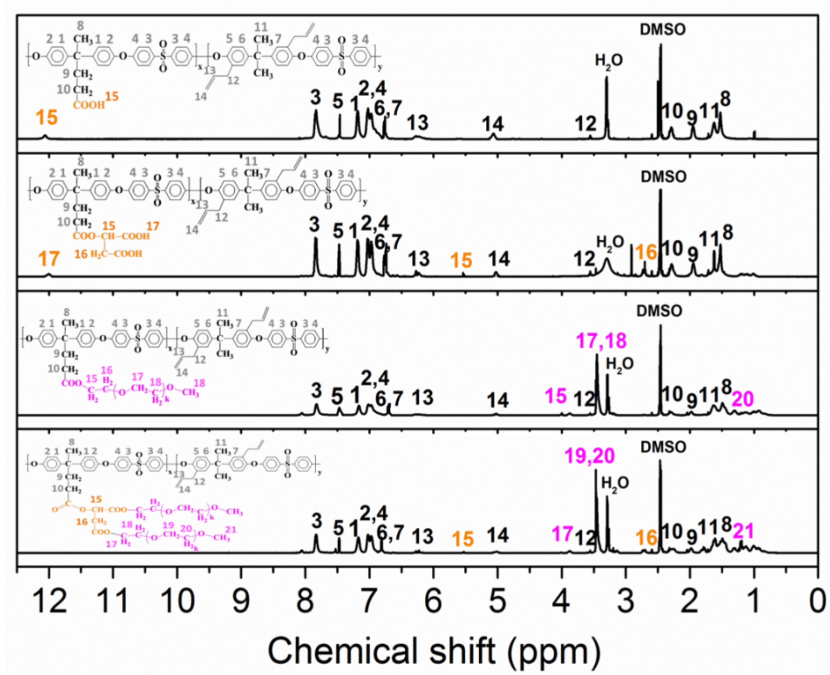
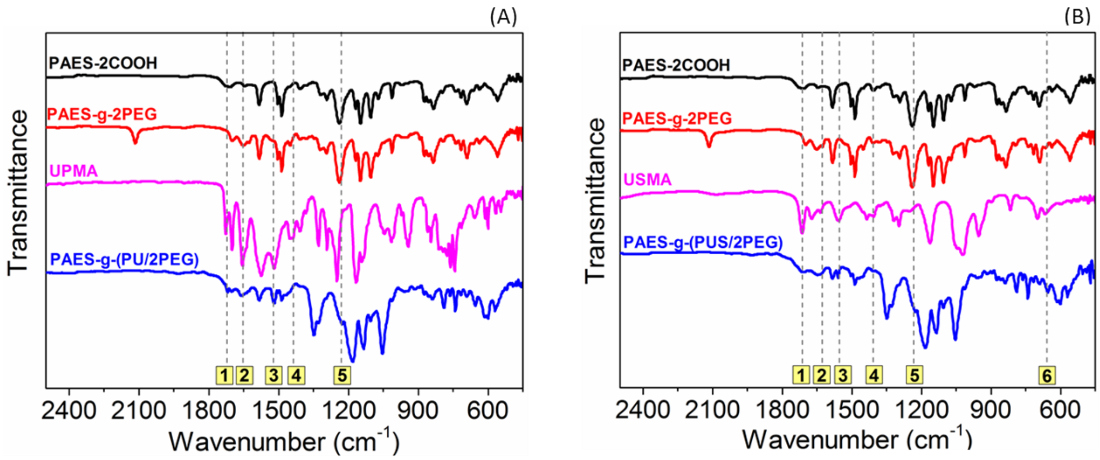


Figure S4. NMR spectra of PAES-COOH, PAES-2COOH, PAES-g-PEG, and PAES-g-2PEG.



- ○ Peak (**1**): cacbonyl (**C=O**) in methacrylate (1720 cm^{-1})
- ○ Peak (**2**): cacbonyl (**C=O**) in urea group (1650 cm^{-1})
- ○ Peak (**3**): amino (**N-H**) vibration (1560 cm^{-1})
- ○ Peak (**4**): (**C=C**) in vinyl groups (1425-1400 cm^{-1})
- ○ Peak (**5**): **Ar-O-Ar** (Aromatic) (1285-1240 cm^{-1})
- ○ Peak (**6**): disulfide (**S-S**) band (648 cm^{-1})

Figure S5. FTIR spectra of (A) PAES-2COOH, PAES-g-2PEG, UPMA, PAES-g-(PU/2PEG); and (B) PAES-2COOH, PAES-g-2PEG, USMA, PAES-g-(PUS/2PEG).

