

Supporting Information for
Stabilizing the interface of PEO solid electrolyte to lithium
metal anode via a g-C₃N₄ mediator

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1. Experimental Section

1.1 Preparation of *g*-C₃N₄

The *g*-C₃N₄ powder was synthesized by directly heating urea (from SCRC, AR) in a muffle furnace. In detail, a known amount of urea in a corundum crucible was heated to 500 °C in a heating rate of 5 °C min⁻¹, and retained at 500 °C for 2 h. After cooling to room temperature, it was further ground to fine powders.

1.2 Preparation of PEO electrolyte

The preparation process was carried out in the glove box. PEO (from Aladdin, M_w 600 000) and LiTFSI powders (the molar ratio of EO: Li⁺ was kept at 15: 1) were dissolved into acetonitrile (AN) and stirred over 24 h. The resulting homogeneous mixture was coated onto a Teflon (PTFE) film and dried at room temperature for about 1 h to allow the solvent to volatilize naturally, and then dried at 60 °C for 24 h in vacuum to completely remove the residual solvent. Thus, the PEO electrolyte membrane was obtained.

1.3 Preparation of double-layer polymer electrolyte

Weigh a certain amount of PEO, LiTFSI powders (the molar ratio of EO: Li⁺ was kept at 15: 1) and as-prepared *g*-C₃N₄ powders. The *g*-C₃N₄ and LiTFSI powders were first added into AN and dispersed under ultrasonic for 1 h. The PEO powder was then dissolved into the mixture and stirred for 24 h. The obtained homogeneous mixture was coated on the surface of an as-prepared PEO electrolyte membrane and dried at room temperature for 1 h, then it was dried at 60 °C for 24 h in vacuum. The obtained double-layer polymer electrolytes of different *g*-C₃N₄ contents (10%, 30% and 50% of the total weight of the modified layer) are denoted as 10CN-PEO, 30CN-PEO and 50CN-PEO, respectively.

1.4 Characterizations

Phase analysis was performed by X-ray diffraction (XRD) (Bruker D2 Phaser, Cu Ka X-ray source) in the 2θ range of 10° to 60°. The morphologies of the samples were characterized using a FEI Sirion 200 field emission scanning electron microscope (FE-SEM).

1.5 Electrochemical tests

Symmetric cells using stainless steel (SS) as electrode were prepared. The ionic conductivity was obtained by AC impedance measurement on symmetric SS/SS cells at different temperatures from 30 to 80 °C. It was calculated according to the Eq. (1).

$$\sigma = L/RS \quad (1)$$

where σ , L , R and S denote the ionic conductivity, thickness of the membrane, the resistance of SPE at different temperatures and contact area between stainless-steel sheet and the SPE.

Li/SS cells were prepared, in which lithium metal was used as the counter and reference electrode while stainless steel was the working electrode. The linear sweep voltammetry (LSV) tests were conducted from 2.5 V to 6 V (vs Li⁺/Li) at a scan rate of 1 mV s⁻¹ to evaluate the electrochemical stability of the electrolyte. The cyclic voltammetry (CV) was conducted at a scan rate of 10 mV s⁻¹ under a voltage range of -0.5~6 V.

Symmetric Li/Li cells were assembled using Li foil as the electrodes. The EIS tests were carried out on Solartron E 1287+1260 in the frequency range of 10⁻¹~10⁶ Hz at an amplitude of 10 mV to detect the change of the interface resistance.

The LiFePO₄ cathode was prepared by coating a mixture of active material, carbon black (super-P), and PVDF at a weight ratio of 8: 1: 1 on Al foil and then dried in a vacuum oven at 80 °C for 12 h to remove the solvent before pressing. The cycling performance of cells with different electrolytes was recorded by the automatic battery testing system of Neware CT-4008 mode. All assemblies were carried out in an argon filled glove box.

