

Supporting Information

An efficient Lithium-metal Battery Based on Graphene Oxide-Modified Heat Resistant Gel Polymer Electrolyte with Superior Cycling Stability and Excellent Rate Capability

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Section SI. Experimental materials and methods

Materials

The selected PVDF-HFP was bought from Shanghai Aichun Co. Ltd., China. Graphene Oxide (GO) nanosheets were purchased from Jiangsu XFNANO Materials Technology Co., Ltd. And the used PMIA spinning solution was supplied by Yantai Taihe New Materials Co., Ltd. China. The *N, N*-dimethylacetamide (DMAc) was purchased directly from Tianjin Kermel Chemical Reagent Co., Ltd. Moreover, the lithium-metal anode was obtained from Taiyuan Liyuan lithium electric technology center Co., Ltd. The adopted liquid electrolyte for lithium-metal batteries was supplied by Suzhou Sai fluorine New Material Co., Ltd. China. Meanwhile, a 38 μm thick Celgard 2340 separator (Shanxi Li Zhi Yuan Co., Ltd., China) was used as the commercial separator for a comparative study. All other chemical reagents were of analytical grade.

Membrane preparation

Firstly, the PVDF-HFP powders was dissolved in the DMAc solvent to get a homogenous solution. Then, a defined amount of GO nanosheets (0%, 0.1%, 0.3%, 0.5%, 0.7 wt% on the basis of the added PMIA mass) was suspended in the above solution with the assistance of ultrasonic and intensive stirring. After that, the PMIA solution was introduced into the above mixtures by vigorous stirring for 3 hours to obtain the GO doped F-PMIA spinning solutions. The corresponding nanofiber membranes were prepared through the electrospinning technique at an optimized condition of a constant flowing rate of $0.8 \text{ ml}\cdot\text{h}^{-1}$, a high voltage power of 30 kV and a tip-collector distance of 18 cm. The as-prepared nanofiber membranes were finally dried under vacuum oven at 60 °C for 24 h to remove the residual solvents. In the meantime, the gel PMIA membranes could be gained after the hot-pressing and electrolyte-soaking processes. And the electrospun pure PMIA membrane was also prepared as above-mentioned method to be a contrast sample.

Structure characterization

Scanning electron microscopy (SEM: Hitachi S-4800, Japan) was used to observe

the morphologies of nanofiber membranes. The specific surface areas of the as-prepared nanofiber membranes were determined by the Brunauer-Emmett-Teller (BET) method at 77 K (Quantachrome Instruments Autosorb-iQ). The contact angle measuring instrument (JYSP-180, Shanghai Zhongchen Digital Technology Apparatus Co., Ltd., China) was applied to investigate the adopted liquid electrolyte wettability of the obtained membranes. The thermal behavior was analyzed by differential scanning calorimetry (DSC) performed on a Q5000IR TA machine with the temperature gradually increased from 25 °C to 275 °C.

The tensile strength (T) of these samples was performed on YG005 Electronic Single Fiber Strength Tester (Fangyan Instrument Co., Ltd., China) at a stretching speed of 10 mm·min⁻¹, which was calculated in the light of the following **equation (1)**:

$$T (MPa) = A (cN)/(B (cm) \times C (\mu m)) \quad (1)$$

Where A was the tensile load of different samples, B and C were the width and thickness of the nanofiber membranes, respectively. And the membrane thickness was measured by the 0-10-3Q thickness gauge (Shanghai chuanlu measuring tool Co., Ltd., China).

The electrolyte uptake behavior (ε) of all prepared samples was evaluated by recording the mass differences of separators before (M_a) and after (M_b) soaked in liquid electrolyte for 24 h, which was calculated according to **equation (2)**:

$$\varepsilon = \frac{M_b - M_a}{M_a} \times 100\% \quad (2)$$

To measure the overall porosity, five groups of PMIA/P-G and Celgard separators were measured the same quality and dried for 2 h at 60 °C in a vacuum oven and weighed. The overall porosity (ε) was calculated according to the commonly used method based on density measurements:

$$P = 1 - \frac{V_p}{V} \times 100\% \quad (3)$$

where P is the porosity of membrane, V is the total volume of membrane, and V_p is the

volume of PMIA/P-G nanofibers (Celgard separators) (i.e., the mass divided by the density (1.064 g cm⁻³) of PMIA/P-G polymer). The electrolyte uptake and porosity values of each type of electrospun PMIA/P-G nanofibrous membranes (Celgard separators) were finally determined from averaging the values of 5 samples.

