

Electronic Supplementary Information (ESI)

In situ Constructing Asymmetric Composite Electrolyte with Structural Gradients for Dendrite-Free Lithium Metal Batteries

Tao You^a, Lehao Pan^a, Jingchao Liu^a, Yifan Zhao^a, Fengquan Liu^a, Chen Wang^{a,*} and Lin Li^{a,b,*}

^a College of Textiles & Clothing, State Key Laboratory of Bio-Fibers and Eco-Textiles, Qingdao University, Qingdao 266071, PR China

^b Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China

Experimental Section:

Materials:

Polyethylene glycol monomethyl ether acrylate (PEGMEA), polyethylene glycol diacrylate (PEGDA), Succinonitrile (SN, 99 %), lithium difluoro (oxalate) borate (LiDFOB, 99 %), Lithium bis (trifluoromethanesulfonyl) imide (LiTFSI, 99 %), 2,2'-Azobis (2-methylpropionitrile) were purchased from Shanghai Macklin Biochemical Co., Ltd. LLZTO Particles (300 nm), Poly (vinylidene fluoride) (PVDF), LiFePO₄ (LFP) powder, Carbon-coated Al foil (C-Al) were purchased from Suzhou Duo Duo Chemical Technology Co., LTD. Conductive agent (Super P) and N-methyl pyrrolidone (NMP, 99.9 %) were purchased from Shanxi Power source battery material Co., Ltd. LiCoO₂ (LCO) powder were purchased from Guangdong Canrd New Energy Technology Co., Ltd. Li metal foil (d=15.6 mm) were purchased from Tianjin Zhongneng Lithium Co., LTD. All experimental materials were stored in AR-filled glove boxes without further purification before use.

Preparation of SPE:

First of all, according to the previous research results of the laboratory, SN, LiTFSI and LiDFOB were mixed according to the mass ratio of 1:0.8:0.2, and stirred at 60 °C for 2 h to fully dissolve the lithium salt to obtain a double-salt deep eutectic solution, which was recorded as SN-DES. Then PEGDA and PEGMEA were mixed at a mass ratio of 1:1 to obtain a mixed solution, GDA-MEA and SN-DES were stirred according to a mass ratio of 1:5 for 3 h to obtain a uniform precursor solution, which was recorded as GDA-MEA. The content of initiator AIBN was 0.3 %. The precursor liquid is cast in the groove of a customized PTFE plate and heated at 60 °C for 8 h to fully polymerize the polymer electrolyte, named SPE.

Preparation of CSE:

LLZTO powder with different mass ratios was dispersed into GDA-MEA solution. Stir the mixture vigorously for 24 hours to form a sticky paste. After adding AIBN, the fluid slurry is cast in the groove of the PTFE plate, the thickness of the electrolyte film is controlled by controlling the amount of slurry and the diameter and depth of the groove. After being heated at 60 °C for 8 h and fully polymerized, the organic and inorganic composite solid electrolyte film was obtained with the order of GDA-MEA-LLZTO-CSE, named CSE.

Preparation of LCO and LFP Electrolyte:

LCO, Super P and PVDF were mixed according to the mass ratio of 0.8:0.1:0.1, dispersed in NMP to form a uniform slurry, coated on aluminum foil, and dried at 80 °C in a vacuum oven for 12 h, the pole sheet was cut into a circle with a diameter of 10 mm as the positive electrode of the battery. The process of preparing LFP positive electrode is the same. The actual load mass of the active material is about 2.5 mg cm⁻². Then the cut pole piece is placed in a vacuum oven, kept at 110 °C for 12 h,

and transferred to the glove box for use. Therefore, the batteries are assembled in the glove box, and the battery is encapsulated by a pressure machine.

Material characterization:

The surface morphology of electrolyte was studied by field emission scanning electron microscopy (Hitachi-Regulus 8100). The evolution of polymer functional groups at 700-4000 cm^{-1} was studied by Fourier transform infrared spectroscopy (FTIR) (thermoelectric-Nicolet is50). The thermal behavior was investigated using a differential scanning calorimeter (DSC, TADSC250) at a heating rate of 5 $^{\circ}\text{C}/\text{min}$ under N_2 atmosphere in the temperature range of -70 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$. Thermogravimetric analysis of its thermal stability was carried out using a thermogravimetric analyzer (TG 209 F3) at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in N_2 atmosphere from 30 to 600 $^{\circ}\text{C}$. X-ray diffraction (XRD) was performed by Smart Lab 3 KW to observe the crystal characteristics. The interfacial composition of the lithium anode surface was studied by X-ray photoelectron spectroscopy (XPS) and detected on a Thermo Fisher ESCALAB Xi+.

Electrochemical Characterization:

The electrochemical properties of electrolyte were tested with PMC-1000 interface in an AMETEK electrochemical workstation. Electrochemical impedance spectroscopy (EIS) was recorded in the range of 30 to 90 $^{\circ}\text{C}$ with a frequency range of 1 MHz to 0.1 HZ and an AC amplitude of 10 mV. The ionic conductivity σ is calculated by the following equation:

$$\sigma=L/(R\times S)$$

where L represents the thickness (cm) of the electrolyte membrane, R represents the bulk resistance (Ω), and S corresponds to the contact area (cm^2) between SS and electrolyte.

LSV measurements were conducted at a sweep rate of 1 mV/ S from 2 to 6 V.

The effect of direct current (DC) polarization and AC impedance of lithium ions

in Li/Li symmetric batteries on the migration number of lithium ions t_{Li^+} was tested at room temperature, and the value could be calculated according to the Bruce-Vincen-Evans equation:

$$t_{Li^+} = I_s (\Delta V - I_0 R_0) / I_0 (\Delta V - I_s R_s).$$

Where ΔV is the applied direct current potential (10 mV), I is the direct current and R is the charge transfer resistance. The subscripts "0" and "s" denote the initial and steady states, respectively. The Li//Li symmetric cells and LCO//Li full cells were charged and discharged on a LAND-CT3002A battery tester (Wuhan LAND Electronic Co. Ltd.).



