

Janus nanofibers with multiple Li⁺ transport channels and outstanding thermal stability for all-solid-state composite polymer electrolyte

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Experimental Section

Fabrication of the Janus nanofiber membrane

The Janus nanofiber membrane was prepared by the side-by-side electrospinning process. For the preparation of one side of the PMIA electrospinning solution: The 15 g PMIA solution was added to 10.7 g N, N-dimethylacetamide (DMAc) solution with magnetic stirring for 5 h, obtaining the PMIA spinning solution. This was followed by the preparation of the other side YSZ-based nanofibers spinning solution. Concretely, the 8YSZ (8%Y₂O₃) doping ceramic nanoparticle, lithium bis-trifluoromethanesulfonimide (LiTFSI, Mw=287.09 g mol⁻¹, 99%, Macklin), and polyethylene oxide (PEO, Mw=600,000 g mol⁻¹) powder was added to suitable anhydrous acetonitrile solvent, keeping stirring for 12 h after the ultrasound for 20 min. The weight percentage of 8YSZ was 60 wt.% of the whole solute system. The ratio of ethylene oxide [EO] to [Li] was fixed at 12:1. Subsequently, the PMIA solution and 8YSZ-based solution were drawn in appropriate amounts to two pipettes, respectively. And tightly stuck the parallel spinning needle on the pipette for side-by-side electrospinning. Specifically, the PMIA and 8YSZ-based solution were extruded at a rate of 0.2 mL h⁻¹ and 0.4 mL h⁻¹ using a booster pump and then drawn into fibers under the action of a 30 kV high-voltage electric field. The distance between the needle and the receiving roller was 16 cm. Finally, the PMIA*YSZ60 Janus nanofiber membrane obtained from the collector was dried at 60°C for 48 h under a vacuum condition to preferably eliminate the residual solvent. It was worth noting that LiTFSI salt was very sensitive to moisture in the air, so the entire electrospinning process was carried out in the drying room to prevent LiTFSI from reacting with moisture in the air. For the comparison, a pure PMIA nanofiber membrane was obtained by electrospinning the above PMIA solution with the extruded rate of 0.6 mL h⁻¹ under a high voltage of 30 kV.

Fabrication of composite electrolytes

The poly (ethylene oxide) (PEO, MW=600000, Aladdin) and Lithium bis-trifluoromethanesulfonimide (LiTFSI, 99.99%, Aladdin) were purchased commercially and without further purification before being used. The all-solid-state composite electrolyte was obtained by the solution-casting method. The pouring solution was firstly prepared by dissolving PEO and LiTFSI in anhydrous acetonitrile in

subsequence and then stirring for 4 h, where the ratio of ethylene oxide [EO] to [Li] was fixed at 12:1. Then the homogeneous solution was poured into the PMIA*YSZ60 Janus nanofiber membrane, and then the obtained composite electrolyte was placed under vacuum at 60 °C for 48 h to remove the solvent. Finally, in order to remove as much residual moisture and solvent as possible, the composite polymer electrolyte was further placed in an argon-filled glove box for at least 48 h before its electrochemical characterization and measurement.

Preparation of cathodes

LiFePO₄ (LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811)), LITFSI, carbon black, and PEO (polyvinylidene fluoride (PVDF)) were added into a certain amount of acetonitrile at the mass ratio of 6:1:1:2, and then continuously stirred for 48 h to obtain a homogeneous solution. Subsequently, the mixed solution was coated onto a carbon-coated aluminum foil and dried in a vacuum oven for 72 h. Finally, the prepared cathode electrodes were cut into 14 mm diameter discs for the application of the assembled cell. The loading of the LiFePO₄ active material was approximately 1.2 mg cm⁻², and the NMC811 active material was approximately 1 mg cm⁻².

