Supporting Information

A Functional Separator Coated with Sulfonated SEBS to Synergistically Enhance the Electrochemical Performance and Anti-self-discharge Behavior of Li-S Batteries

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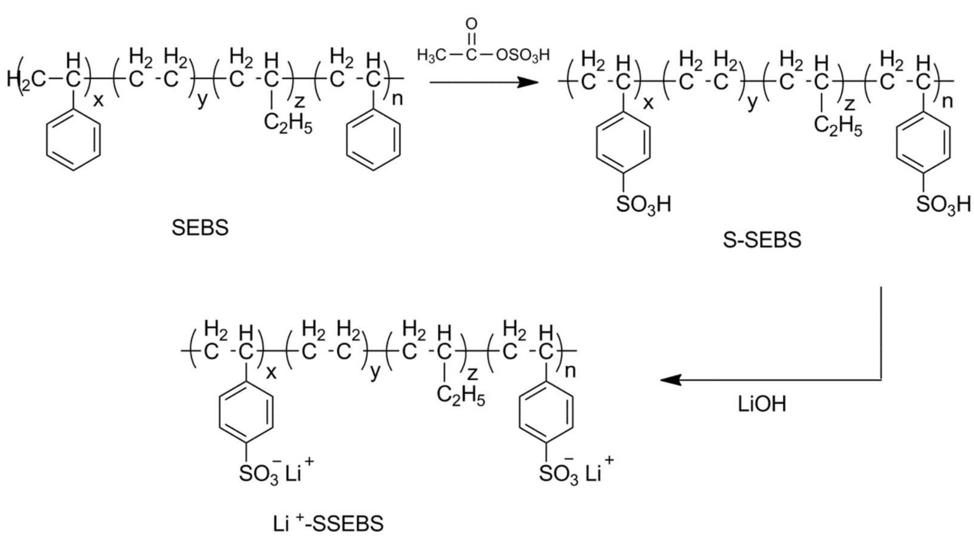

