

# Supplementary Material

## Enabling stable interphases via In-Situ Two-Step Synthetic Bilayer Polymer Electrolyte for Solid Li Metal Batteries

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### 1. Experimental Section

#### Materials

All reagents and solvents were purchased from Sigma-Aldrich and Alfa Aesar and used without further purification unless otherwise stated. The  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  cathode material was supplied by Beijing Easpring Material Technology Co., Ltd. The  $\text{LiFePO}_4$  cathode material was supplied by Changchun Jinneng Co., Ltd. The Li foils with the thickness of 600  $\mu\text{m}$  were purchased from China Energy Lithium Co., Ltd.

#### Prepare of PAN-SPE film

PAN-SPE was prepared by solvent evaporation. PAN (0.3 g, 85000 MW) , LiTFSI and TEGDME were dissolved in Dimethylformamide (DMF) and stirred for 20 h. The obtained homogeneous dispersion was coated onto the Al foil. The Al foil coated with precursor solution dried at 80 °C in vacuum oven. The PAN-SPE was adherent to the surface of Li foil.

### **Prepare of PEO-SPE film**

PEO-SPE was prepared by UV crosslinking. PEO (1 g, 200000 MW), LiTFSI and TEGDME were dissolved in acetonitrile and stirred for 20 h. The obtained homogeneous dispersion was coated onto the PTFE plate. The PTFE plate coated with precursor solution was later dried at 80 °C in vacuum oven, then exposed under a 500 W Hg lamp (CEL-M500, Beijing China Education Au-light co., Ltd) for 15 min. The UV light with a main wavenumber of 365 nm was used, and the radiation exposure energy was about 150 mW cm<sup>-2</sup>. The PEO-SPE was adherent to the surface of PTFE plate.

### **Prepare of DLPE film**

DLPE was prepared by in-situ two-step synthesis. The cathode coated with PAN-SPE precursor solution was dried at 80 °C in vacuum oven, then the obtained PEO-SPE homogeneous dispersion was coated onto the PAN-SPE. The cathode and PAN-SPE coated with PEO-SPE precursor solution was later dried at 80 °C in vacuum oven, then exposed under a 500 W Hg lamp for 15 min. The DLPE was obtained.

## **2. Electrochemical measurements**

Electrochemical tests were carried out using 2025-type coin cells assembled in an Ar-filled glovebox (Mbraun, PRS380/S11-0736) with H<sub>2</sub>O and O<sub>2</sub> < 0.1 ppm. In the assembly of Li // Li cells, the Li metal foils are with a diameter of 16.0 mm, the electrolytes are with a diameter of 17.0 mm.

Electrochemical impedance spectroscopy (EIS) analyses were taken during cycling. The stability test of Li electrode was measured by Li // Li cells, and the current density is 0.1 mA

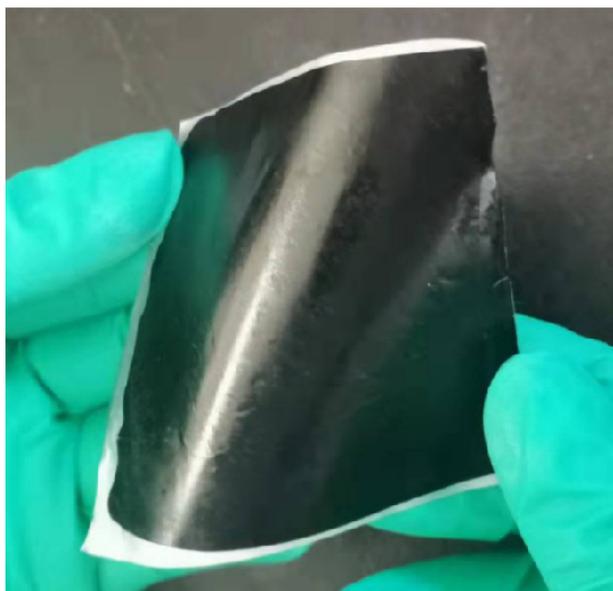
cm<sup>-2</sup> with capacities of 0.1 mAh cm<sup>-2</sup>, respectively.