Electrochemical performance evaluation

The ionic conductivities of all obtained membranes were characterized through the electrochemical impedance spectroscopy (EIS). And the impedance measurements were evaluated on the liquid electrolyte-soaked membranes sandwiched between two stainless steel (SS) blocking electrodes in the frequency range of 0.1-10⁵ Hz. The specific ionic conductivity (σ) values was calculated on the basis of **equation (4)**:

$$\sigma = \frac{d}{R_0 S} \quad (4)$$

where d (μm), S (cm^2) and R_0 (Ω) were the membranes thickness, the contact area between separators and SS and the bulk resistance of separators, respectively. The electrochemical stability windows were measured by linear sweep voltammetry (LSV) using the lithium/separator/SS sandwich structure cells, ranging over 2.5~6 V with a scan rate of 5 $\text{mV}\cdot\text{s}^{-1}$. All of the above tests were performed on a CHI660D electrochemical workstation system. The lithium-metal batteries were prepared by assembling the lithium cobalt oxide cathode, separators and lithium anode together in an Ar-filled glove box. Subsequently, the cycling stability and rate capability were conducted on a LAND-CT2001A multichannel battery tester within a potential ranging over 2.75~4.2 V. In addition, the adopted liquid electrolyte contained 1 $\text{mol}\cdot\text{L}^{-1}$ lithium hexafluorophosphate (LiPF_6) dissolving in ethylene carbonate (EC)/ diethyl carbonate (DEC)/ethylmethyl carbonate (EMC) (1/1/1, v/v/v).