Figure S1 Synthesis of Li^+-SSEBS

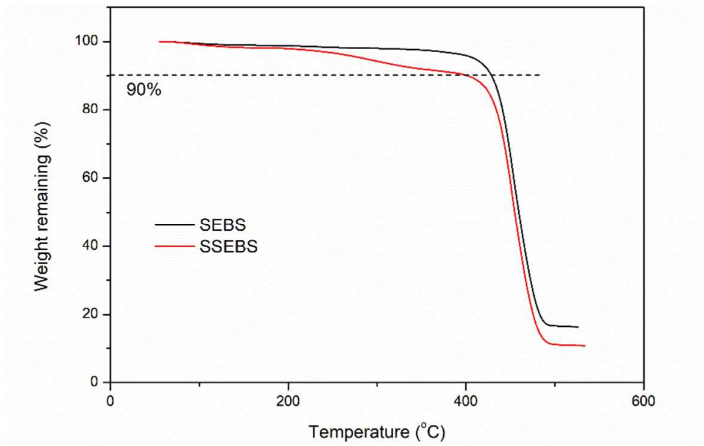

Figure S2 TGA curves of SEBS and SSEBS

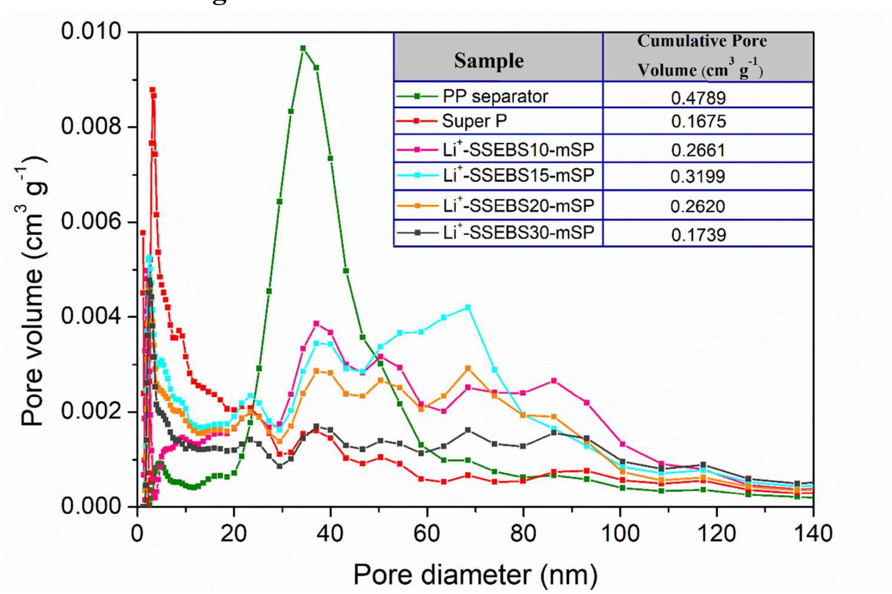

Figure S3 Pore size distribution and cumulative pore volume (inset table) of different samples.

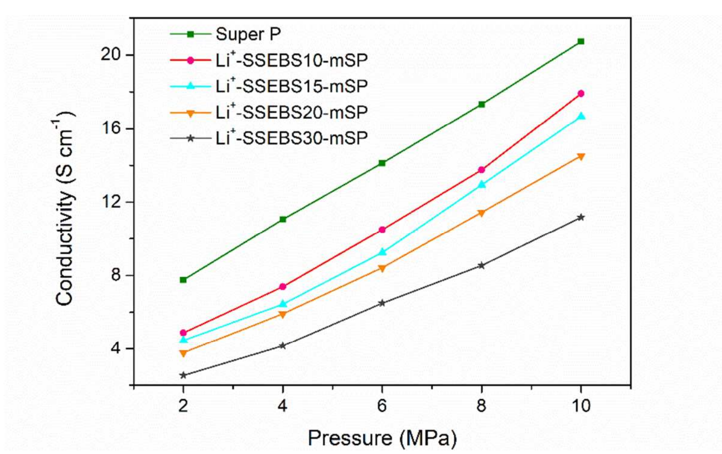

Figure S4 Conductivity test of different coating layer by four point probe resistivity tester at different pressure.

Lithium ion diffusion coefficient:

According to reference,[1-2] lithium ion diffusion coefficient can be obtained by the ion-diffusion resistance (the Warburg impedance, W_c), which corresponds to a straight inclined line in the low-frequency region. The diffusion coefficient σ_W could be obtained by equation (1):

$$Z' = R_e + R_{ct} + \sigma_W \omega^{-0.5} \quad (1)$$

σ_W is the slope for the plots of Z' vs. the reciprocal root square of the lower angular frequencies ($\omega^{-0.5}$), as shown in Figure S3 and Figure S4. The diffusion coefficient values of the lithium ions (D) can be calculated as equation (2):

$$D = 0.5(RT/AF^2\sigma_W C)^2 \quad (2)$$

Where R is the gas constant (8.314 J mol^{-1} K^{-1}), F is the Faraday's constant (96,500 C mol^{-1}), T is the testing temperature (298.5 K), A is the area of the electrode surface and C is the molar concentration of Li ions. The diffusion coefficient values of the lithium ions (D) are listed in Table S1 and S2.