2. Supporting Figures

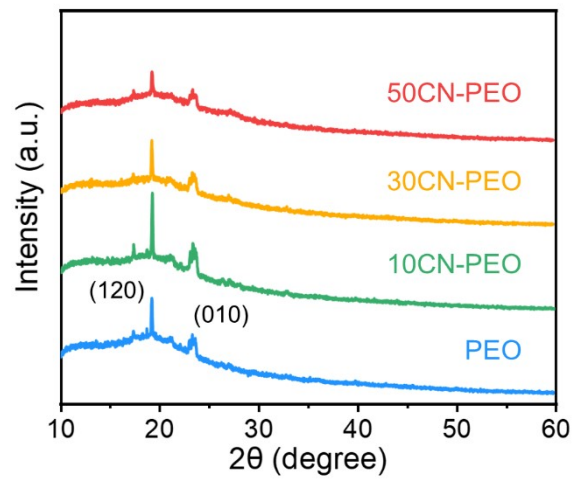


Fig. S1 XRD patterns of PEO, 10CN-PEO, 30CN-PEO and 50CN-PEO electrolytes

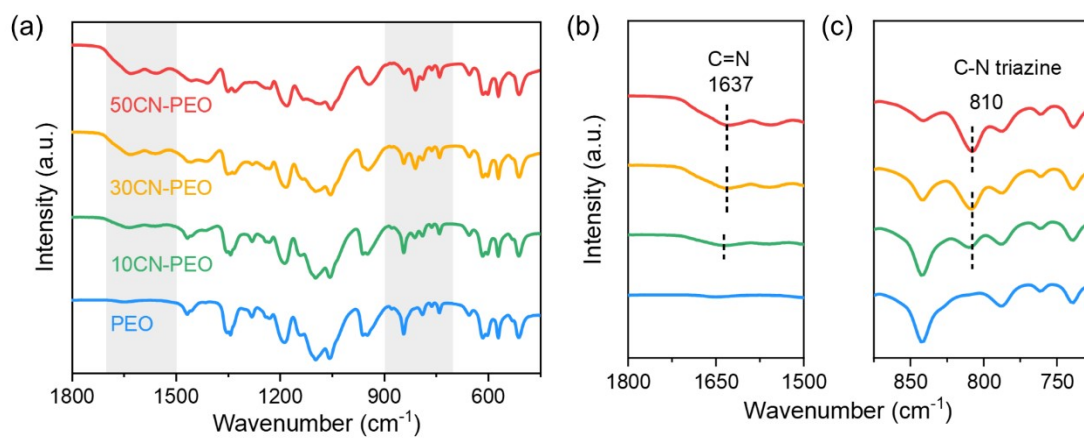


Fig. S2 (a) Fourier transform infrared spectrum of PEO, 10CN-PEO, 30CN-PEO and 50CN-PEO electrolytes with (b and c) partial enlargement

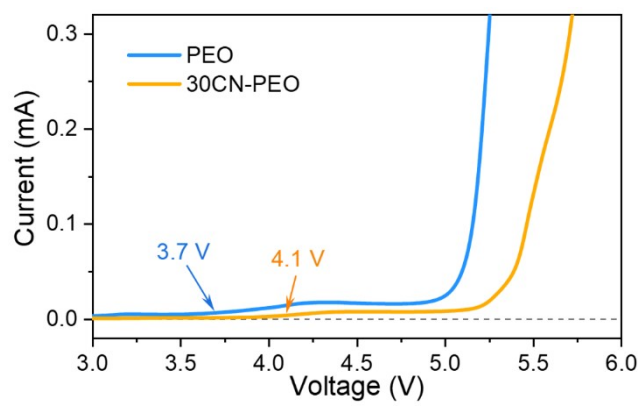


Fig. S3 Linear sweep voltammetry curves of PEO and CN-PEO electrolytes

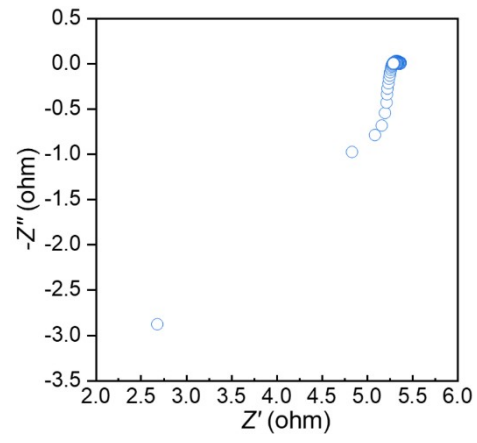


Fig. S4 Nyquist plot of the shorted Li/PEO/Li cell (cycled for 115 h)