Characterization of the composite electrolytes

The surface morphologies of the prepared nanofiber membrane and composite polymer electrolytes were carried out on the field emission scanning electron microscope (GeminiSEM 500, England), in which the acceleration voltage was set to 10 kV and the distribution of the corresponding elements was analyzed by the energy dispersive spectrometer (EDS). A transmission electron microscope (TEM, Hitachi H7650, Japan) was used to characterize the crystallographic features of the electrolytes. X-ray diffraction (XRD) measurements were performed on the Bruker AXS D8 Discover machine with a Ni-filtered Cu K α radiation (1.5418 Å) to characterize the crystal structure of the composite electrolytes, and the 2 θ range was changed from 10° to 80°. The thermogravimetric analyzer (TG 209 F3 Tarsus) was used to analyze the decomposition temperature and decomposition rate of the electrolytes. During the test, the heating rate was 10°C min⁻¹, the gas atmosphere was nitrogen, and the temperature range was 25°C~ 800°C. The mechanical properties of the composite electrolytes were tested on the YG004A/N electronic single-fiber strength meter with a tensile speed of 20 mm min⁻¹.

Electrochemical measurements of the composite electrolytes

The ionic conductivities of the composite electrolytes were measured through the

electrochemical impedance spectroscopy (EIS) method, where the test frequency changed from 10^6 to 10^{-1} Hz and the temperature increased from 30°C to 70°C . The specific conductivity value (σ) was calculated according to the **formula (1)**,

$$\sigma = \frac{L}{RS} \quad (1)$$

where L , R , and S represented the thickness of the composite electrolytes, the impedance of the stainless steel (SS)/electrolyte/SS sandwich batteries measured by the EIS method, and the area of the stainless steel (2 cm^2), respectively.

Using linear sweep voltammetry (LSV) to characterize the electrochemical stability window of the composite electrolyte on a CHI660D electrochemical workstation at 50°C , and the battery assembly of a lithium sheet/electrolyte/steel sheet. The voltage range of the test was set to 2.5-6.0 V with a scan rate of 1 mV s^{-1} .

By combining the alternating-current (AC) impedance (from 10^6 to 10^{-1} Hz) and direct-current (DC) polarization (10 mV) curve on the CHI660D electrochemical workstation, the Li^+ transference number (t_{Li^+}) was obtained, and the specific results were calculated by **formula (2)**,

$$t_{\text{Li}^+} = \frac{I_{\text{ss}}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{\text{ss}} R_{\text{SS}})} \quad (2)$$

in which ΔV represents the magnitude of the applied polarization potential, and I_0 and I_{ss} are the initial and steady-state polarization currents, respectively. Meanwhile, R_0 and R_{ss} are the resistance before and after applying the DC voltage, respectively.

The cycle stability of lithium symmetrical batteries and all-solid-state lithium metal batteries was tested by the LAND-BT2013C battery test system. The cycling performance of the LiFePO_4 assembled all-solid-state battery was tested at different temperatures with various current densities ($1 \text{ C} = 170 \text{ mA g}^{-1}$) in the voltage range of 2.80-3.85 V. The cycling performance of the NCM811 assembled all-solid-state battery was tested at 50°C with a current density of 0.5 C ($1 \text{ C} = 280 \text{ mA g}^{-1}$) in the voltage range of 3-4.3 V. Noticeably, the entire assembly process of the all-solid-state lithium symmetrical batteries and lithium metal batteries does not add any liquid electrolyte.