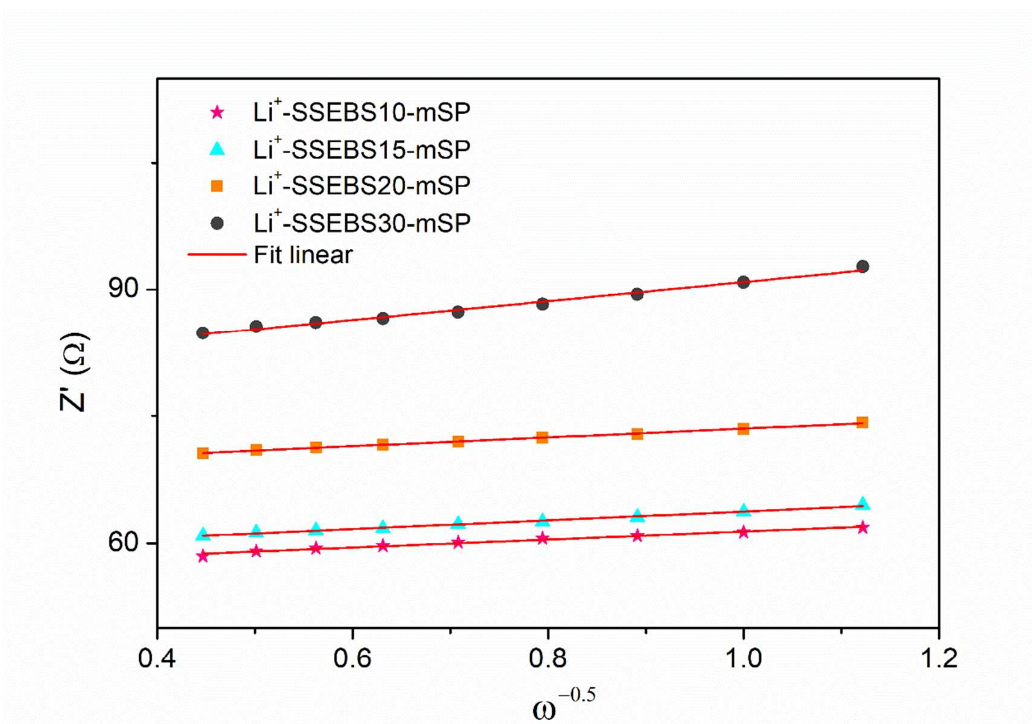

Figure S5 The relationship between Z' and $\omega^{-0.5}$ at low frequencies for Li-S batteries with Li^+-SSEBS-mSP separators.

Lithium ion transference number:

The lithium ion transference number (t_+) was investigated by Vincent and Bruce's method: using electrochemical impedance spectra combined with steady-state current technique.[3-5] The cell assembled with Li/separator-liquid electrolyte/Li was subjected to a small DC polarization potential (ΔV=10.0 mV) for enough time to achieve a steady-state current. The interfacial resistances of the cell were measured by AC impedance before and after polarization. The t_+ can be calculated using the equation (3):

$$t_+=\frac{I_S(\Delta V-I_O R_O)}{I_O(\Delta V-I_S R_S)} \quad (3)$$

Where I_o and I_s are the initial and steady-state currents (Figure S), respectively. R_o and R_s are the initial and steady-state interfacial resistances, respectively.