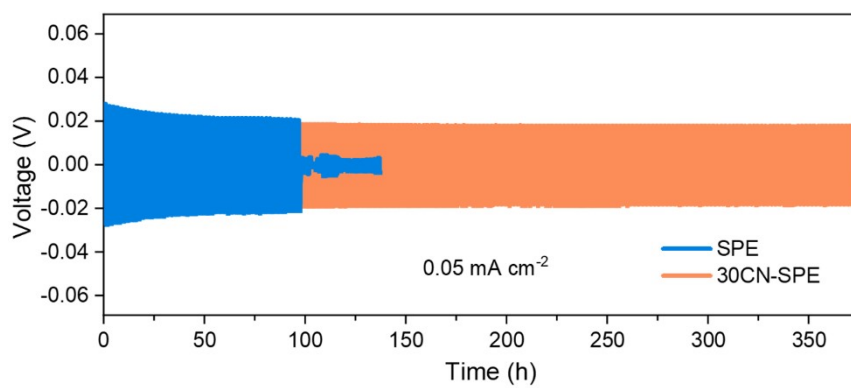


Fig. S5 Li plating/stripping curves of PEO and 30CN-PEO electrolytes at a current density of 0.05 mA cm^{-2}

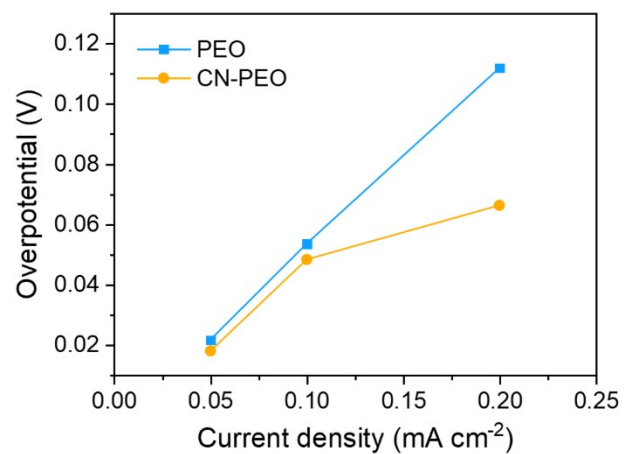


Fig. S6 Li deposition overpotential of Li/Li symmetric cells with PEO and CN-PEO electrolyte under different current densities (0.05, 0.1, 0.2 mA cm⁻²)

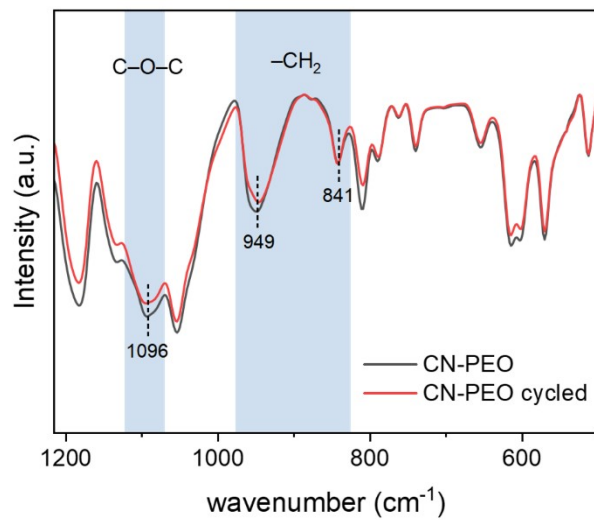


Fig. S7 FTIR spectrum of CN-PEO electrolyte before and after cycling for 180 h