In the assembly of LFP // Li and NCM // Li full cells, The LFP and NCM electrodes were prepared by casting LiFePO<sub>4</sub> and LiNi<sub>0.6</sub>Co<sub>0.2</sub>Mn<sub>0.2</sub>O<sub>2</sub>, C350 and poly(vinylidene difluoride) (PVDF) in a weight ratio of 8:1:1 onto Al foil. The areal loadings of LFP and NCM cathodes were about 1.5 mg cm<sup>-2</sup>. The LFP // Li cells were cycled at the voltage range 2.5~3.8 V vs. Li/Li<sup>+</sup>. The NCM // Li cells were cycled at voltage range 2.8~4.3 V vs. Li/Li<sup>+</sup>. These battery tests were all conducted using a Neware battery testing system, and all the electrochemical tests were conducted using an electrochemical workstation (PARSTAT 4000). The Li foils that were polished with tetrahydrofuran (THF) solvents in our experiments.

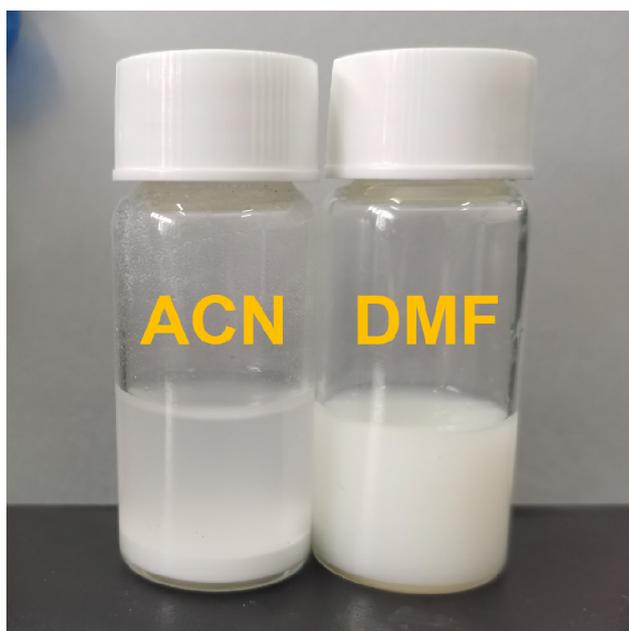
X-ray photoelectron spectroscopy was employed on the Li metal anode and cathode from NCM // Li coin cells after 50 cycles at 0.1 C.

### **3. Characterization**

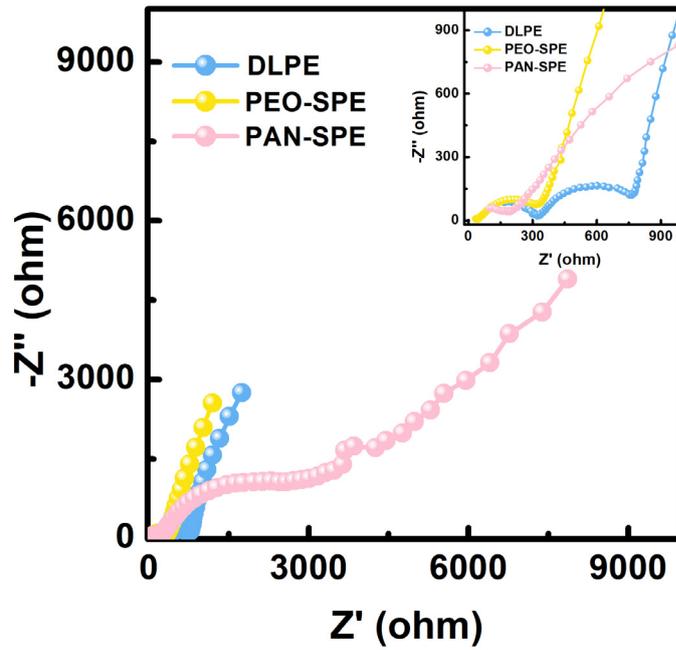
The structural morphology and the in-detail inter-stacked structure of the sample was examined by scanning electron microscopy (SEM) (Hitachi S-5500) coupled with an EDS (Ametek). X-ray photoelectron spectroscopy (XPS) analysis was carried out an ESZALB 250XL spectrometer using a twin-anode Al K (1486.7 eV) and an emission angle of 90°. The binding energy scale was calibrated using C 1s peak assigned to the C-H bond at 284.3 eV.