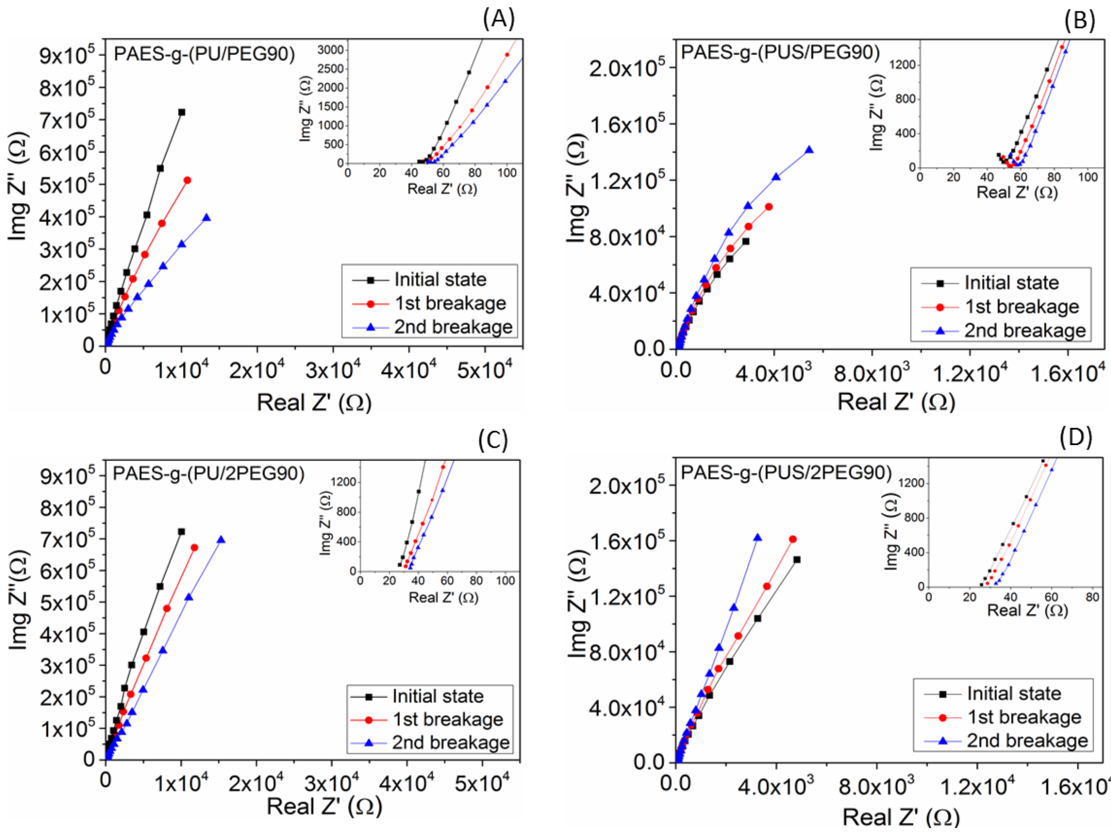


Figure S6. Nyquist plots before and after healing of (A) PAES-g-(PU/PEG90); (B) PAES-g-(PUS/PEG90); (A) PAES-g-(PU/2PEG90); and (A) PAES-g-(PUS/2PEG90) solid electrolytes containing 60 wt.% of (IL-EC) mixture.

