Supporting Information

In-situ extracted poly(acrylic acid) contributing to electrospun nanofiber separators with precisely tuned pore structures for ultra-stable lithium-sulfur batteries

Xiaobo Zhu, Yue Ouyang, Jiawei Chen, Xinguo Zhu, Xiang Luo, Feili Lai, Hui Zhang, Yue-E Miao*, Tianxi Liu

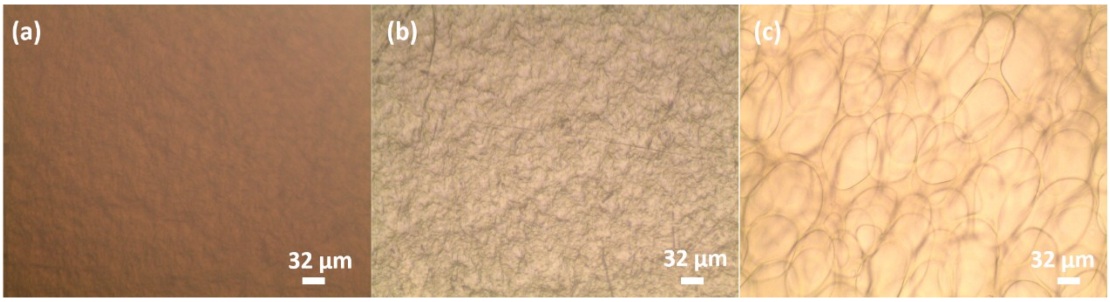

Fig. S1 Microscope photographs of different electrospinning precursor solutions: (a) PAN, (b) PAA and (c) PAN_6/PAA_4.

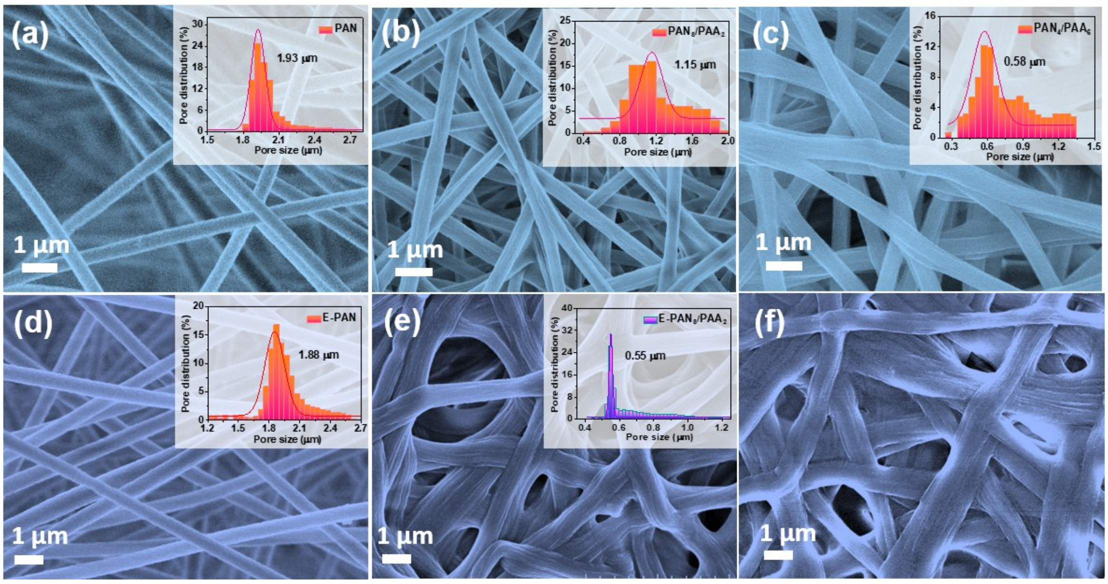

Fig. S2 SEM images and the corresponding pore size distributions (inset) of different membranes: (a) PAN, (b) PAN_8/PAA_2, (c) PAN_4/PAA_6, (d) E-PAN, (e) E-PAN_8/PAA_2, (f) E-PAN_4/PAA_6.