**Figure S1.** Optic photos of DLPE by in-situ two-step method.

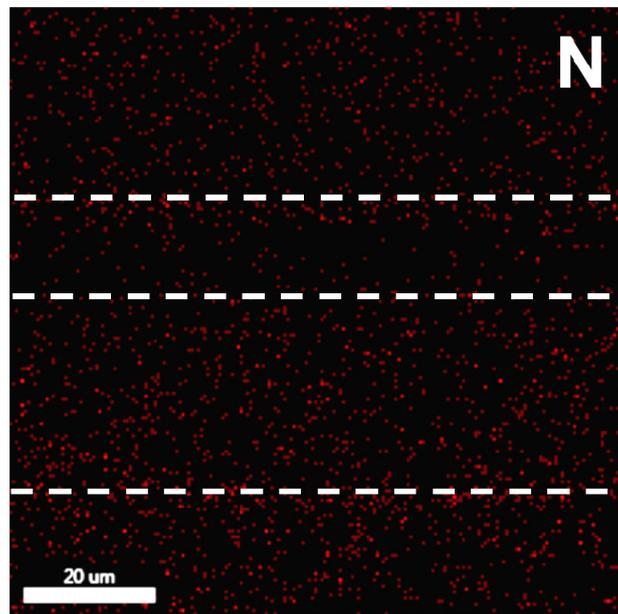


**Figure S2.** Photos of PAN dissolution in ACN and DMF.



**Figure S3.** The Nyquist plot of NCM622/DLPE/Li, NCM622/PEO-SPE/Li and NCM622/PAN-SPE/Li.

The interfacial resistance of DLPE is larger than that of PEO-SPE electrolyte, because the former introduces the PAN-SPE, which adds a new electrolyte-electrolyte interface. Besides, PAN-SPE has a large interfacial resistance which is larger than that of DLPE.



**Figure S4.** The EDS mapping of N element for the DLPE membrane.

There is no obvious two-layer structure in the EDS mapping of N element, because both PAN-SPE and PEO-SPE contain a large amount of LiTFSI which contains N element.

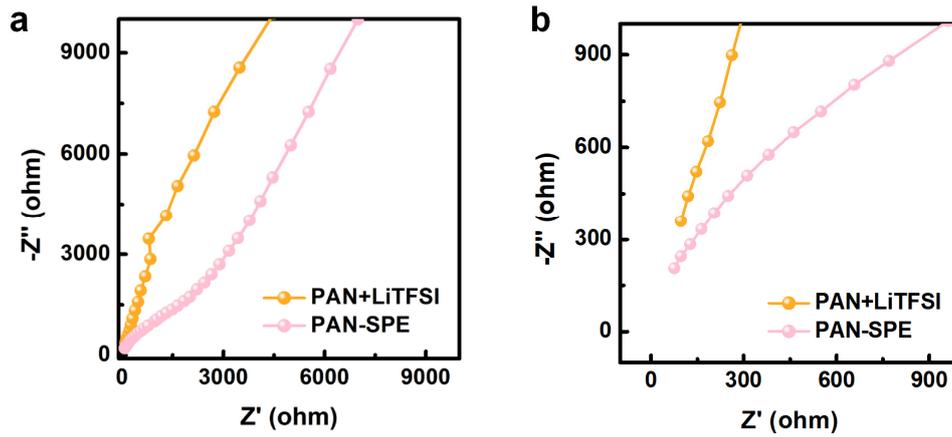


Figure S5. (a) The Nyquist plot of PAN and PAN-SPE, (b) the initial of the Nyquist plot.