Section SII. Supporting Figures and Tables

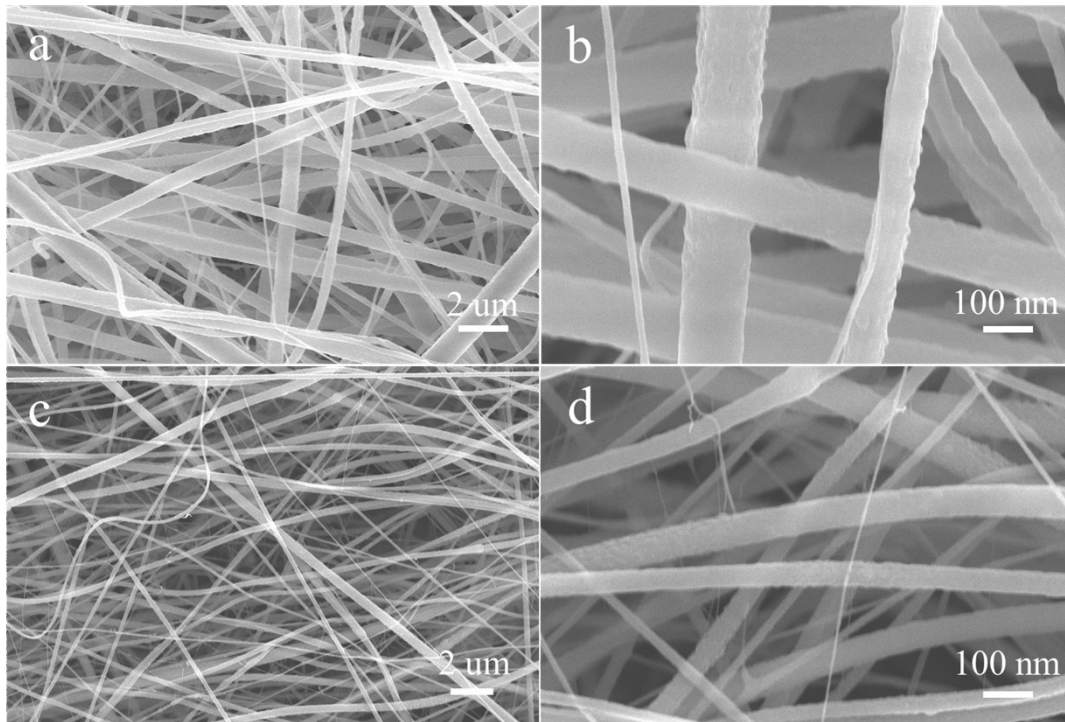


Fig. S1. SEM images of the prepared various PMIA/P nanofiber membranes, (a), (b) PMIA: PVDF-HFP = 5:1; (c), (d) PMIA: PVDF-HFP = 15:1

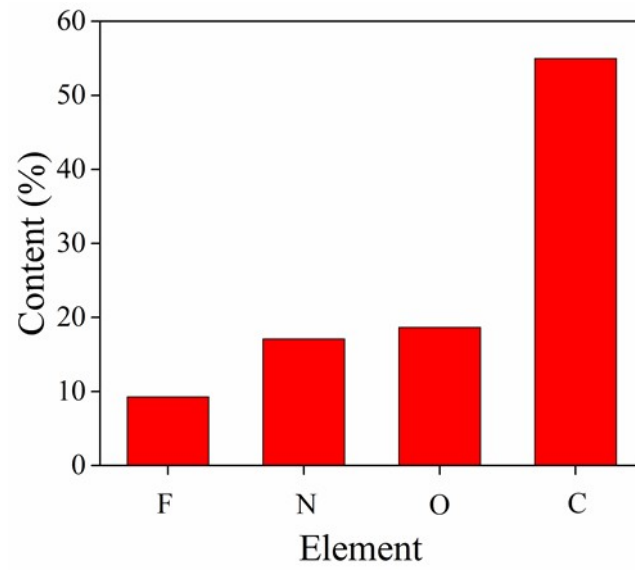


Fig. S2. Element content distribution of the PMIA/P Fiber membrane for XPS

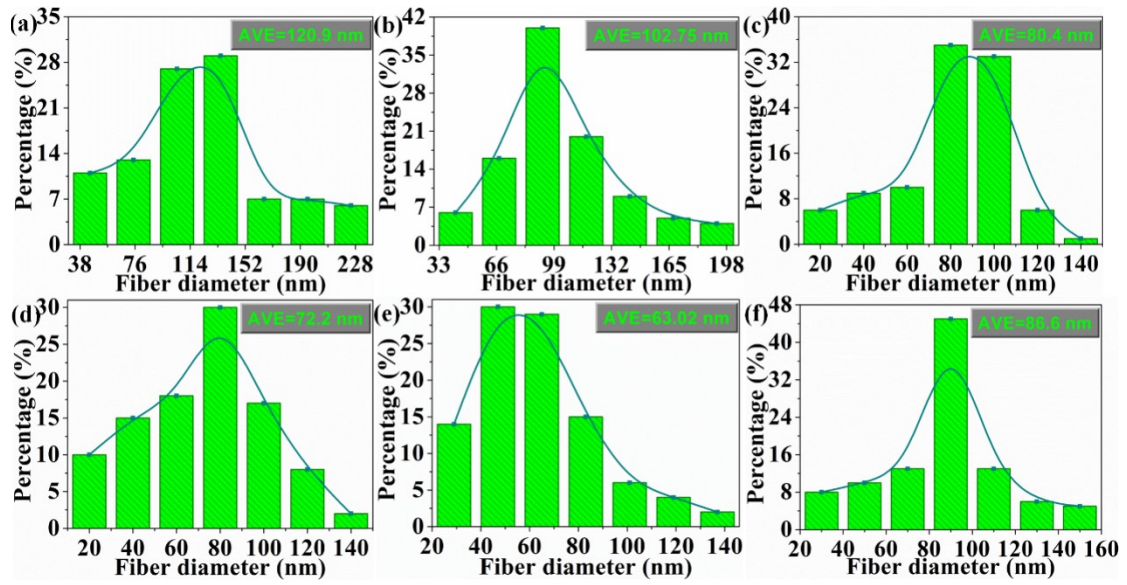


Fig. S3. The fibers diameter distribution of the prepared (a) PMIA; (b) PMIA/P; (c) PMIA/P-1G; (d) PMIA/P-3G; (e) PMIA/P-5G and (f) PMIA/P-7G nanofiber membranes.