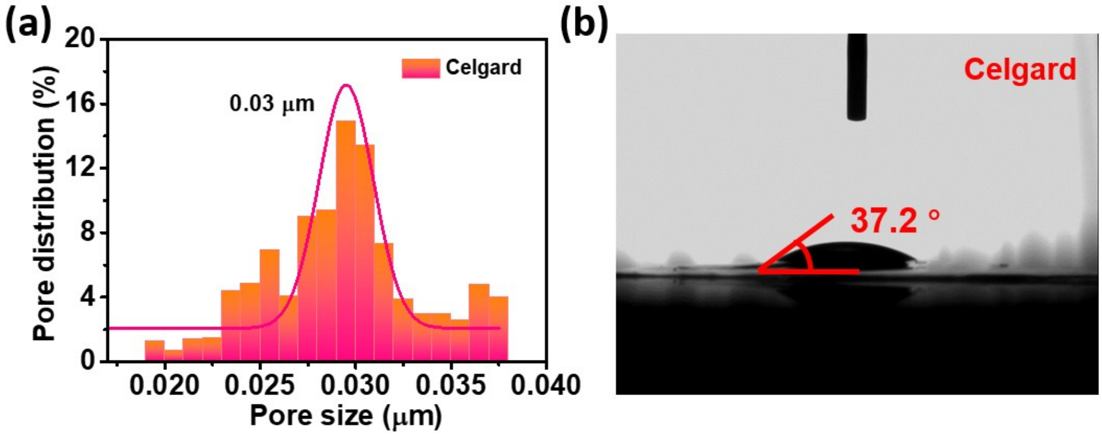

Fig. S3 (a) The pore size distribution, and (b) electrolyte contact angle of Celgard.

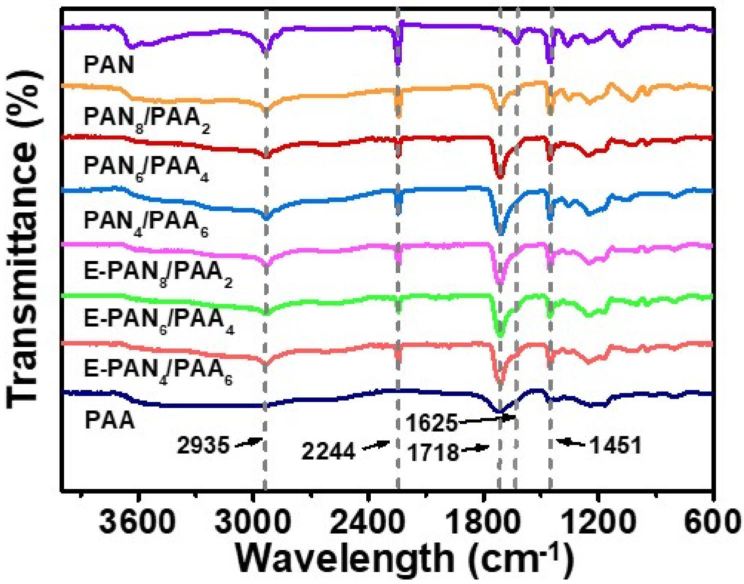

Fig. S4 FTIR spectra of different membranes.