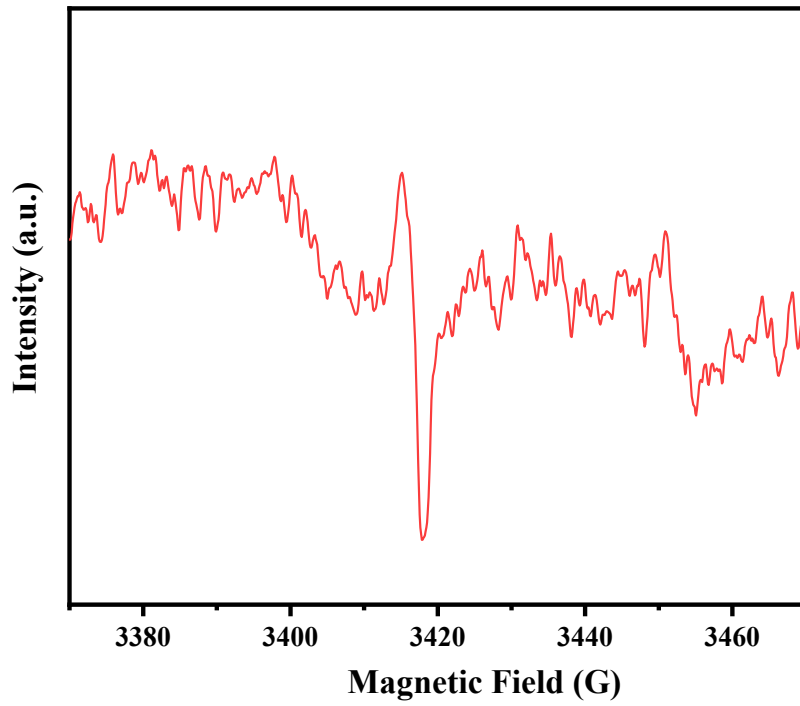


Fig.S1 EPR spectra for the prepared YSZ nanoparticle.

Fig. S2a shows the FTIR spectra for the prepared PEO SPE and PEO/PMIA*YSZ60

CPEs in the range of 4000-400 cm^{-1} . To better observe the differences caused by adding the PMIA*YSZ60 Janus nanofiber to the PEO matrix, the deconvoluted FTIR spectra in **Figs. S2b-c** presents the stretching vibrational modes of the C-O-C, $-\text{SO}_2$, and $-\text{CF}_3$ groups in the frequency ranges 1160-1000 cm^{-1} and 1400-1150 cm^{-1} , respectively. From **Fig. S2b**, the C-O-C characteristic peaks of the prepared PEO/PMIA*YSZ60 CPEs shifted to 1035.23, 1075.12, 1102.40, 1123.63 and 1140.67 cm^{-1} when compared with those of PEO electrolyte (1036.10, 1076.57, 1098.02, 1119.44, and 1141.20 cm^{-1} , respectively). The evolution of this C-O-C characteristic peak also indicated a change in the chemical environment of the $-\text{EO}$ group in PEO can be realized, further proving the interactions between C-O-C and PMIA*YSZ60 Janus nanofiber [1]. Furthermore, in the 1400-1150 cm^{-1} range (**Fig. S2c**), after introducing the PMIA*YSZ60 Janus nanofiber to the PEO, the $-\text{SO}_2$ stretching corresponding to the peaks at 1331.15 and 1302.03 cm^{-1} shifted to 1131.21 and 1302.82 cm^{-1} , respectively. And the $-\text{CF}_3$ symmetric stretching corresponding to the peaks at 1253.98 and 1227.71 cm^{-1} , and the $-\text{CF}_3$ asymmetric stretching corresponding to the peaks at 1193.88, and 1178.03 cm^{-1} all shifted to varying degrees, respectively. All of these shifts and results about the corresponding $-\text{SO}_2$ and $-\text{CF}_3$ groups demonstrated that the prepared PMIA*YSZ60 Janus nanofiber had strong interactions with TFSI $^-$, which effectively promoted the dissociation of LiTFSI and released more lithium ions [2].

