

## Supplementary Material

### **An electrospun three-layer nanofibrous membrane-based in-situ gel separator for efficient lithium-organic batteries**

Mingyu Yin,<sup>a</sup> Xi Liu,<sup>\*a,c</sup> Caiting Li,<sup>a</sup> Deyi Liao,<sup>a</sup> Yichao Yang,<sup>a</sup> Shaobo Han,<sup>\*a</sup> Longfei Fan,<sup>a</sup> Jing Zhao,<sup>a</sup> Hui Yu,<sup>a</sup> Qingguang Zeng,<sup>b,c</sup> and Da Wang<sup>\*b,c</sup>

<sup>a</sup>*College of Textile Science and Engineering, Wuyi University, Jiangmen 529020, China.*

<sup>b</sup>*School of Applied Physics and Materials, Wuyi University, Jiangmen, 529020, China.*

<sup>c</sup>*Institute of Carbon Peaking and Carbon Neutralization, Wuyi University, Jiangmen, 529020, China.*

\*Corresponding author.

E-mail address: [liuxi@wyu.edu.cn](mailto:liuxi@wyu.edu.cn) (X. L.); [hanshaobo@wyu.edu.cn](mailto:hanshaobo@wyu.edu.cn) (S. H.); [dawang@mail.ustc.edu.cn](mailto:dawang@mail.ustc.edu.cn) (D. W.)

### **Experimental**

*Materials:* All reagents were obtained from commercial sources and used without further purification. Polystyrene sulfonic acid (PSSH, Mw ~45,000-70,000), polyethylene oxide (PEO, Mw ~100,000), 1,1'-Iminodanthraquinone (IDAQ) and multi-walled carbon nanotubes (MWCNTs) were purchased from Shanghai Macklin Biochemical Co., Ltd. Polyvinylene difluoride (PVDF, Mw ~1,000,000) was purchased from Beijing Huawei Ruike Chemical Co., Ltd. *N, N*-Dimethylformamide (DMF) was purchased from Guangzhou Chemical Reagent Factory. Anhydrous ethanol was purchased from Sun Chemical Technology(shanghai) Co., Ltd. The components of the electrolyte, including bis(trifluoromethylsulfonyl)amine lithium salt (LiTFSI), 1,3-dioxolane (DOL), and 1,2-dimethoxyethane (DME) were purchased from Dodochem.

*Characterization:* Fourier-transform infrared (FTIR) spectra data were collected with a Nicolet iS50 Fourier transform infrared spectrometer. Scanning electron microscopy (SEM) characterization was conducted using a Hitachi SU8200 instrument. X-ray diffraction (XRD) characterization was collected on a Rigaku SmartLab 1.6kW. Gel Permeation Chromatography (GPC) was performed by using a Waters GPC-1515. Mass spectroscopy (MS MALDI-TOF) was performed by using a Waters Vion IMS QToF. <sup>1</sup>H NMR spectra were measured using a Bruker AV-500. Cyclic voltammetry (CV) was performed on an electrochemical workstation (CHI660E). Galvanostatic charge/discharge curves and rate capability tests were carried out on a Land test system (CT3001A, China).

*Preparation of PVDF nanofiber:* The PVDF nanofiber was prepared by electrospinning technique. 2.0 g of PVDF was dissolved in 18.0 g DMF under intensive stirring. After stirring for 12 h, the solution was loaded into a 5.0 mL syringe for electrospinning with an applied voltage of 19 kV, a receiving distance of 16 cm, a flow rate of 1 mL h<sup>-1</sup> and a needle of 18 G. This fiber sample was named PVDF nanofiber.