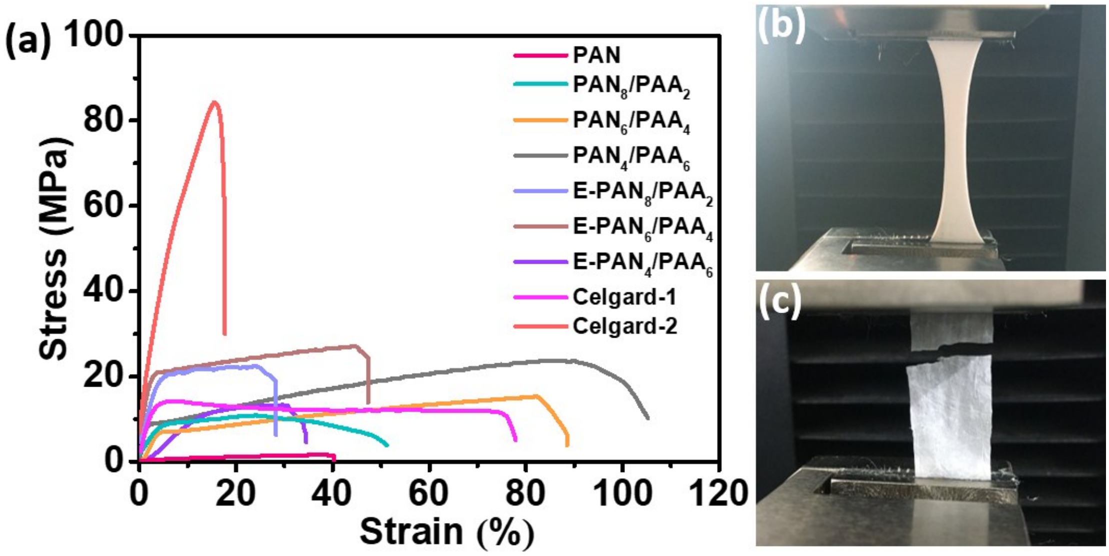

Fig. S5 (a) Representative stress - strain curves for various membranes. Tensile fracture photos of (b) PAN_6/PAA_4 and (c) E-PAN_6/PAA_4 separators.

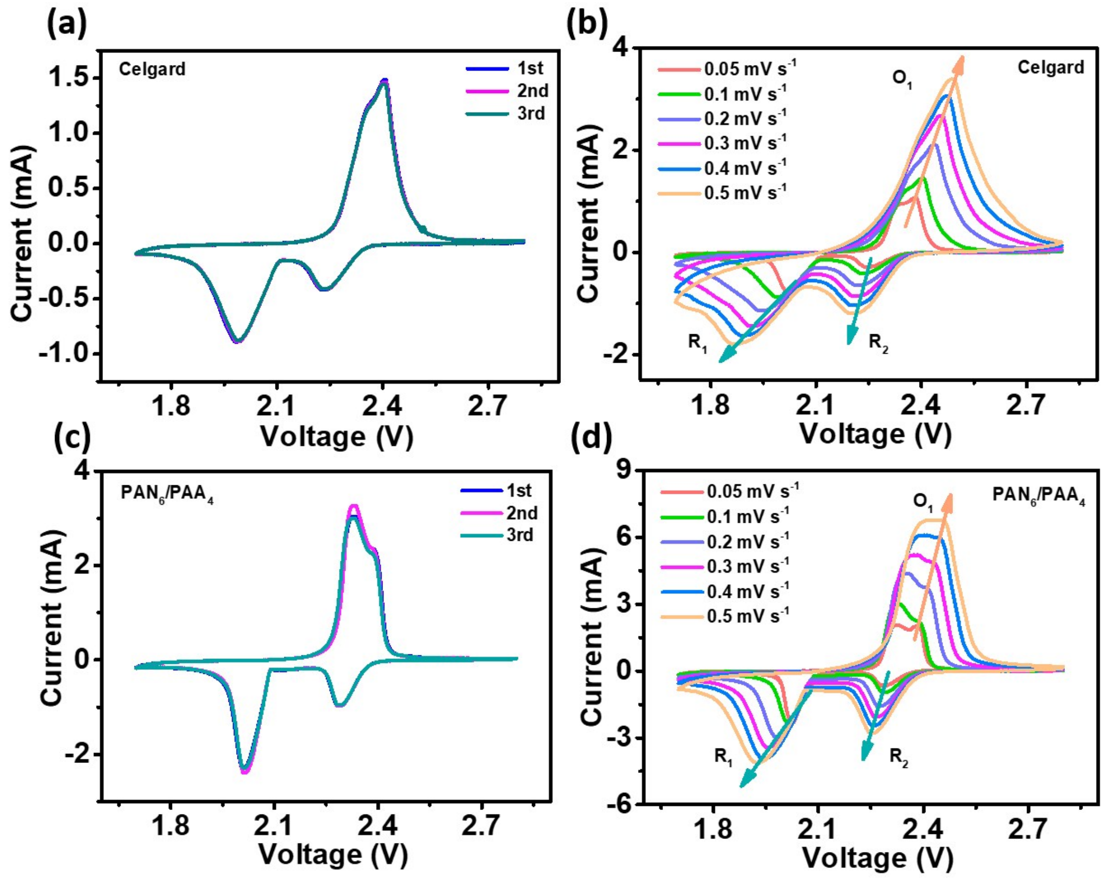

Fig. S6 CV curves of (a, b) Celgard and (c, d) PAN_6/PAA_4 separators obtained at a scanning rate of 0.1 mV s^{-1} and different scanning rates.