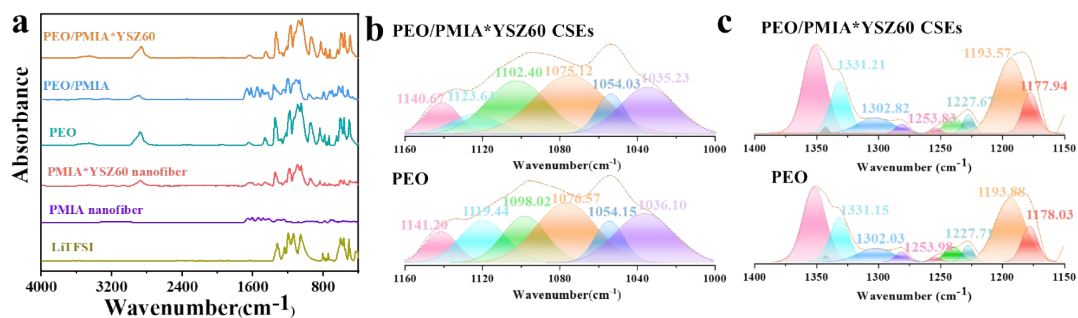


Fig. S2 (a) FTIR spectra for PMIA nanofibers, LiTFSI, PEO, PEO/PMIA, and PEO/PMIA*YSZ60 at 4000-400 cm^{-1} . FTIR spectra for PEO, PEO/PMIA*YSZ60 at (b) 1160-1000 cm^{-1} . and (c) 1400-1150 cm^{-1} .

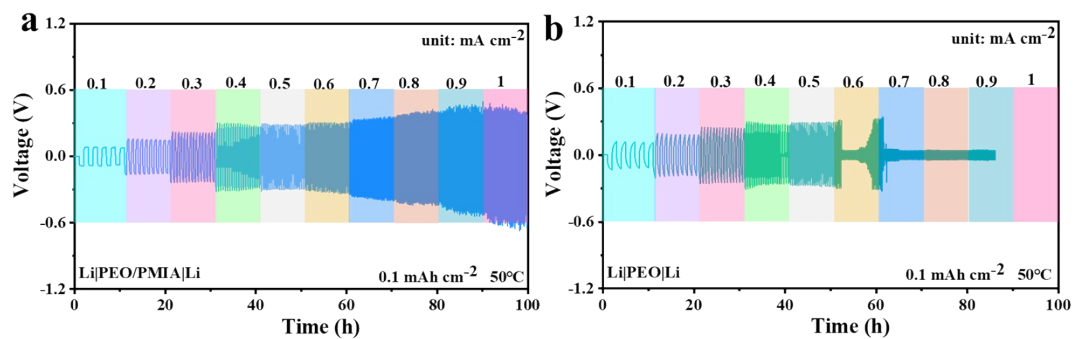


Fig. S3 The cycling performance of the Li|SPEs|Li batteries under 50 °C and different current densities at 0.1 mAh cm⁻².