*Preparation of PSSH@PEO11 nanofiber:* The PSSH@PEO11 nanofiber was prepared by electrospinning technique. Firstly, 0.03 g of PEO was dissolved in 2.97 g of mixed solution of anhydrous ethanol and deionized water, where the volume ratio of anhydrous ethanol and deionized water is 5 : 1. Then, 3.0 g of PSSH was added, and the weight percentage of PSSH relative to the total composition was set to 50%. After intensive stirring for 12 h, the solution was loaded into a 5.0 mL syringe for electrospinning with an applied voltage of 8 kV, a receiving distance of 16 cm, a flow

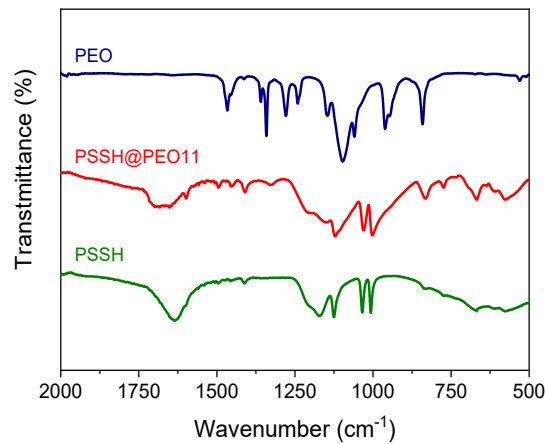
rate of 1 mL h<sup>-1</sup> and a needle of 18 G. This fiber sample was named PSSH@PEO11 nanofiber.

*Preparation of PSE11 nanofiber membrane:* The PSE11 nanofiber membrane was prepared by electrospinning 10.0 g PVDF solution, 6.0 g PSSH@PEO11 solution, and 10.0 g PVDF solution in turn. Before electrospinning the top layer PVDF, the ambient humidity was adjusted to less than 10%. The electrospinning parameters were the same as mentioned above.

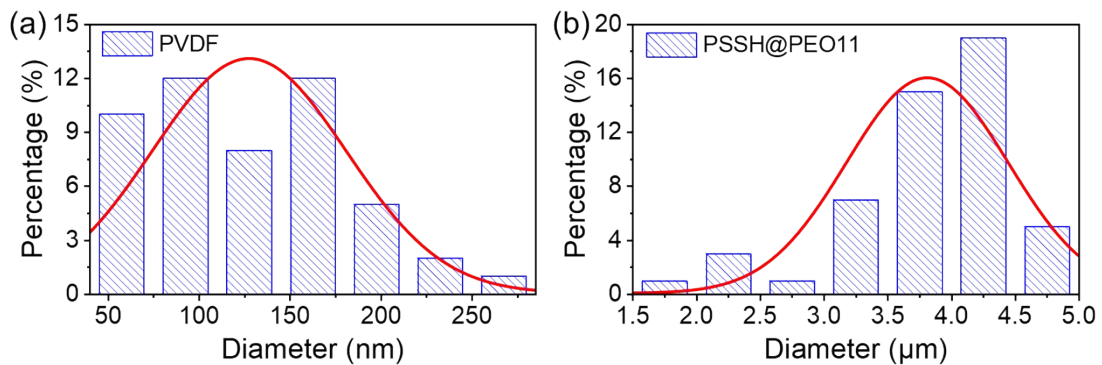
*Preparation of separator:* The dried electrospun PSE11 and PVDF nanofiber membranes were rolled under a pressure of 6 MPa three times with a final membrane thickness of 30–40 μm. Then, the PSE11, PVDF, and Celgard 2400 were punched into circular sheets with 19 mm in diameter to obtain the separator. All final separators were dried at 60 °C in a vacuum oven for over 48 h before assembling coin-type cells in an argon-filled glovebox.