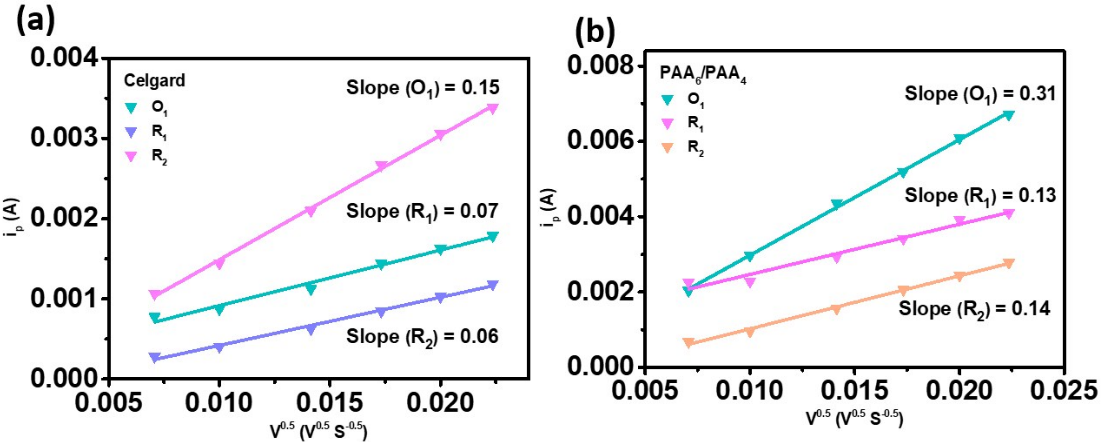

Fig. S7 Linear fits of the peak currents of Li-S batteries with (a) Celgard and (b) PAN_6/PAA_4 separators.

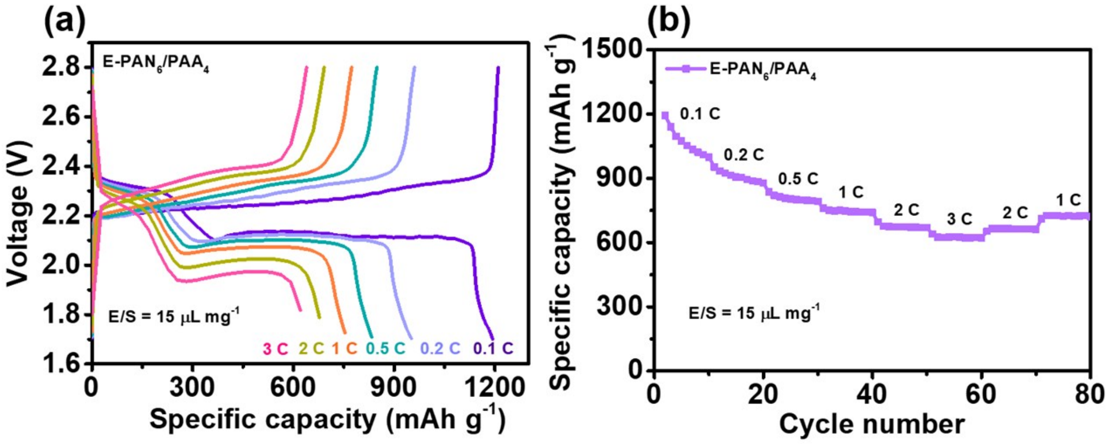

Fig. S8 Electrochemical performance of the batteries assembled by E-PAN_6/PAA_4 at a low electrolyte addition (the ratio of electrolyte/sulfur is about 15 μL mg^{-1}). (a) First cycle discharge/charge curves and (b) rate performance at 0.1, 0.2, 0.5, 1, 2 and 3 C.