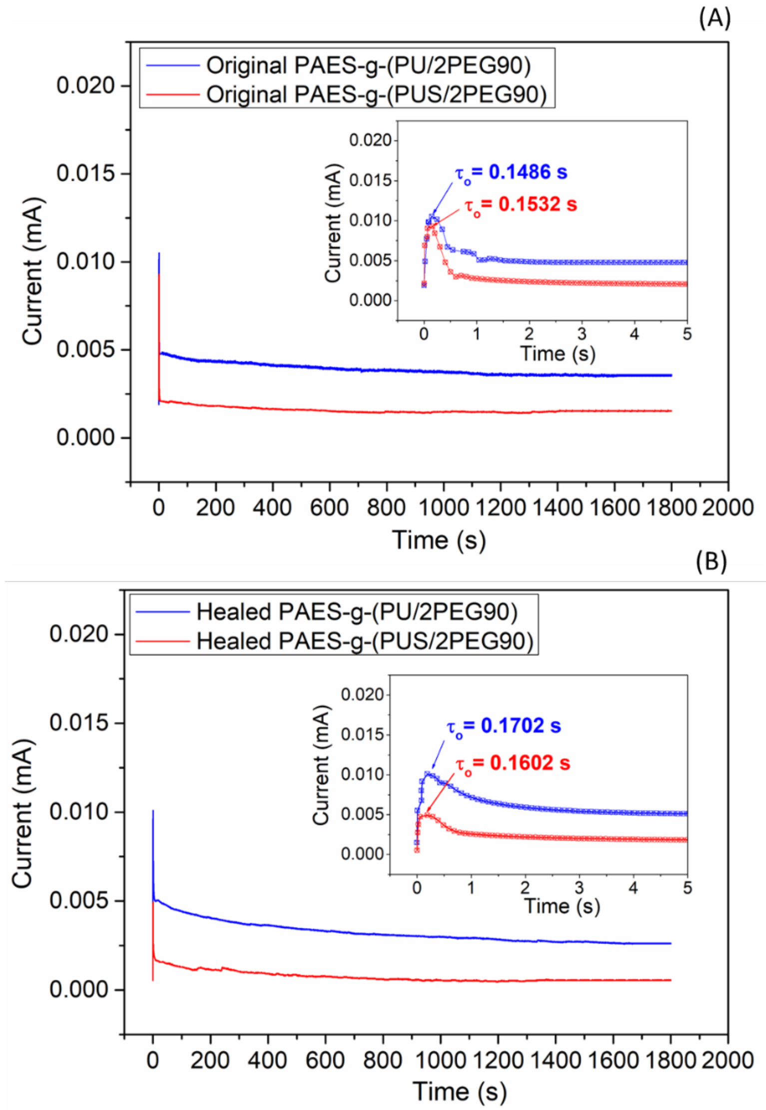


Figure S7. Transient ion current (TIC) curves of PAES-g-(PU/2PEG90) and PAES-g-(PUS/2PEG90) solid electrolytes (A) at original state and (B) after 2nd healing.

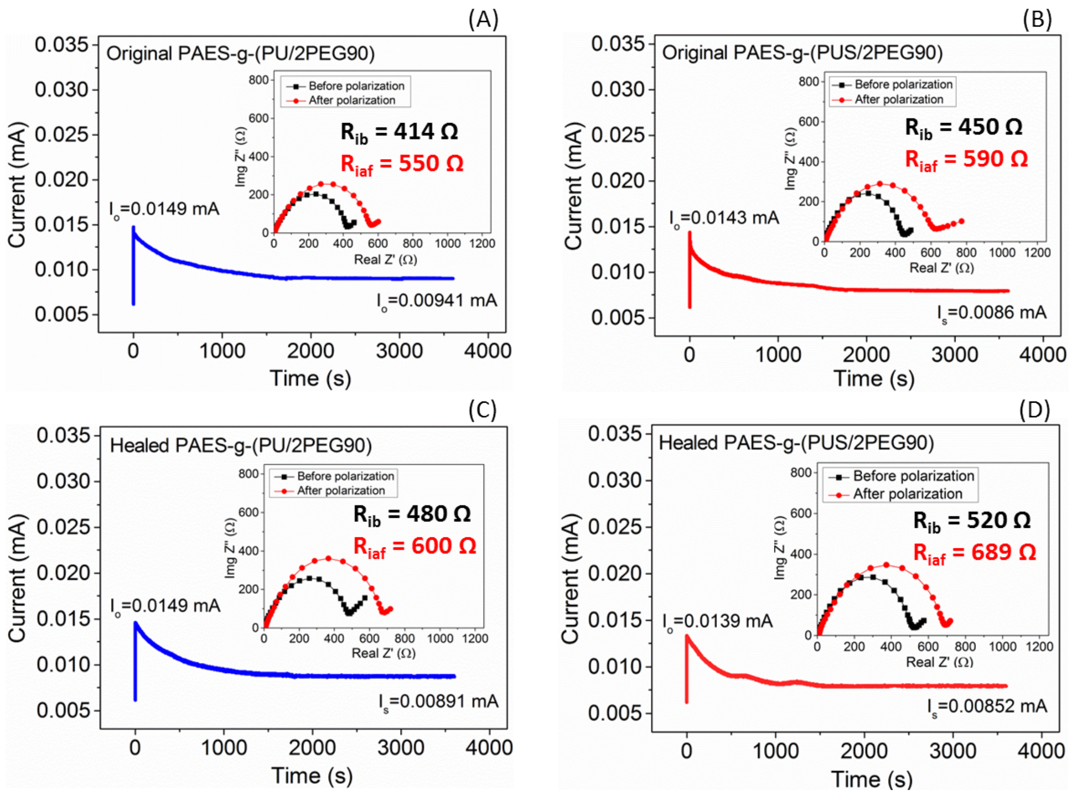


Figure S8. Current-time plots and impedance spectra before and after polarization of (A) original PAES-g-(PU/2PEG90); (B) original PAES-g-(PUS/2PEG90); (C) healed PAES-g-(PU/2PEG90); and (D) healed PAES-g-(PUS/2PEG90).