*Cathode fabrication, coin cell assembly and battery test:* The organic electrode is composed of a mixture of 30wt% electroactive materials (IDAQ), 60wt% conductive carbon (MWCNTs), and 10wt% binder (PVDF). The mixing process was conducted using a conventional mortar and pestle, during which IDAQ, MWCNTs, and PVDF were added to the mortar in sequence and ground for 20 min. The mixture was poured into a tablet mold and punched into circular sheets with 12 mm in diameter. The electrodes were dried at 80 °C in a vacuum oven for over 8 h before assembling coin-type cells in an argon-filled glovebox. The coin cells were composed of such electrodes as the cathode, lithium metal disc as the anode, PVDF, PSE11, or Celgard 2400 as the

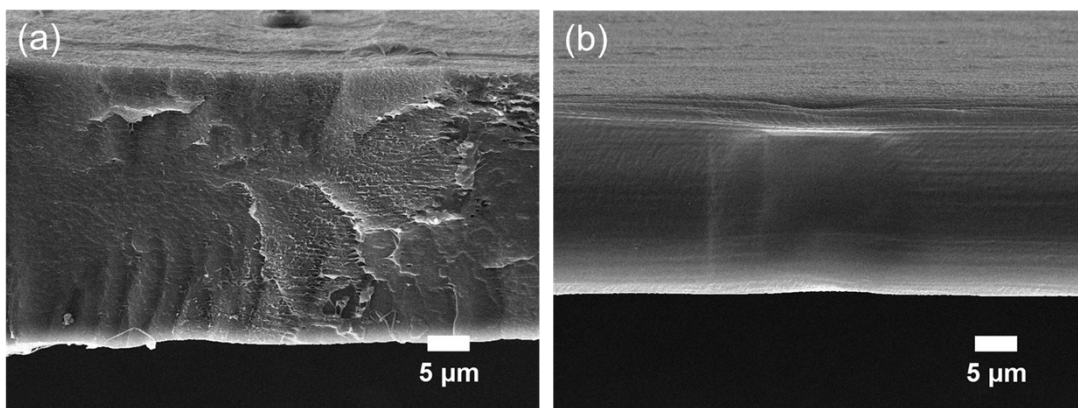
separator, and 1.0 M LiTFSI dissolved in DOL-DME (1:1, v:v) as the electrolyte. The assembled cells were allowed to sit in a 25 °C incubator for 12 h before the related tests, allowing the PSE11 separator to form the PSE11-Gel separator in situ. CV measurement was performed on the CHI660E electrochemical workstation with a scan rate of 0.1 mV s<sup>-1</sup>. Galvanostatic charge-discharge cycling tests, rate capability, and cycle performance were carried out on a Land test system between 1.5 and 3 V at 25 °C.



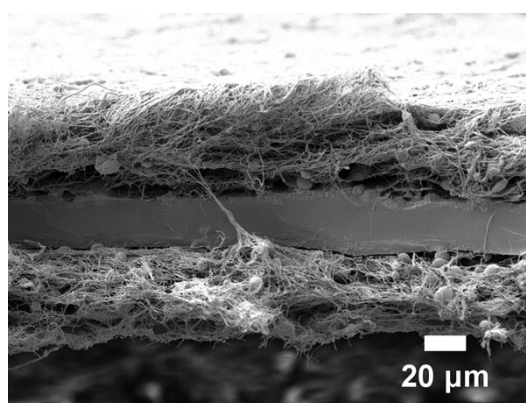
**Fig. S1.** FTIR spectra of PEO, PSSH@PEO11, and PSSH.



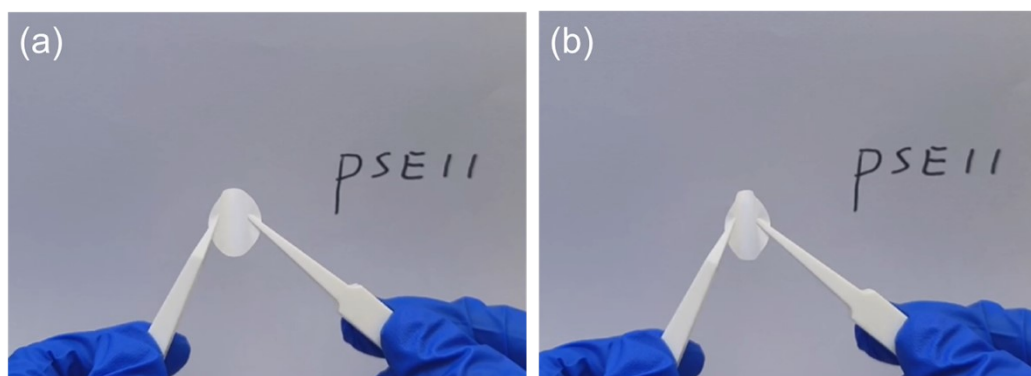
**Fig. S2.** The fiber diameter distributions of PVDF (a) and PSSH@PEO11 (b) nanofibers.