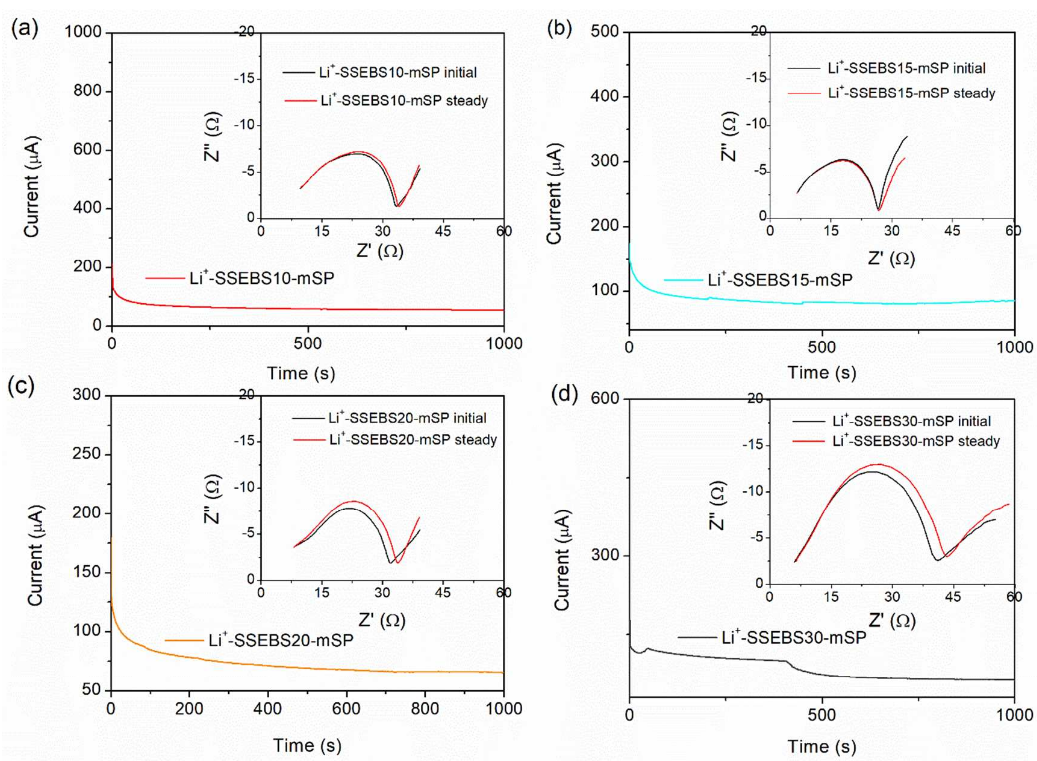

Figure S6 Li ion transference number measurements. Impedances before and after polarization, and polarization profile: (a) Li^+-SSEBS10-mSP, (b) Li^+-SSEBS15-mSP, (c) Li^+-SSEBS20-mSP and (d) Li^+-SSEBS30-mSP, respectively.

Table S1 Impedance parameters and Li^+ transference number of Li^+-SSEBS-mSP separators.

Battery	Re (Ω)	Rct (Ω)	σ_w (Ω $s^{-0.5}$)	D (cm^2 s^{-1})	Li^+ transference number
Li^+-SSEBS10-mSP	2.67	57.01	4.68	1.05×10^{-9}	0.347
Li^+-SSEBS15-mSP	2.45	59.21	5.13	8.7×10^{-10}	0.486
Li^+-SSEBS20-mSP	3.29	68.14	5.11	8.8×10^{-10}	0.431
Li^+-SSEBS30-mSP	5.47	83.60	11.29	1.64×10^{-10}	0.346

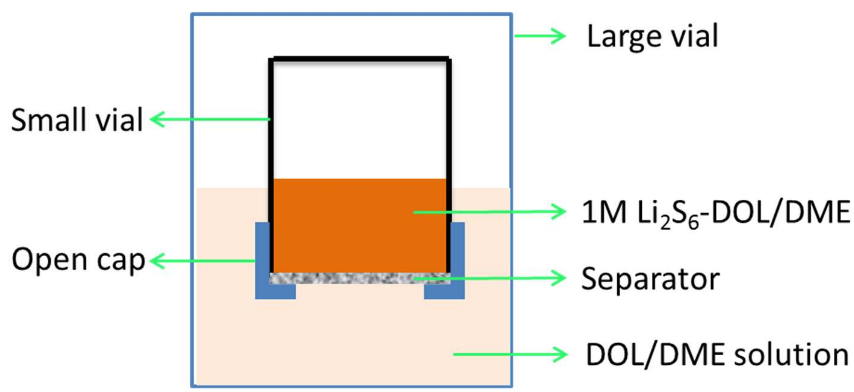

Figure S7 The schematic illustration of visible diffusion experiment.

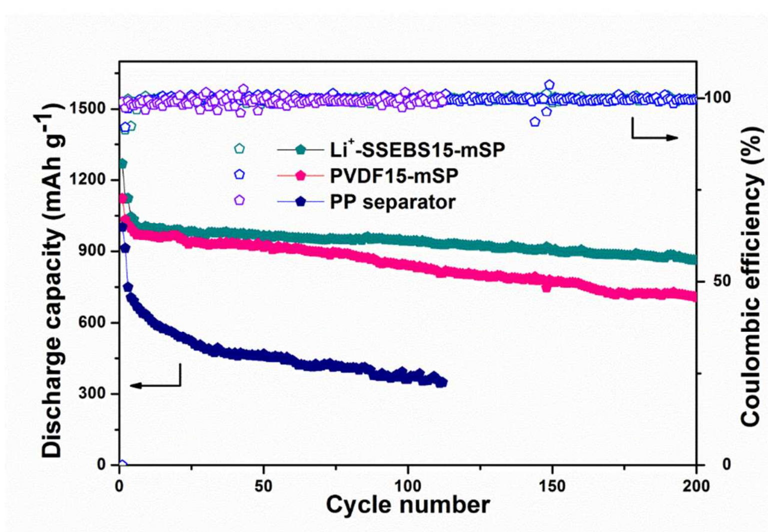

Figure S8 Cycling performances of lithium sulfur batteries with different separator at