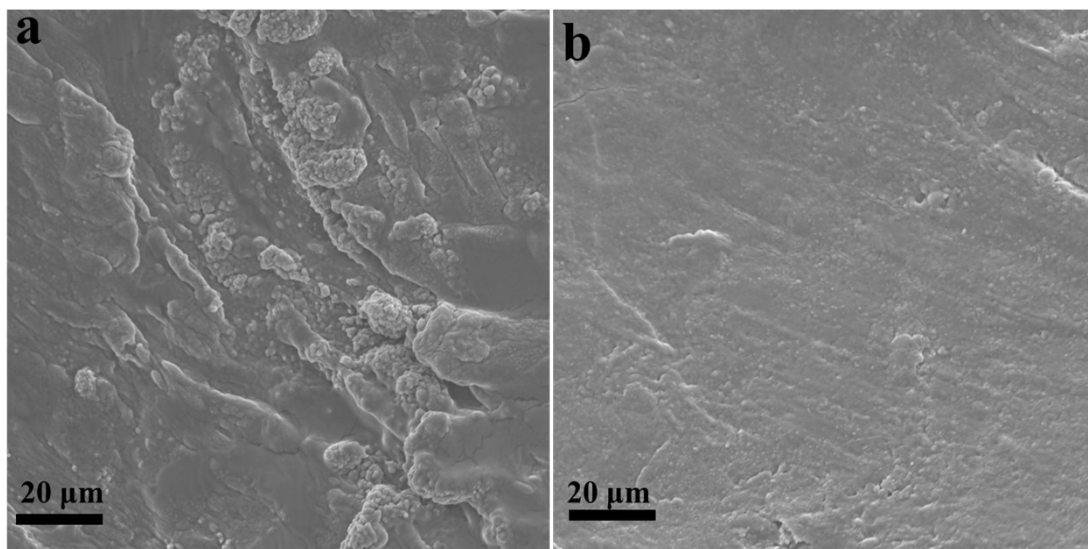


Fig. S4 The surface morphology of the lithium anodes obtained from (a) Li|PEO|Li and (b) Li|PEO/PMIA*YSZ60|Li batteries.

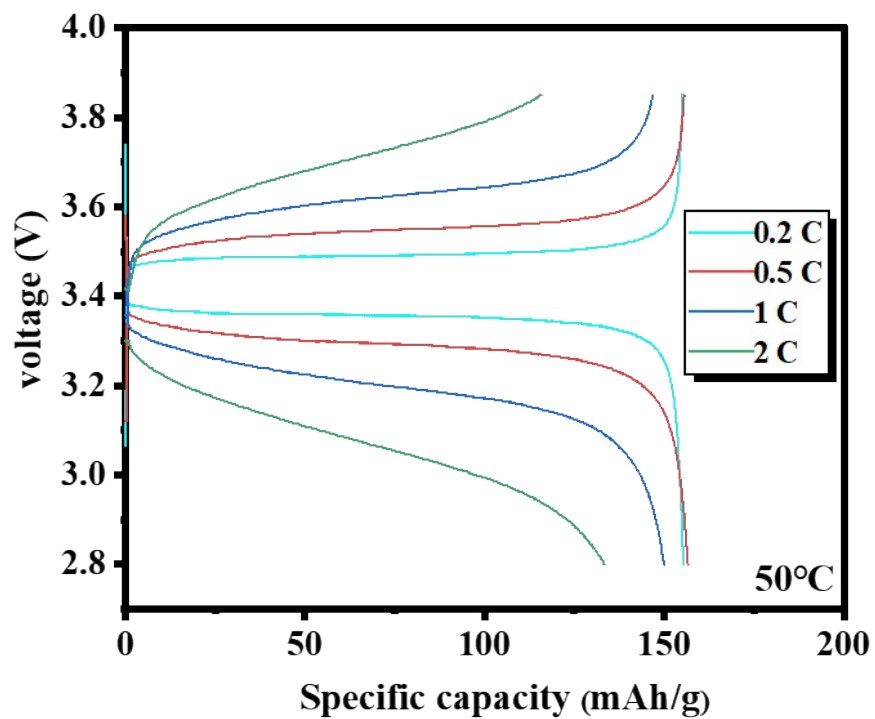


Fig. S5 Charge-discharge voltage profiles of Li|PEO/PMIA*YSZ60|LFP cells at different rates.