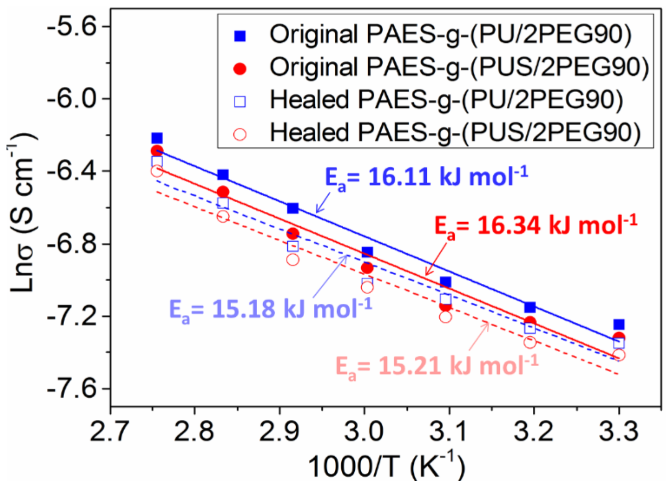


Figure S9. Thermal activation energy of PAES-g-(PU/2PEG) and PAES-g-(PUS/2PEG) electrolyte membranes before and after healing.

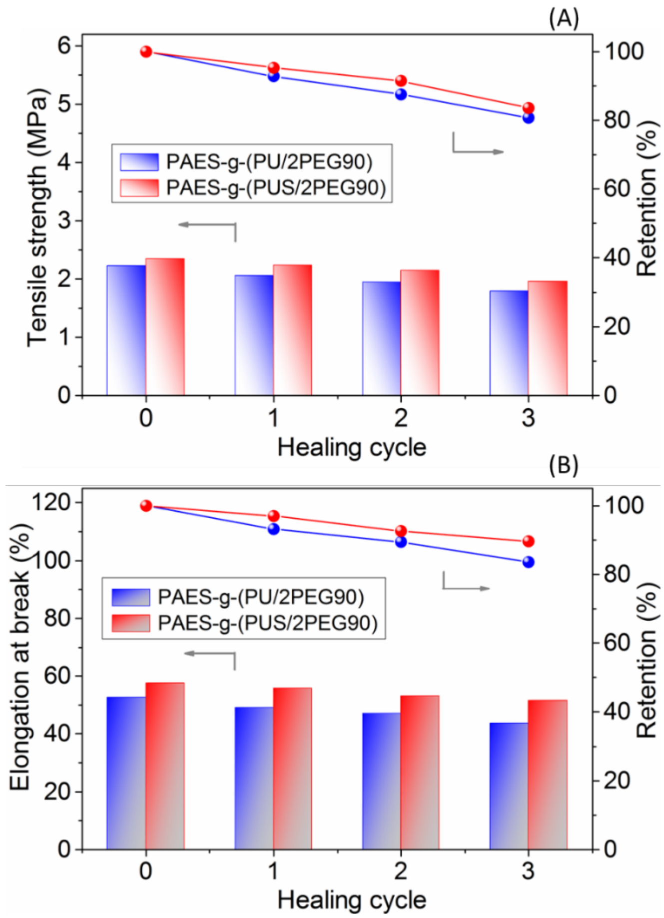


Figure S10. Tensile strength and elongation at break of PAES-g-(PU/2PEG) and PAES-g-(PUS/2PEG) electrolyte membranes before and after healing.

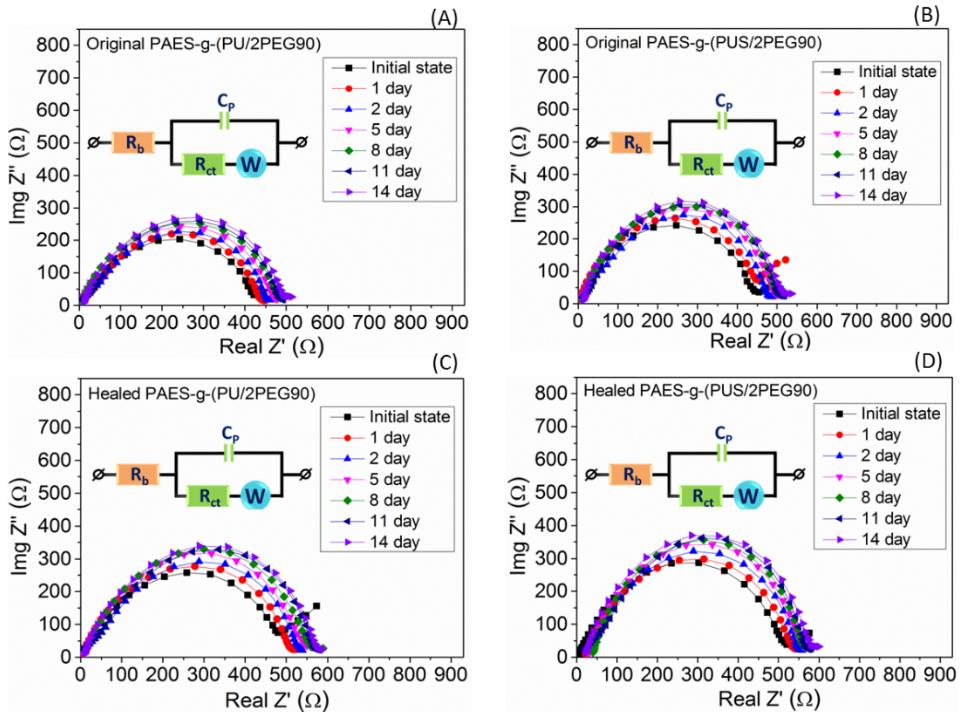


Figure S11. EIS plots of Li/PSE/Li cell assembled with PAES-g-(PU/2PEG) and PAES-g-(PUS/2PEG) electrolyte membranes before and after healing at different storage times.