0.5 C for 200 cycles

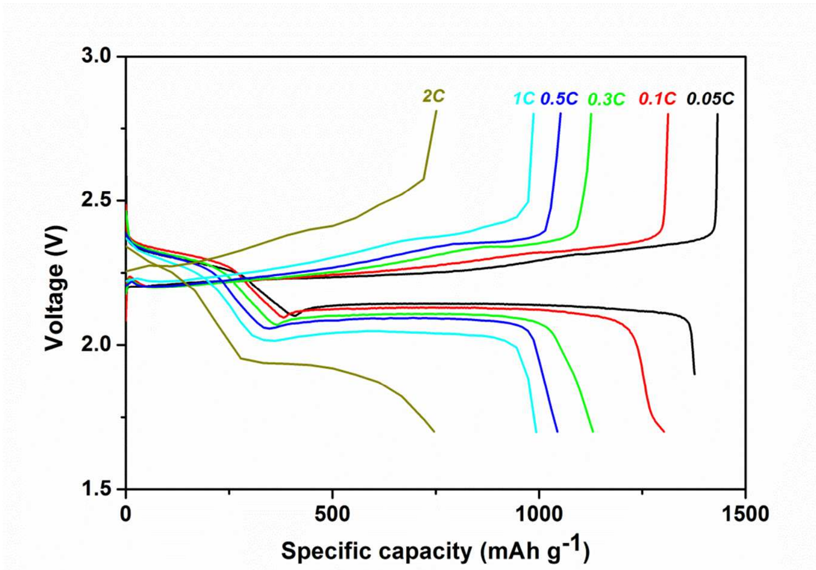

Figure S9 The discharge-charge profiles of the cell with Li^+-SSEBS15-mSP at different current densities.

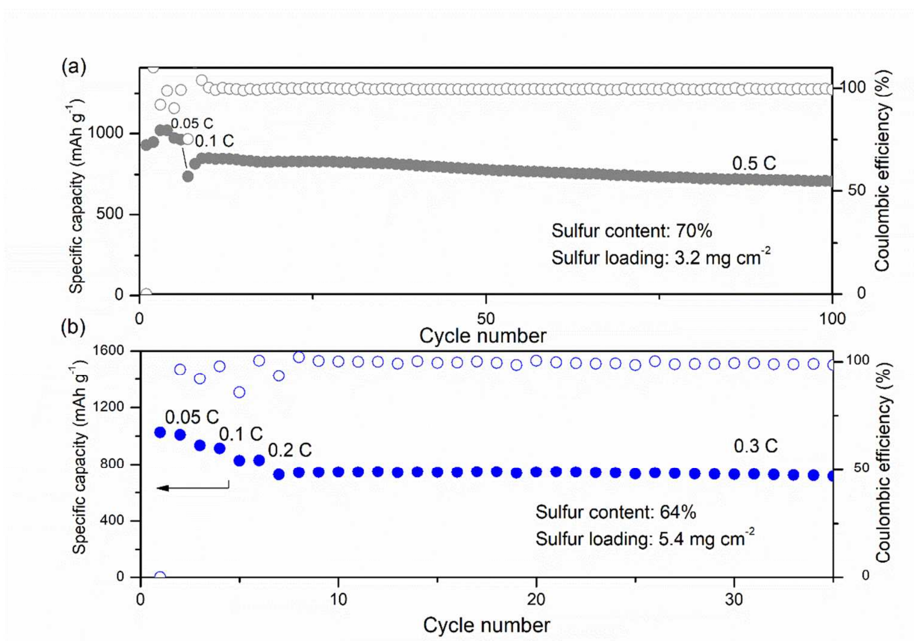

Figure S10 Cycle performance of Li-S battery with high sulfur loading cathodes (a: 3.2 mg cm^{-2}, b: 5.4 mg cm^{-2}) using Li^+-SSEBS15-mSP as a separator.