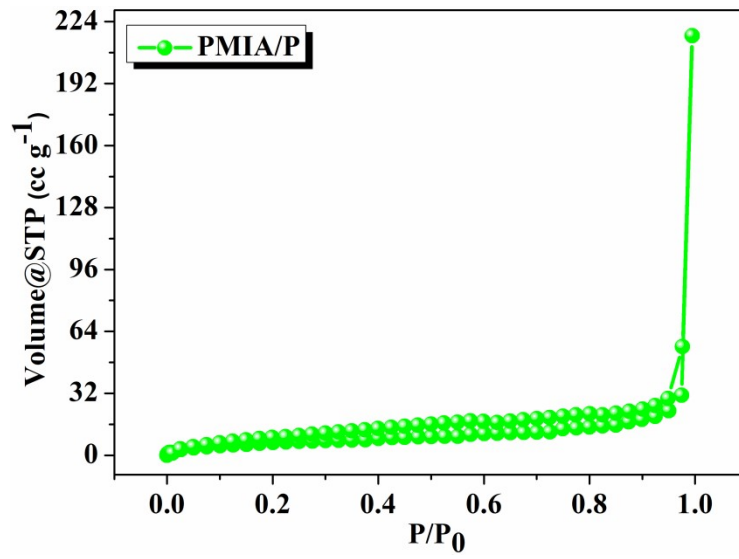


Fig. S4. The nitrogen adsorption-desorption isotherms of the PMIA/P nanofiber membrane.

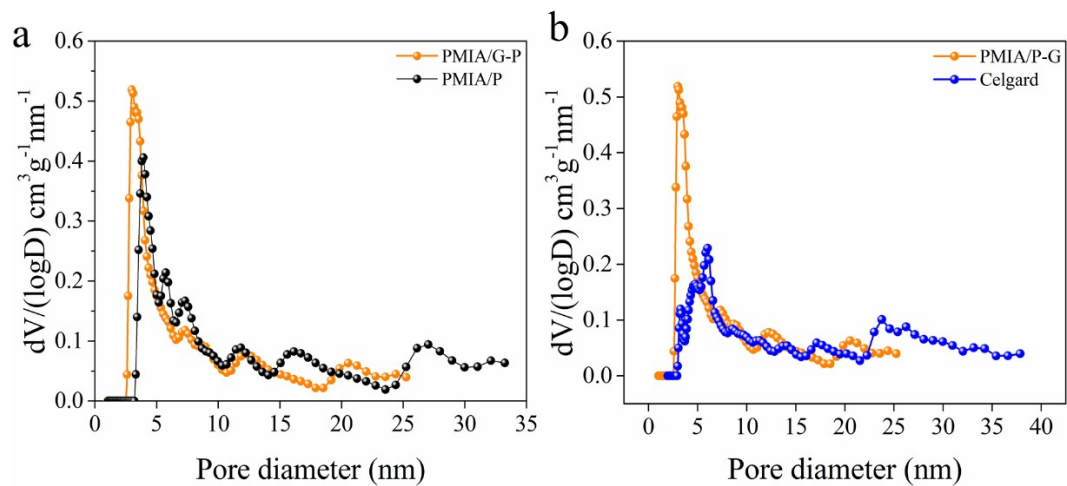


Fig. S5. Pore size distribution of PMIA/G-P, PMIA/P and Celgard for Nitrogen adsorption-desorption isotherms.