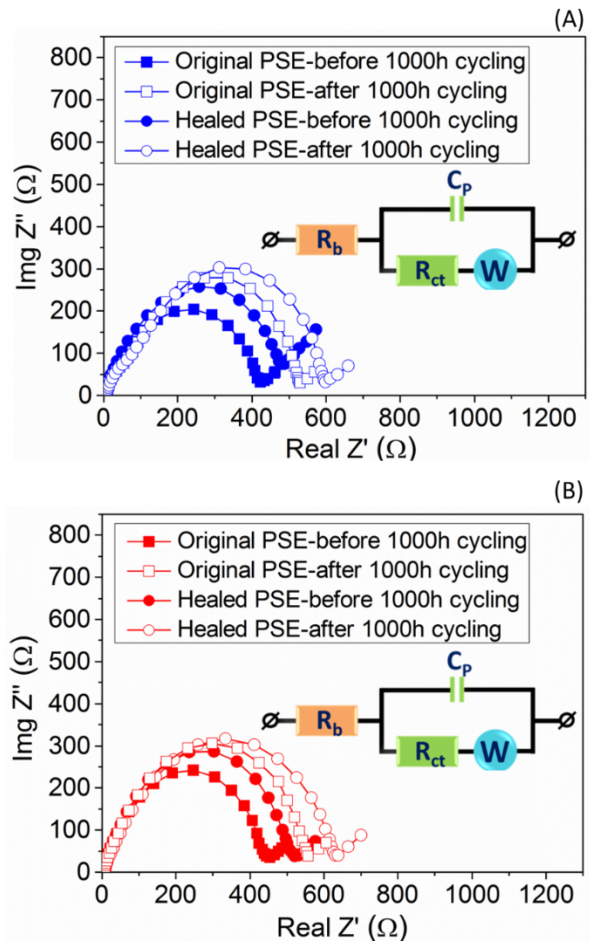


Figure S12. EIS plots before and after 1000 h cycling at 2.0 mA cm^{-1} for Li/PSE/Li cell assembled with (A) PAES-g-(PU/2PEG) and (B) PAES-g-(PUS/2PEG) electrolyte membranes before and after healing.