**Fig. S3.** The sectional SEM images of PVDF (a) and Celgard 2400 (b) separators.



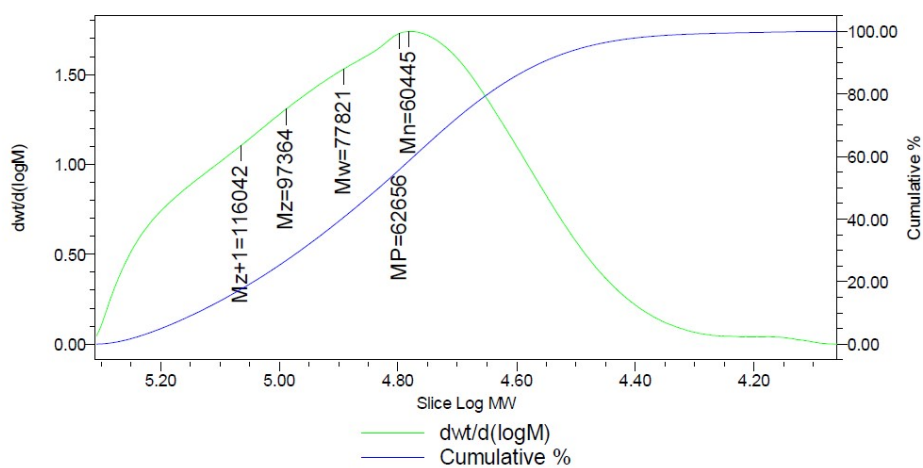
**Fig. S4.** The sectional SEM image of fresh PSE11 membrane without rolled.



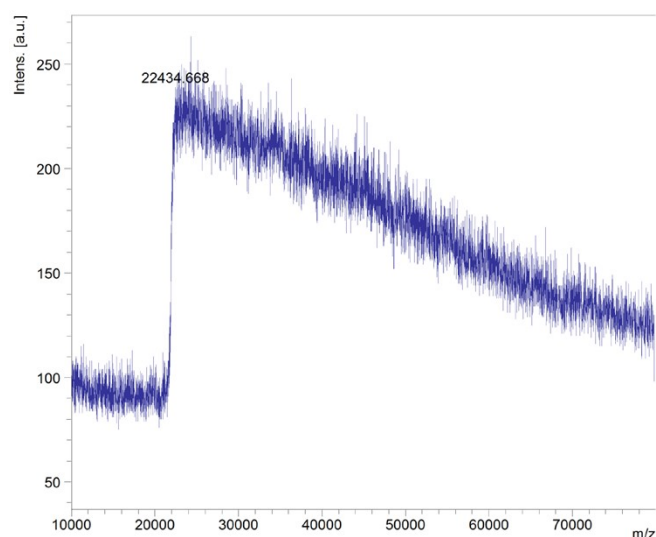
**Fig. S5.** Display of bending mechanical properties of PSE11 separator under different bend angles.