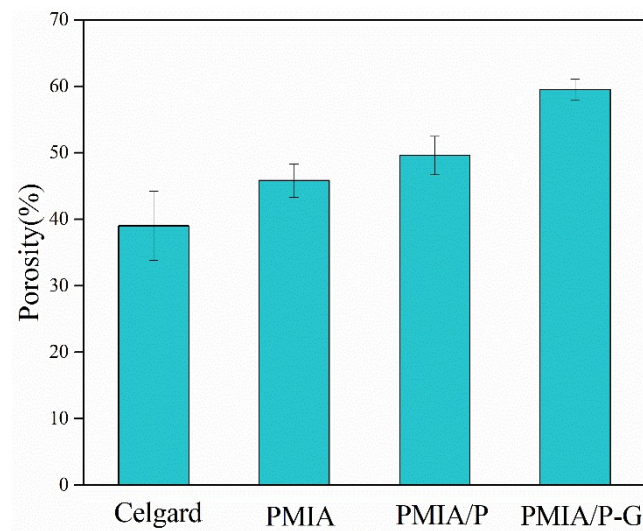


Fig. S6. Porosity of Celgard separator and various fiber membranes

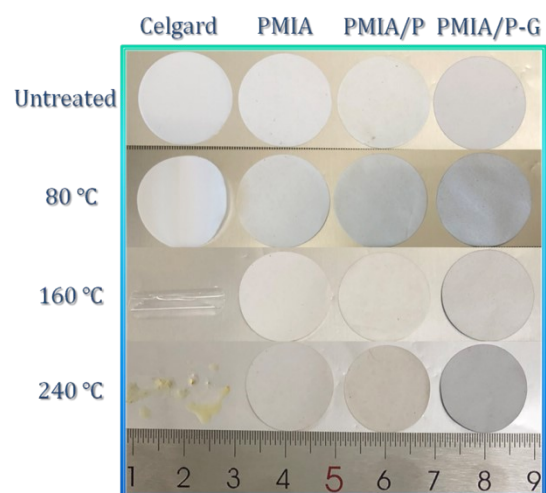


Fig. S7. The heat-treatment pictures of the Celgard, PMIA, PMIA/P and PMIA/P-5G membranes.