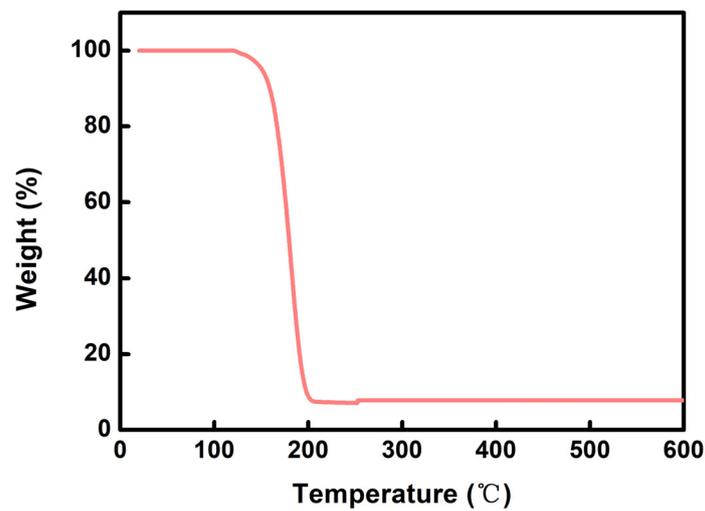


Figure S6. TGA curves of pure PEO.

Pure PEO has 92.8 % weight loss at 350 °C, which is in accordance with the TGA curves of DLPE and PEO-SPE. They have a weight loss at 350 °C .

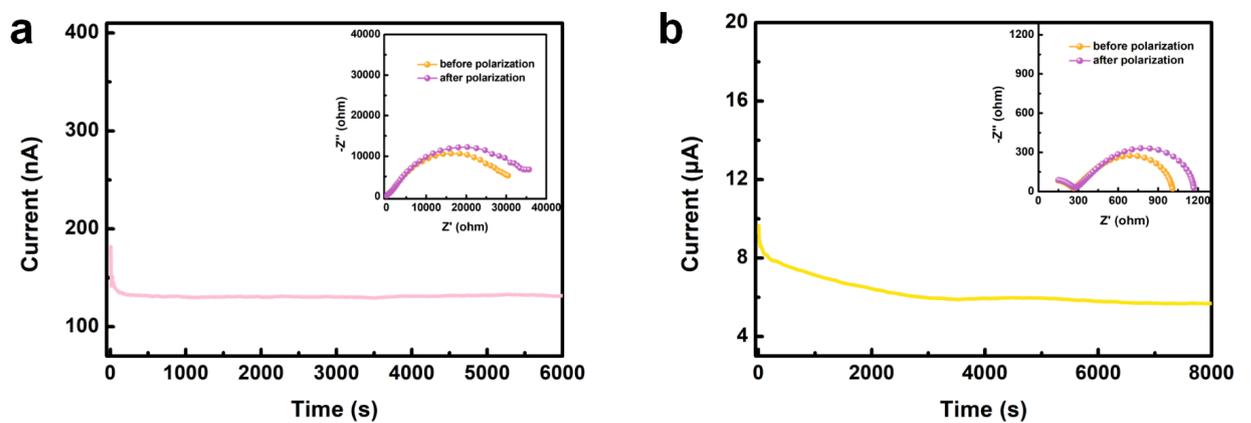


Figure S7. AC curve and impedance spectra before and after polarization of (a) PAN-SPE and (b) PEO-SPE.