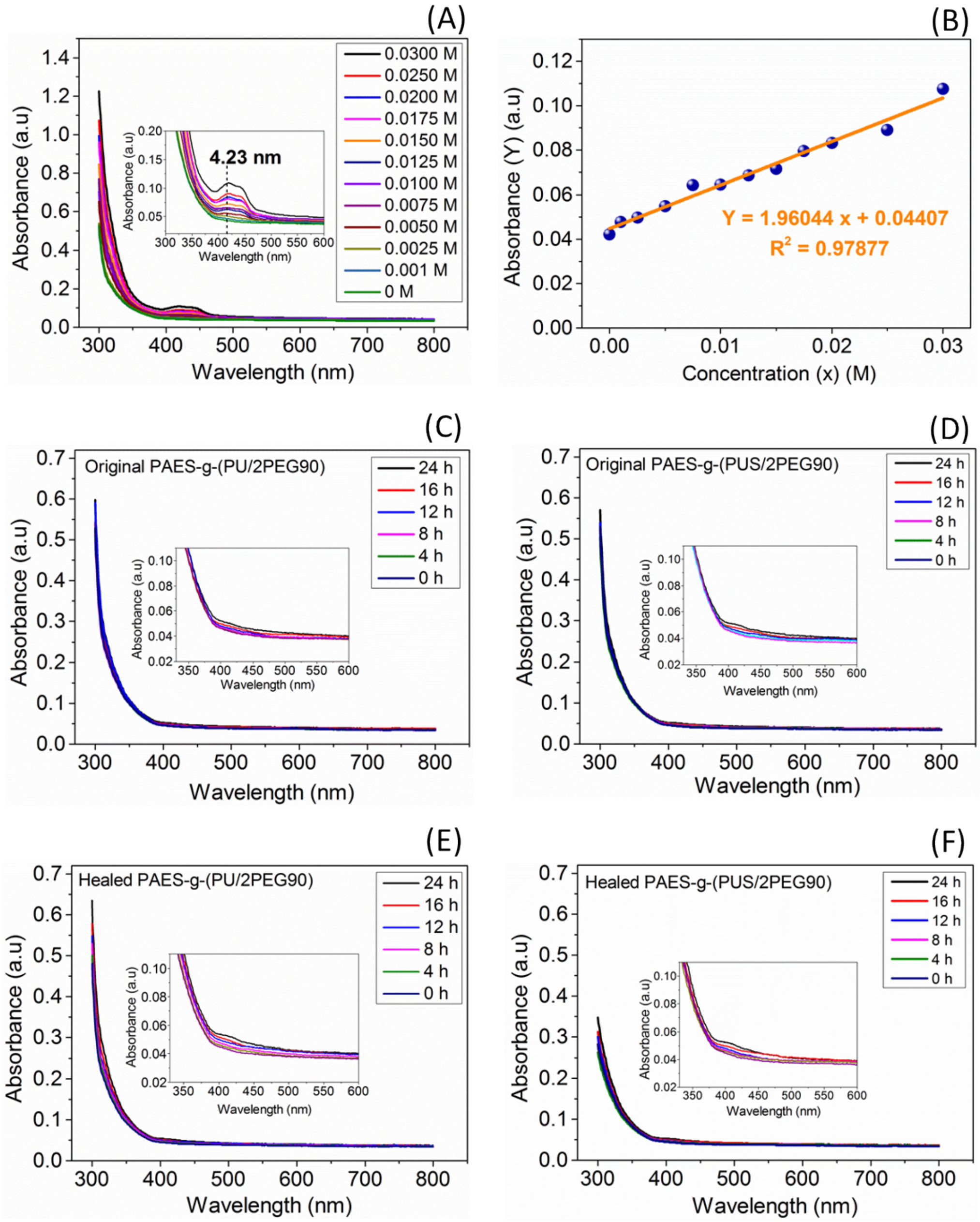


Figure S13. (A) UV-vis spectra of PS solution at different concentrations; (B) calibration plot of absorbance vs. PS concentration with the linear regression; (C-F) UV-vis spectra of PS solution diffused through PAES-g-(PU/2PEG) and PAES-g-(PUS/2PEG) electrolyte membranes before and after healing.

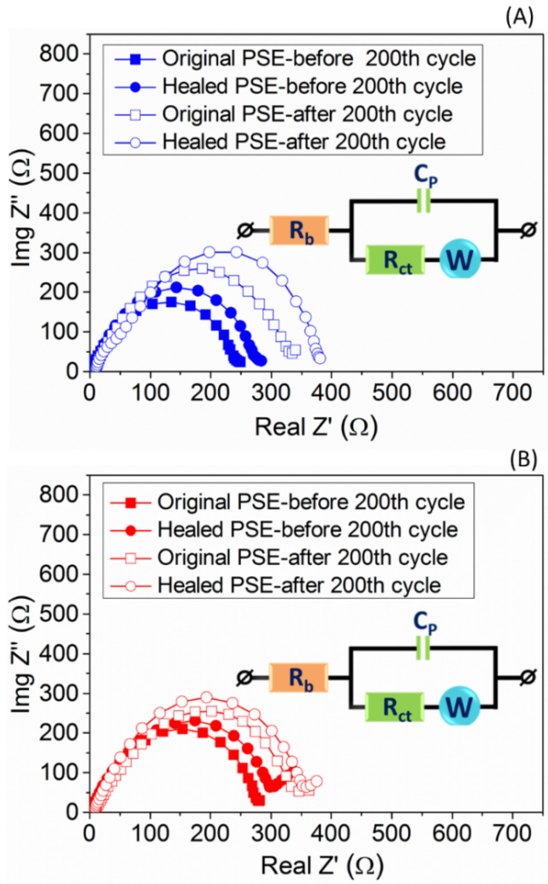


Figure S14. Interfacial resistance before and after 200 cycles of S/PSE/Li cells assembled with (A) PAES-g-(PU/2PEG); and (B) PAES-g-(PUS/2PEG) electrolyte membranes before and after healing.