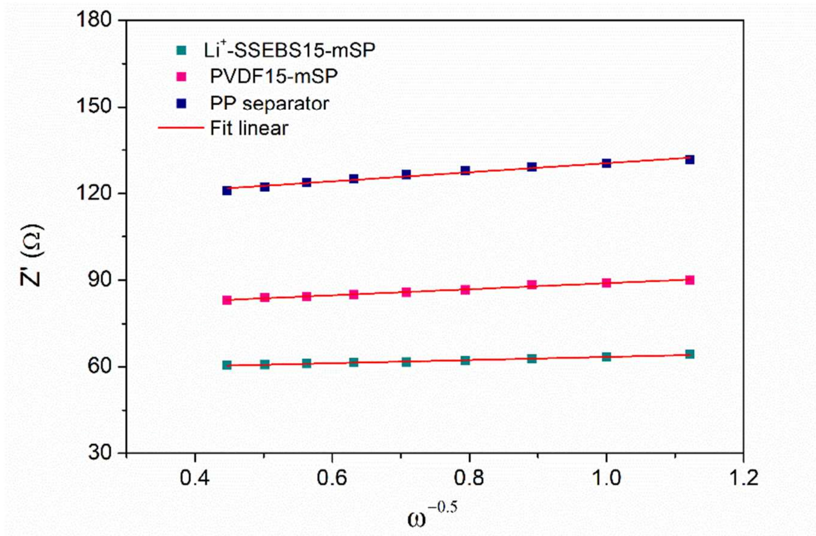

Figure S11 The relationship between Z' and $\omega^{-0.5}$ at low frequencies for batteries with different separator.

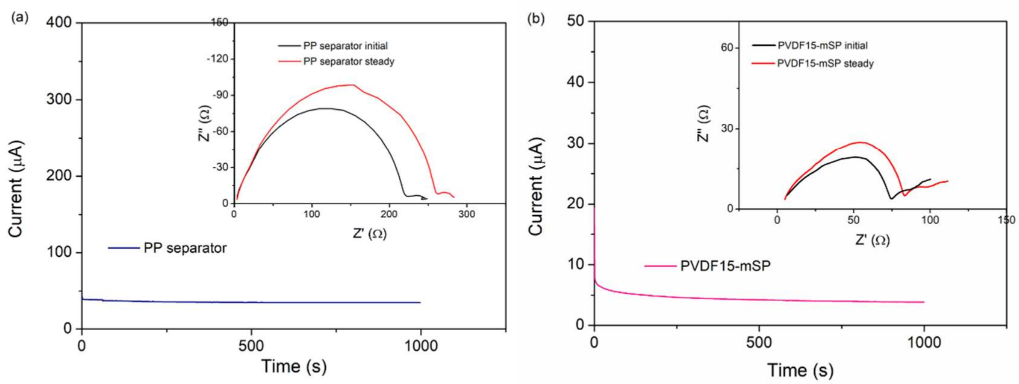

Figure S12 Li ion transference number measurement. Impedance before and after polarization, and polarization profile: PP separator (a) and PVDF15-mSP (b).

Table S2 Impedance parameters and Li^+ transference number of batteries with different separator.

Battery	Re (Ω)	Rct (Ω)	σ_w (Ω $s^{-0.5}$)	D (cm^2 s^{-1})	Li^+ transference number
Li^+-SSEBS15-mSP	2.45	59.21	5.13	8.7×10^{-10}	0.486
PVDF15-mSP	3.31	74.96	10.38	2.13×10^{-10}	0.317
PP separator	5.72	111.80	15.61	9.43×10^{-11}	0.199