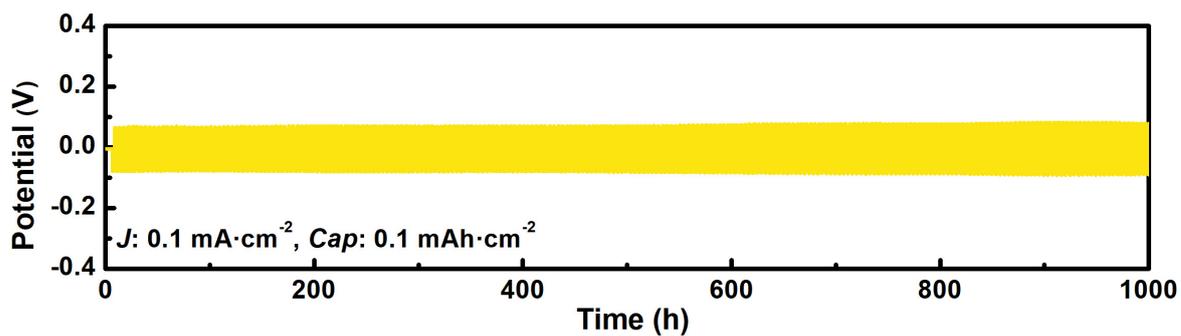


Figure S8. Voltage profiles of the Li/PEO-SPE/Li symmetric batteries at a current density of  $0.1 \text{ mA cm}^{-2}$ .

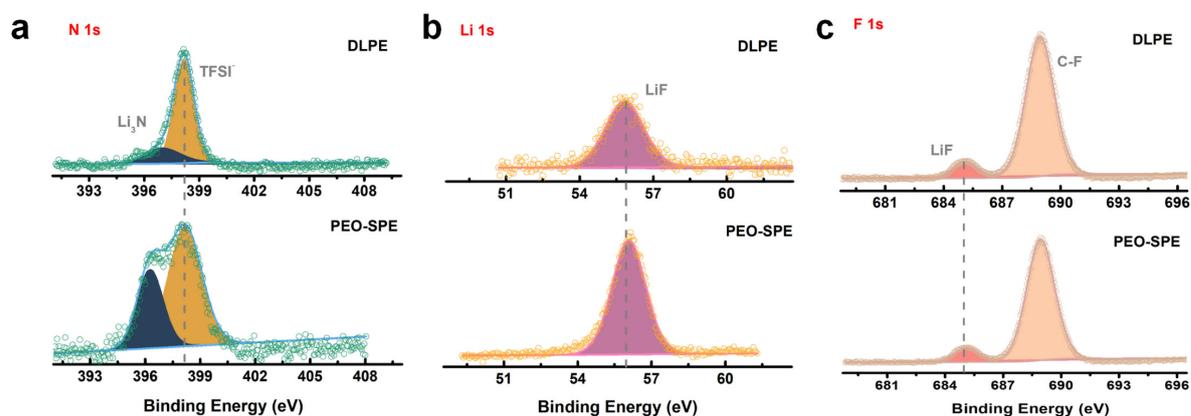


Figure S9. (a-c) High-resolution XPS spectra of DLPE and PEO-SPE anode after 50 cycles.

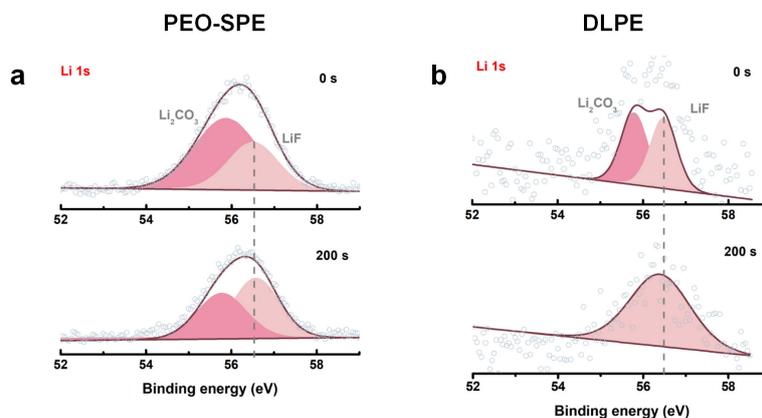


Figure S10. High-resolution XPS spectra of (a) PEO-SPE and (b) DLPE cathode after 50 cycles before and after sputtering for 200 s.