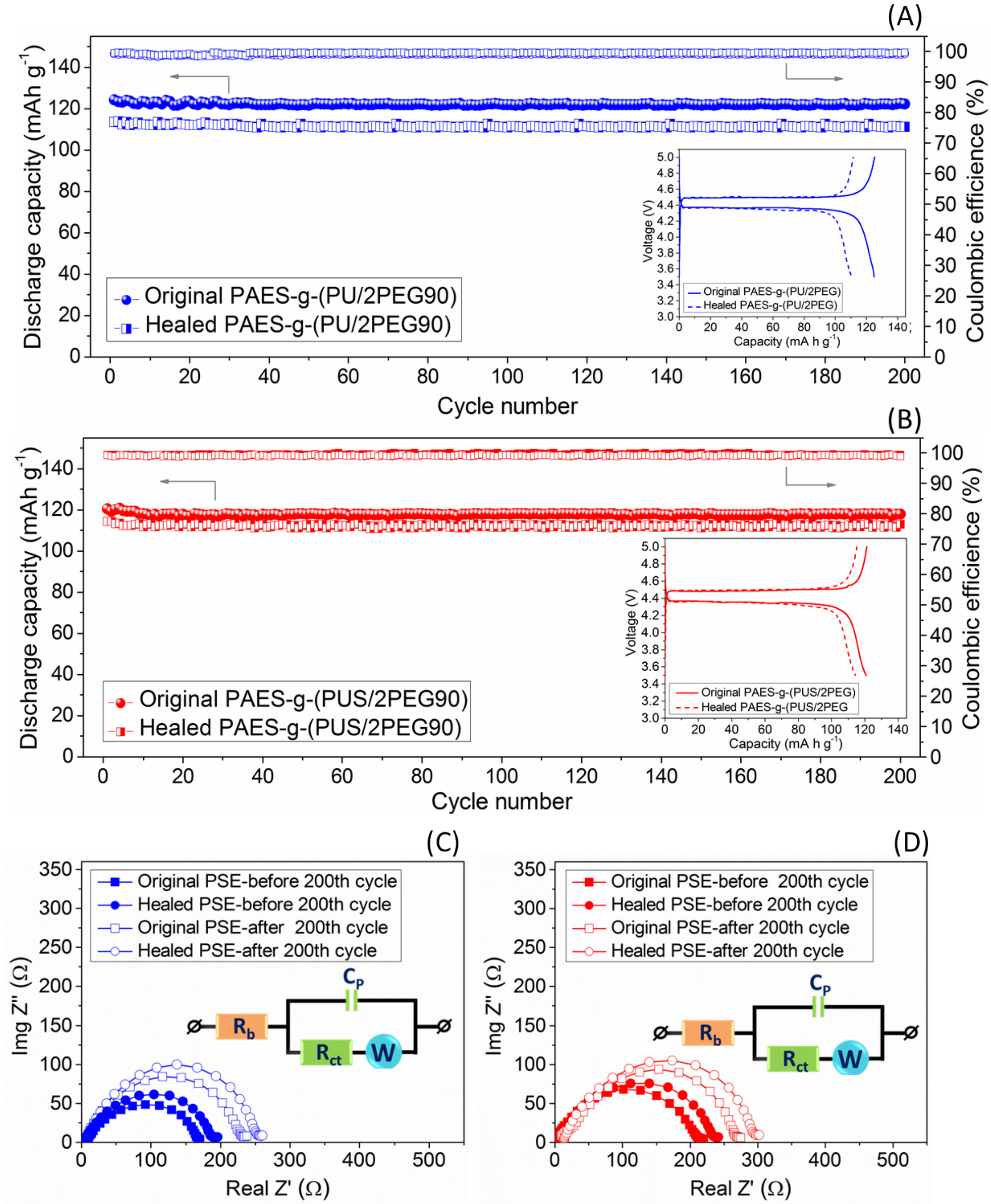


Figure S15. (A-B) Lithium storage performance at 0.2 C of LNMO/PSE/Li cells containing PAES-g-(PU/2PEG) and PAES-g-(PUS/2PEG) electrolyte membranes before and after healing; (C-D) Interfacial resistance of LNMO/PSE/Li cells before and after 200 cycles in voltage range of 3.5 -5.0 V.