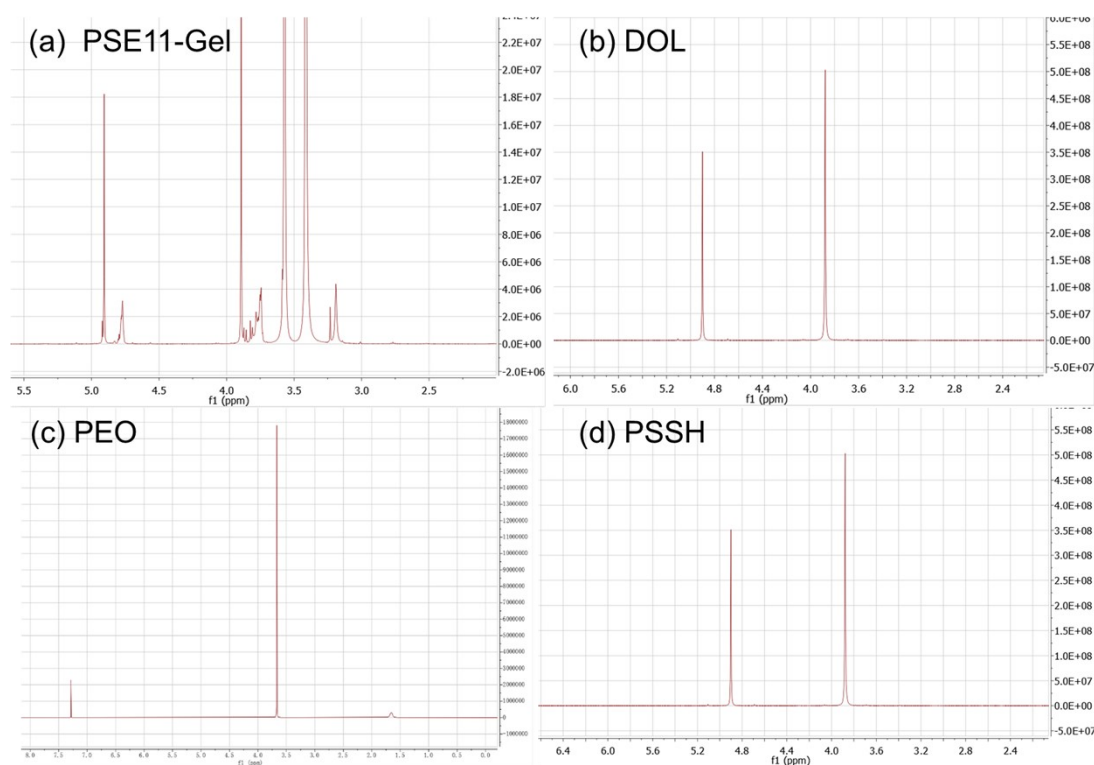
**Fig. S6.** Optical photograph of a pale white quasi-solid state by liquid electrolyte (1.0 M LiTFSI-DOL/DME) soaked with PSE11 over 36 hours.



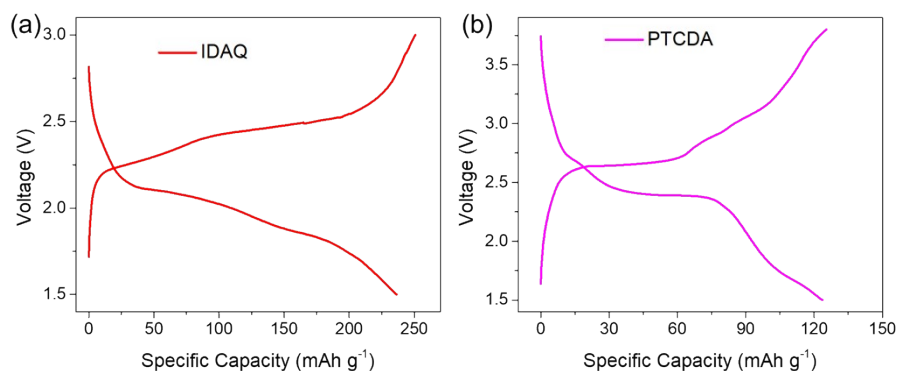
**Fig. S7.** GPC distribution plot of PSE11-Gel measured with  $\text{CHCl}_3$  as eluent.