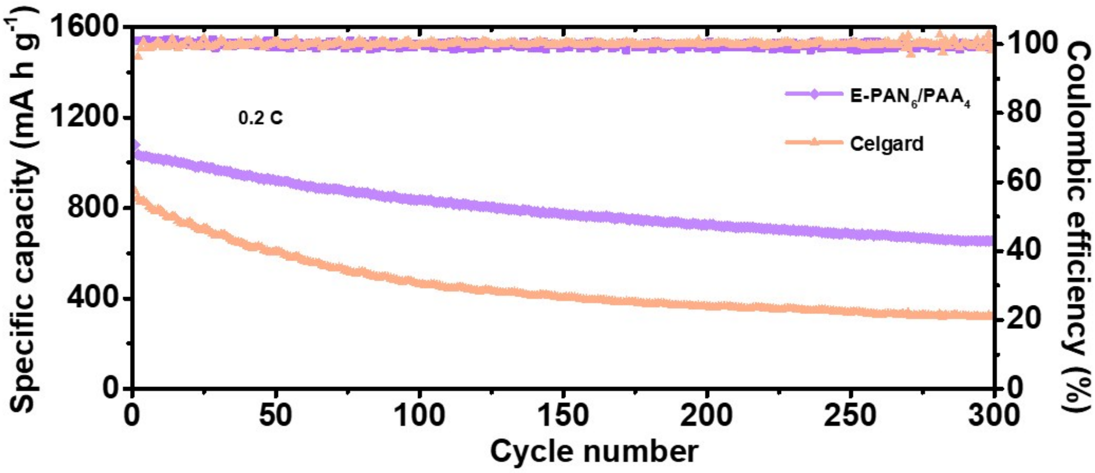

Fig. S9 The cycling performance of batteries with E-PAN_6/PAA_4 and Celgard separators at a low rate of 0.2 C.

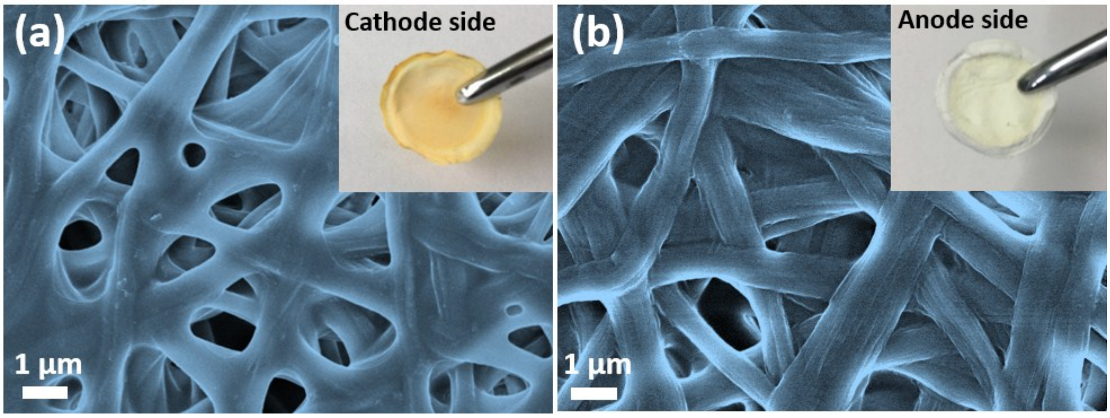

Fig. S10 SEM images with the corresponding digital photographs (inset) of (a) the cathode side and (b) anode side of E-PAN_6/PAA_4 separator after 500 cycles of discharge/charge tests.