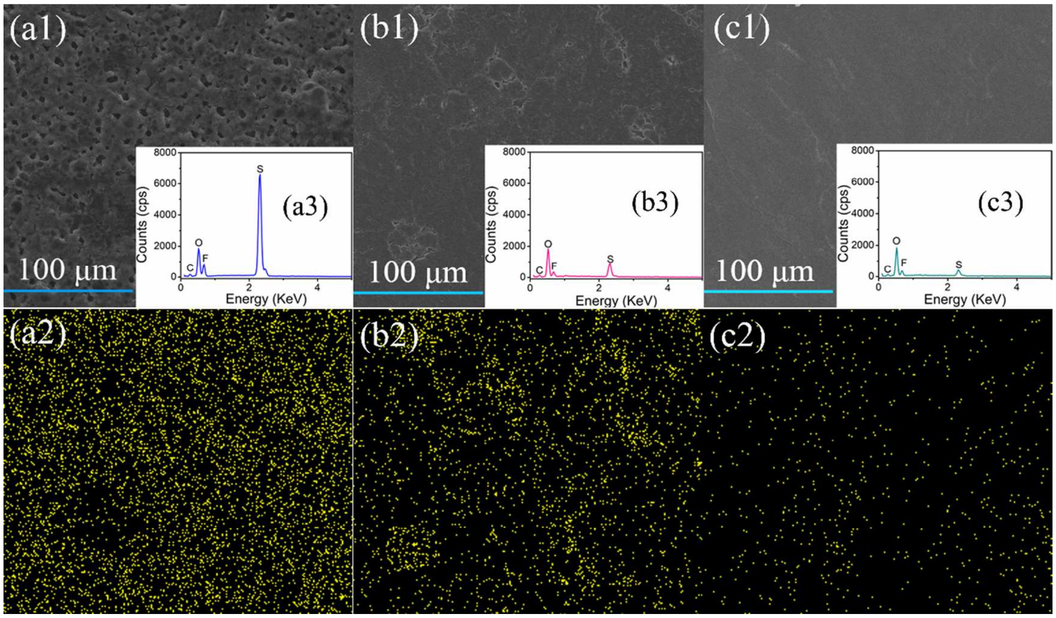

Figure S13. SEM image and corresponding EDS mapping of surface and line scanning results of Li anode after 20 cycles (0.5 C) in batteries with PP separator (a); PVDF15-mSP (b); Li^+-SSEBS15-mSP (c).

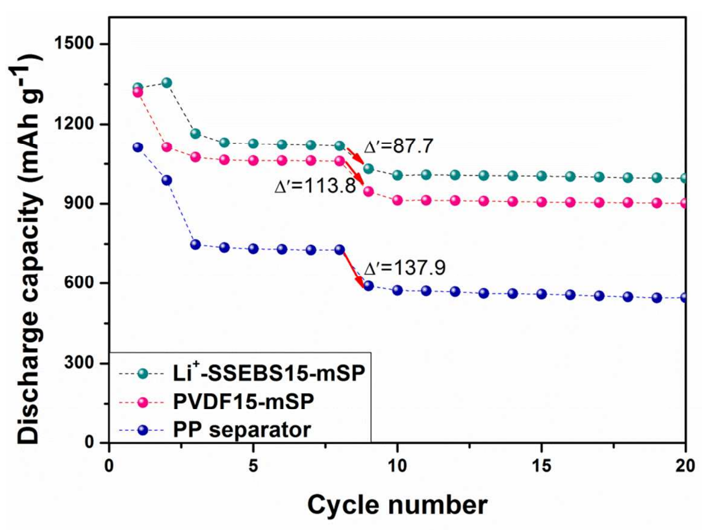

Figure S14 Discharge capacity-cycle index plots of self-discharge behavior test by the reference's method (interrupted at 2.1 V and rest 72 h during discharge).

Table S3 Capacity Loss rate values of Li-S batteries with different separators from different self-discharge test method.

Loss rate value	Li^+-SSEBS15-mSP	PVDF15-mSP	PP separator
Reference's method	7.8%	10.7%	18.9%
This work' method	8.8 %	12.3%	26.4%

Reference

(1) Xu, R.; Huang, X.; Lin, X.; Cao, J.; Yang, J.; Lei, C., The functional aqueous slurry coated separator using polyvinylidene fluoride powder particles for Lithium-ion batteries. *J. Electroanal. Chem.* **2017,** *786*, 77-85.

(2) Zhao, D.; Qian, X.; Jin, L.; Yang, X.; Wang, S.; Shen, X.; Yao, S.; Rao, D.; Zhou, Y.; Xi, X., Separator modified by Ketjen black for enhanced electrochemical performance of lithium–sulfur batteries. *Rsc.Adv.* **2016,** *6*, 13680-13685.

(3) Evans, J.; Vincent, C. A.; Bruce, P. G., Electrochemical measurement of transference numbers in polymer electrolytes. *Polymer* **1987,** *28*, 2324-2328.

(4) Lin, C.-E.; Zhang, H.; Song, Y.-Z.; Zhang, Y.; Yuan, J.-J.; Zhu, B.-K., Carboxylated polyimide separator with excellent lithium ion transport properties for a high-power density lithium-ion battery. *J. Mater.Chem. A* **2018,** *6*, 991-998.

(5) Ma, L.; Nath, P.; Tu, Z.; Tikekar, M.; Archer, L. A., Highly Conductive, Sulfonated, UV-Cross-Linked Separators for Li–S Batteries. *Chem. Mater.* **2016,** *28*, 5147-5154.