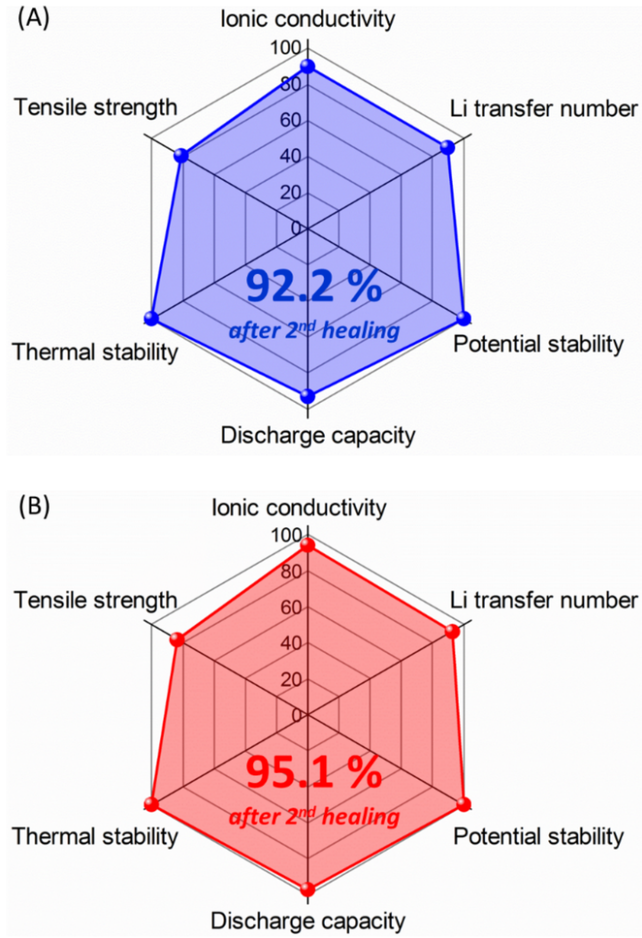


Figure S16. Radar diagram for important aspects related to self-healing efficiency of (A) healed PAES-g-(PU/2PEG); and (B) healed PAES-g-(PUS/2PEG) electrolyte membranes after 2nd damage.

Table S1. Comparison of ionic conductivity (σ), tensile strength and electrochemical stability window of 2nd-healed PAES-g-(SHP/2PEG) membranes with those of other electrolytes recently reported.[1–16]

Electrolyte membranes	σ (mS cm^{-1})	TS a) (MPa)	ESW b) (V)	[Ref]
Poly(PEG-co-BTA)/zwitterion	4.79	0.05	4.5	[1]
PIL-UPy/ LiTFSI (DOL+DME)	1.57	0.047	5.3	[2]
Poly(PEO-co-TFB)/ LiTFSI	0.784	0.137	5.0	[3]
Healed PAES-g-(PU/2PEG90)	**0.641**	**1.98**	**5.4**	**Our work**
Healed PAES-g-(PUS/2PEG90)	**0.659**	**2.14**	**5.6**	**Our work**
Poly(MPC-co-SBVI)	0.60	0.116	5.4	[4]
DPIL-6/ LiTFSI	0.347	0.490	4.9	[5]
PVA-UPy-PEG *co-grafting*	0.287	0.13	5.2	[6]
Sulfide SS-PMSS/ SiO_2 *composite*	0.279	0.15	4.82	[7]
Cross-linking PBA-co-PMMA/LiTFSI	0.169	15.0	4.8	[8]
PEG-g-UPyMA/ LiPS	0.145	0.50	4.6	[9]
PVT/EMIMTFSI (IL)	0.126	0.04	4.5	[10]
Poly(UPy-BCDMA)	0.0293	0.13	5.2	[11]
PEG-UPy/ UPy-modified SiO_2 *composite*	0.0088	0.51	5.1	[12]
Poly(HFBM-co-SBMA)/IL	0.0063	0.08	4.7	[13]
PEGDA-UPyMA/ HCP	0.0056	0.40	4.85	[14]
PEG-UPy/ LiTFSI	0.0021	0.274	4.8	[15]
PEG/BPIL	0.0011	2.50	5.0	[16]

a) Tensile strength and b) electrochemical stability window.

Table S2. Comparison of the S/SPE/Li cell performance based on PAES-g-(SHP/2PEG) membranes with those based on some other electrolytes recently reported.[17–29]

Electrolyte membranes	Discharge capacity (mAh g^{-1})					[Ref]
	0.2C	0.5C	1.0C	2.0C	5.0C	
PEO/ PIM-8% *gel electrolyte*	1200	1100	910	600		[17]
SO_3Li *grafted* UIO (MOF) /LiTFSI +IL	985	*890*	*749*	-	-	[18]
PEGDA /$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$ *composite*	968	*780*	*600*	*585*	-	[19]
PEO-$Li_4(BH_4)_3I$/ SiO_2 (5%wt) *composite*	950	*817*	*613*	*583*	-	[20]
***Healed* PAES-g-(PUS/2PEG90)**	**929.8**	**891.6**	**837.9**	**776.6**	**683.3**	**Our work**
***Healed* PAES-g-(PU/2PEG90)**	**919.9**	**885**	**832.5**	**769.2**	**674.1**	**Our work**
PETT-DA/ (PEO + PVDF-HFP) *nano-fiber*	910	766	624	543	-	[21]
In-situ S-DCBQ organosulfur	890	795	750	600	-	[22]
PEO/(LLZO+MWCNT) *composite*	873	810	500	400	-	[23]
PETEA+divinyladipate/(DOL+TEGDME)	779	621	325	220	-	[24]
PEO/ (P_2S_5 + LiTFSI) *gel electrolyte*	750	450	-	-	-	[25]
PEO/ $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$/ PEO (*LbL*)	692.9	428.4	362.3	-	-	[26]
Polydopamine-coated Li_6PS_5Cl *solid*	552.8	226.4	-	-	-	[27]
PEO/TCM+ LiTFSI) *solid electrolyte*	450	300	-	-	-	[28]
LiPS/Li_3HoBr_6 *composite electrolyte*	450	250	140	-	-	[29]

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