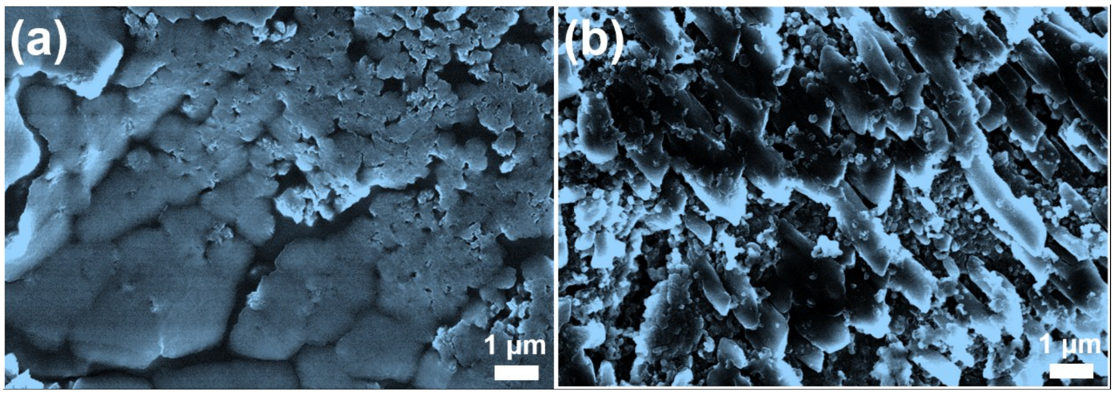

Fig. S11 SEM images of the Li anodes retrieved from Li-S batteries assembled with (a) E-PAN_6/PAA_4 and (b) Celgard separators after the cycling test.

Table S1. Physical properties of different membranes.

Samples	Thickness (μm)	Porosity (%)	Density (g cm^{-3})	Contact angle (°)
Celgard	26	40.1	0.57	37.2
PAN	30	91.2	0.16	0
PAN_8/PAA_2	32	90.5	0.17	0
PAN_6/PAA_4	33	87.3	0.15	0
PAN_4/PAA_6	34	83.1	0.16	0
E-PAN_8/PAA_2	28	37.1	0.17	0
E-PAN_6/PAA_4	30	29.4	0.17	0
E-PAN_4/PAA_6	29	19.6	0.19	0

Table S2. TGA analyses for different samples.

Samples	The remaining weight（wt%）
PAN	53.7
PAN_8/PAA_2	43.0
PAN_6/PAA_4	34.6
PAN_4/PAA_6	34.5
$E\text{-}PAN_8/PAA_2$	41.2
$E\text{-}PAN_6/PAA_4$	34.7
$E\text{-}PAN_4/PAA_6$	31.5
PAA	12.5

Table S3. Summary of the mechanical properties of different membranes.

Samples	**Tensile strength (MPa)**	**Elongation at break (%)**	**Young's modulus (MPa)**
PAN	1.61 ± 0.27	40.17 ± 4.12	4 ± 1
PAN_8/PAA_2	10.88 ± 1.96	53.40 ± 4.31	167 ± 21
PAN_6/PAA_4	15.82 ± 1.31	82.22 ± 2.14	485 ± 26
PAN_4/PAA_6	23.75 ± 2.19	105.23 ± 2.51	541 ± 43
E-PAN_8/PAA_2	22.41 ± 3.07	28.24 ± 1.78	396 ± 34
E-PAN_6/PAA_4	27.17 ± 3.36	47.33 ± 1.59	637 ± 63
E-PAN_4/PAA_6	13.28 ± 1.34	34.50 ± 1.34	95 ± 32
Celgard-1	14.09 ± 2.16	78.64 ± 4.87	485 ± 47
Celgard-2	84.34 ± 4.12	18.44 ± 1.86	642 ± 69

Table S4. Fitted values for the equivalent circuit elements of the electrochemical impedance spectroscopy.

Parameters	**R_0 (Ω)**	**R_{ct} (Ω)**	**R_{sf} (Ω)**
PAN	3.5	3.9	~
PAN_8/PAA_2	4.9	7.2	2.7
PAN_6/PAA_4	6.5	8.4	13.2
PAN_4/PAA_6	5.0	11.4	9.7
E-PAN_8/PAA_2	14.4	23.8	13.6
E-PAN_6/PAA_4	15.6	32.7	15.7
E-PAN_4/PAA_6	33.1	44.2	19.3
Celgard	8.7	12.4	14.4

Table S5. Summary of the Li^+ diffusion coefficient (D_{Li^+}) for Celgard, PAN_6/PAA_4 and E-PAN_6/PAA_4 separators.

Parameters	Celgard	PAN_6/PAA_4	E-PAN_6/PAA_4
D_{Li^+} at peak R_1 ($cm^2\ s^{-1}$)	6.62×10^{-15}	2.28×10^{-14}	8.65×10^{-15}
D_{Li^+} at peak R_2 ($cm^2\ s^{-1}$)	4.87×10^{-15}	2.65×10^{-14}	4.87×10^{-15}
D_{Li^+} at peak O_1 ($cm^2\ s^{-1}$)	3.04×10^{-14}	1.30×10^{-13}	3.46×10^{-14}

Table S6. Comparison of the electrochemical performance of this work with previous works involving different separators using carbon-sulfur cathodes in Li-S batteries.