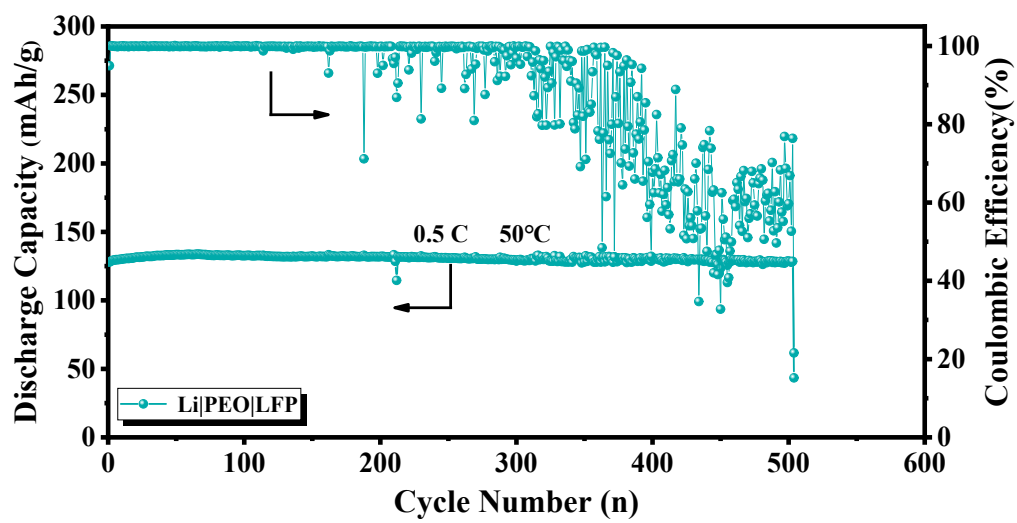


Fig. S6 Cycling performance of Li|PEO|LFP at 0.5 C.

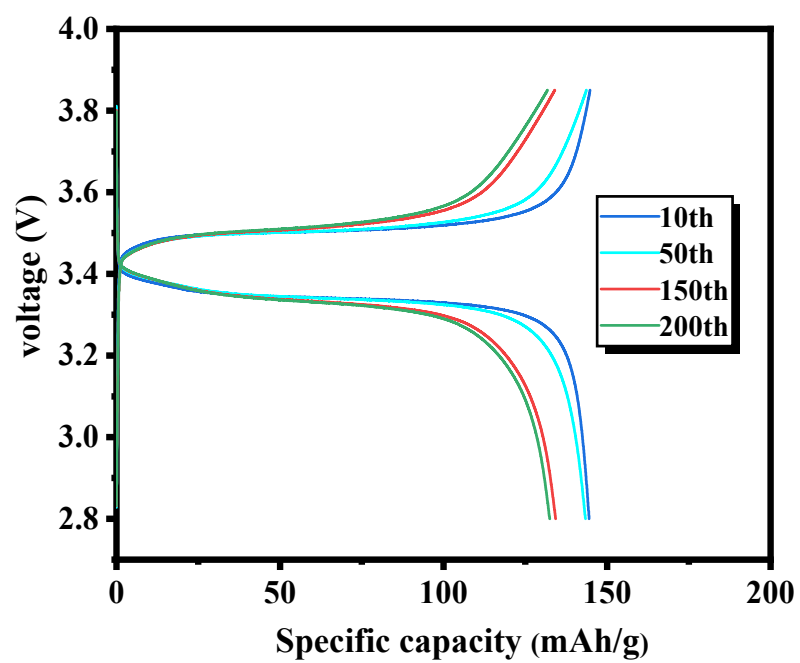


Fig. S7 Charge-discharge voltage profiles of Li|PEO/PMIA*YSZ60|LFP cells at 0.3 C and 40°C.