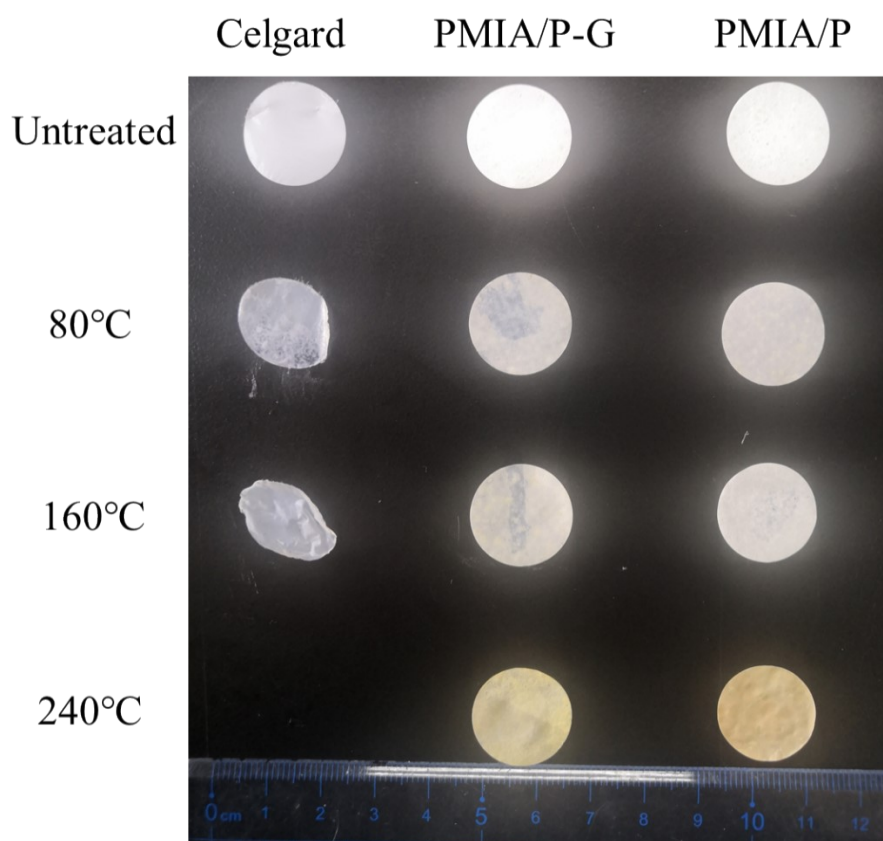


Fig. S8. The heat-treatment pictures of the Celgard, PMIA/P and PMIA/P-5G membranes after associating to the liquid electrolyte.

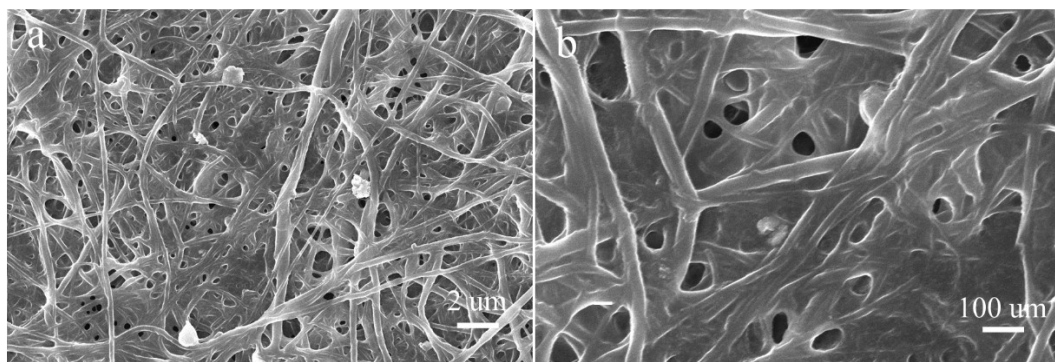


Fig. S9. SEM images of PMIA/P-5G membranes after associating to the liquid electrolyte at 240°C