Separator	Sulfur (%)	Initial capacity (mA h g^{-1})	Rate capability (mA h g^{-1})	Fading rate per cycle (%)	Refs
MoS_2/Celgard	65	1471 (0.1 C)	550 (1 C)	0.08 (0.5 C, 600 cycles)	1
Black phosphorus/Celgard	80	930 (0.4 A g^{-1})	623 (3.5 A g^{-1})	0.14 (0.4 A g^{-1}, 100 cycles)	2
KB@Ir/Celgard [a]	75	1600 (0.1 C)	653 (2 C)	0.11 (1 C, 500 cycles)	3
Janus cation exchange membranes	60	1227 (0.05 C)	610 (2 C)	0.24 (0.2 C, 100 cycles)	4
Graphene/polypropylene/Al_2O_3	60	1067 (0.2 C)	780 (2 C)	0.25 (0.2 C, 100 cycles)	5
PAA-SWNT/Celgard [b]	65	1130 (0.1 C)	592 (2 C)	0.13 (1 C, 200 cycles)	6
COF@CNT/Celgard [c]	75	1130 (0.2 C)	600 (10 C)	0.05 (2 C, 300 cycles)	7
PAA/Celgard [d]	70	713 (0.1 C)	373 (2 C)	0.07 (0.5 C, 600 cycles)	8
GO membrane/Celgard	63	920 (0.1 C)	580 (2 C)	0.26 (0.1 C, 100 cycles)	9
E-PAN/PAA	**60**	**1232 (0.1 C)**	**563 (2 C)**	**0.03 (1 C, 500 cycles)**	**This work**

KB@Ir/Celgard [a]: Ketchen Black and Ir nanoparticle modified Celgard.

PAA-SWNT/Celgard [b]: Poly(acrylic acid) coated single-walled carbon nanotube film on Celgard.

COF@CNT/Celgard [c]: Microporous covalent organic framework (COF) net and mesoporous carbon nanotube (CNT) net modified Celgard.

PAA/Celgard [d]: Poly(acrylic acid) modified Celgard.

References

1. Z. A. Ghazi, X. He, A. M. Khattak, N. A. Khan, B. Liang, A. Iqbal, J. X. Wang, H. Sin, L. S. Li and Z. Y. Tang, *Adv. Mater.*, 2017, **29**, 1606817.
2. J. Sun, Y. M. Sun, M. Pasta, G. M. Zhou, Y. Z. Li, W. Liu, F. Xiong and Y. Cui, *Adv. Mater.*, 2016, **28**, 9797-9803.
3. P. J. Zuo, J. F. Hua, M. X. He, H. Zhang, Z. Y. Qian, Y. L. Ma, C. Y. Du, X. Q. Cheng, Y. Z. Gao and G. P. Yin, *J. Mater. Chem. A*, 2017, **5**, 10936-10945.
4. Z. Li, Y. Han, J. H. Wei, W. Q. Wang, T. T. Cao, S. M. Xu and Z. H. Xu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 44776-44781.
5. R. S. Song, R. P. Fang, L. Wen, Y. Shi, S. G. Wang and F. Li, *J. Power Sources*, 2016, **301**, 179-186.
6. J. H. Kim, J. Seo, J. Choi, D. Shin, M. Carter, Y. Jeon, C. W. Wang, L. B. Hu and U. Paik, *ACS Appl. Mater. Interfaces*, 2016, **8**, 20092-20099.
7. J. T. Yoo, S. J. Cho, G. Y. Jung, S. H. Kim, K. H. Choi, J. H. Kim, C. K. Lee, S. K. Kwak and S. Y. Lee, *Nano Lett.*, 2016, **16**, 3292-3300.
8. S. L. Song, L. Shi, S. Y. Lu, Y. C. Pang, Y. K. Wang, M. Zhu, D. W. Ding and S. J. Ding, *J. Membr. Sci.*, 2018, **563**, 277-283.
9. J. Q. Huang, T. Z. Zhuang, Q. Zhang, H. J. Peng, C. M. Chen and F. Wei, *ACS Nano*, 2015, **9**, 3002-3011.