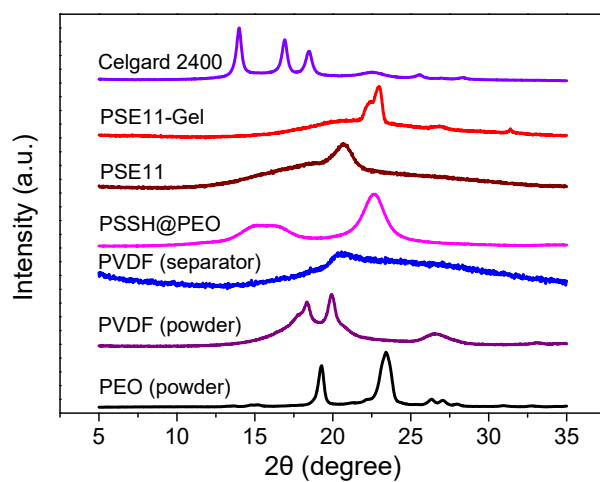
**Fig. S8.** Mass (MALDI-TOF) spectrum of PSE11-Gel.



**Fig. S9.**  $^1\text{H-NMR}$  spectra of the relevant materials. Compared with the  $^1\text{H-NMR}$  spectra of DOL, PEO, and PSSH, the 3–4 ppm broad peaks of PSE11-Gel indicate the formation of a polydisperse gel polymer. In addition, the  $\sim 4.7$  ppm broad peak of PSE11-Gel indicates the presence of residual proton H in the gel polymer, which is the product of ring-opening polymerization induced by PSSH.

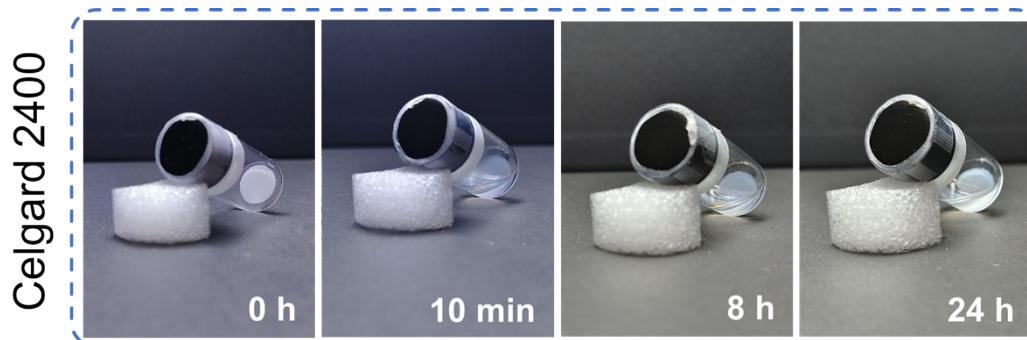


**Fig. S10.** Galvanostatic discharge/charge curves (50 mA g<sup>-1</sup>) of IDAQ (a) and perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) (b) cathodes under 60wt% IDAQ or PTCDA load. According to the literature<sup>[S1, S2]</sup>, the corresponding cathodes were prepared by the coating method, and graphene was used as the conductive agent.



**Fig. S11.** XRD patterns of the relevant materials. Compared to the polymer powders of PEO and PVDF, as well as the commercial Celgard 2400, the nanofibrous membranes (PVDF separator, PSSH@PEO, and PSE11) and PSE11-Gel display broad and weak XRD peaks, which should be attributed to their amorphous structures.





**Fig. S12.** Optical photographs of the liquid electrolyte (1.0 M LiTFSI-DOL/DME) soaked with Celgard 2400.

### References

- [S1] Mengjie Li, Jixing Yang, Yeqing Shi, Zifeng Chen, Panxing Bai, Hai Su, Peixun Xiong, Mingren Cheng, Jiwei Zhao, Yunhua Xu, *Adv. Mater.* 2022, 34, 2107226.
- [S2] Zongshuai Gong, Silin Zheng, Jin Zhang, Yueqin Duan, Zhiqiang Luo, Fengshi Cai, Zhihao Yuan, *ACS Appl. Mater. Interfaces* 2022, 14, 11474–11482.