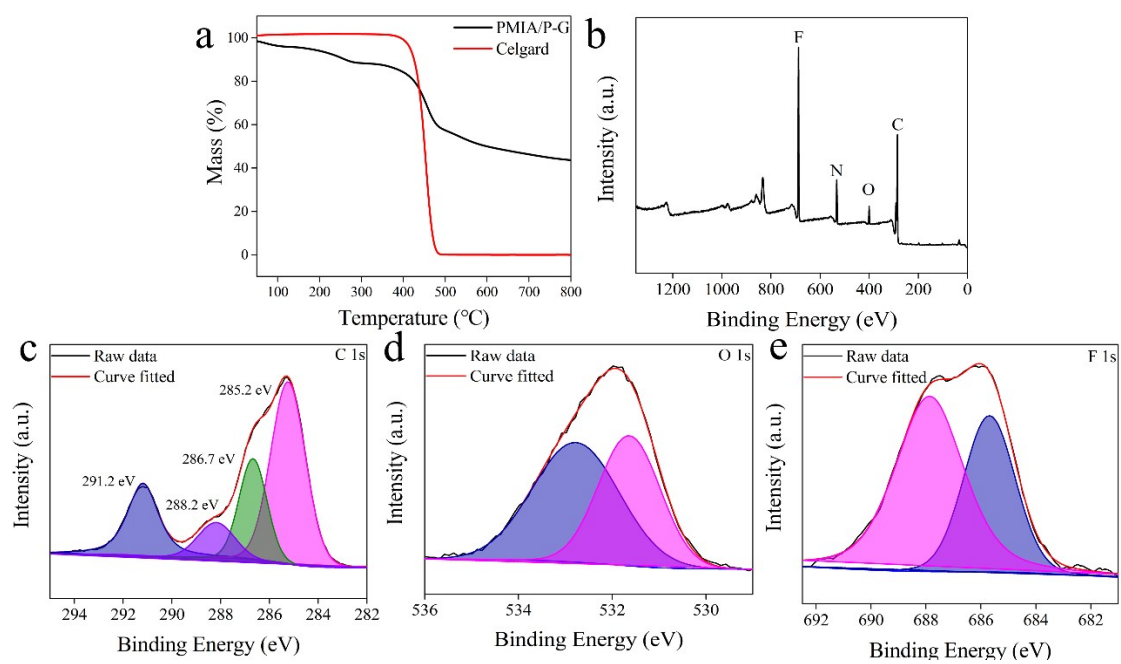


Fig. S10. (a) TG of PMIA/P-5G membranes after associating to the liquid electrolyte; (b) XPS full spectra of PMIA/P-5G; High-resolution spectra of C1s(c), O 1s(d) and F1s (e) of PMIA/P-5G.

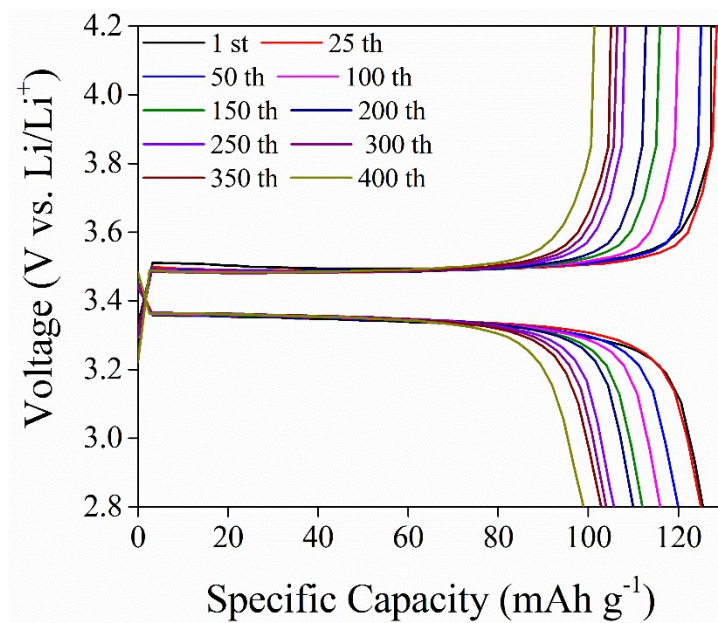


Fig. S11. The galvanostatic discharge/charge profiles of the as-assembled lithium-metal cells with PMIA/P-G separators at 2C.

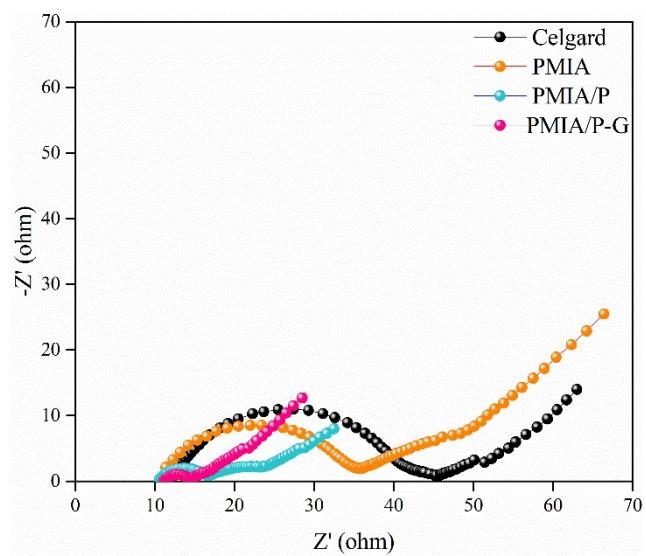


Fig. S12. EIS results of the as-assembled lithium-metal cells with different separators after 200 cycles.

Table S1 Thickness (d), bulk resistance (R_0), and ionic conductivity (σ) of polymer electrolytes with different separators.

Samples	d (μm)	R_0 (Ω)	σ (10^{-3} S/cm)
Celgard	38	2.57	0.47
PMIA	51	1.78	0.91
PMIA/P	42	1.08	1.24
PMIA/P-5G	49	0.75	2.08