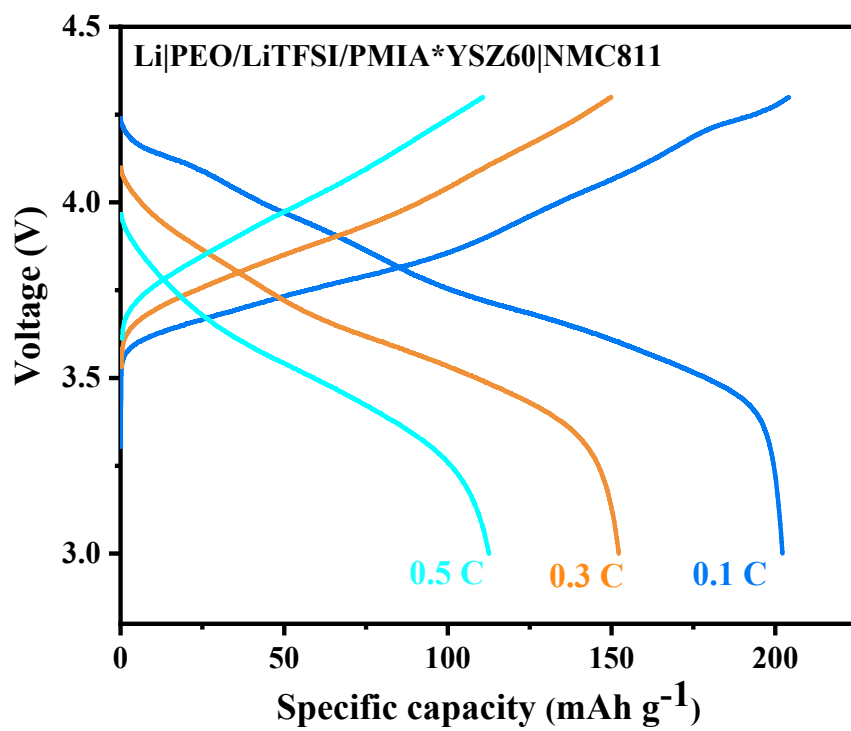


Fig. S8 Charge-discharge voltage profiles of Li|PEO/PMIA*YSZ60|NMC811 cells at different rates.

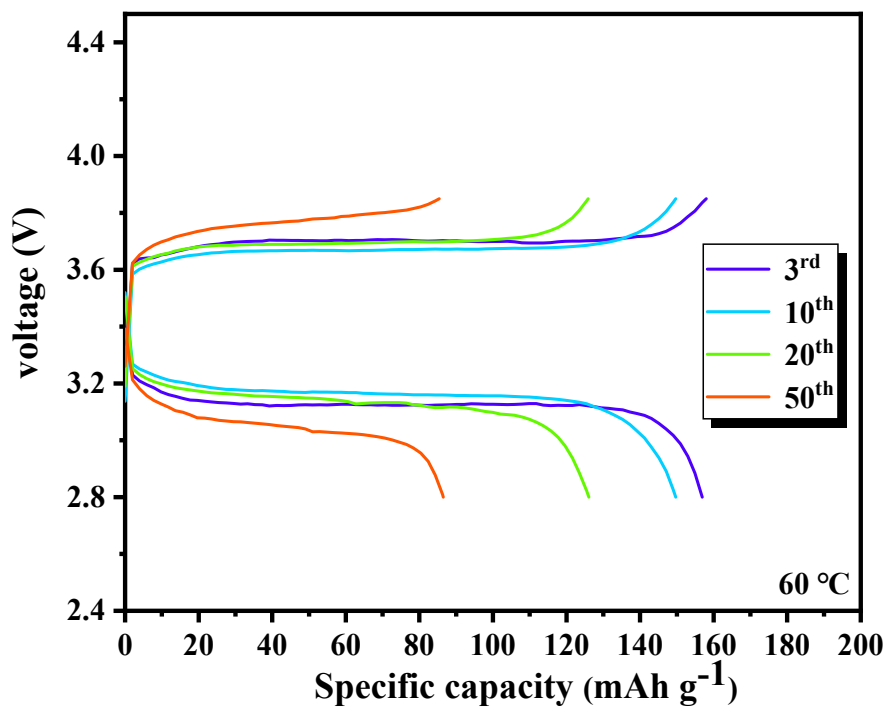


Figure S9 Charge-discharge voltage profiles of LiFePO₄|PEO/PMIA*YSZ60|Li pouch cell after different cycles at 0.3 C and 60 °C.

References

- [1] M. Lei, X. Wu, Y. Liu, K. Chen, J. Hu, C. Li, Nano Res. 16 (2023) 8469-8477.
- [2] H. Chen, D. Adekoya, L. Hencz, J. Ma, S. Chen, C. Yan, H. Zhao, G. Cui, S. Zhang, 10 (2020) 2000049.