Figure S1. Optical image of CSE before and after polymerization.



Figure S2. Photographs of the SPE

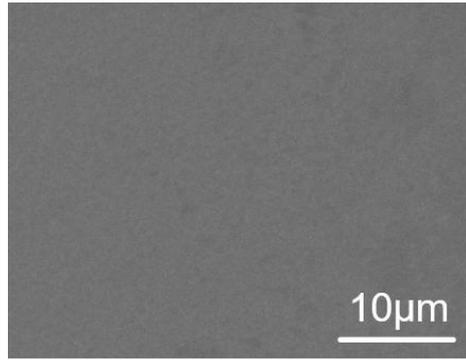


Figure S3. SEM image of the SPE.



Figure S4. Photographs of the CSE electrolyte under original and folding states.

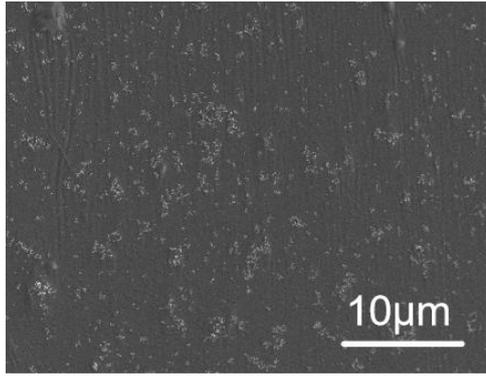


Figure S5. SEM image of the CSE.

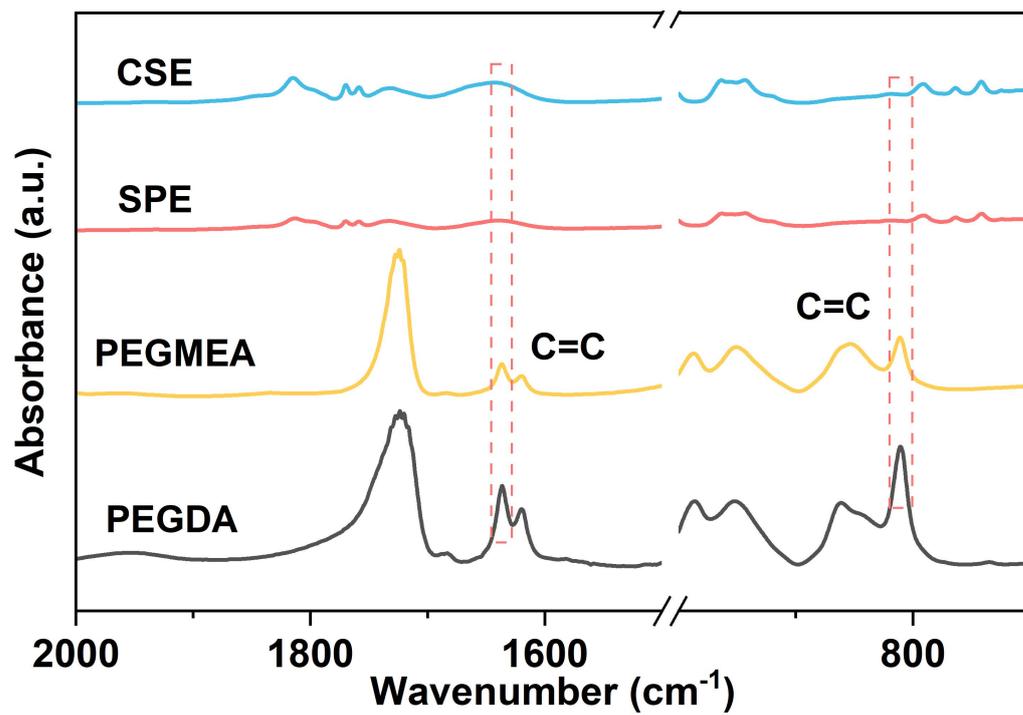


Figure S6. locally magnified FTIR spectra of PEGDA, PEGMEA, SPE, and CSE.

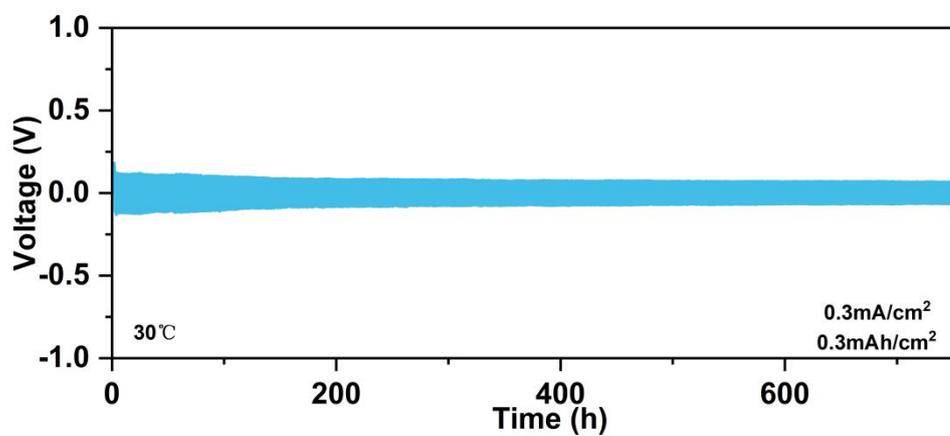


Figure S7. Galvanostatic cycling curves of Li/CSE/Li symmetric cell at 30 °C.

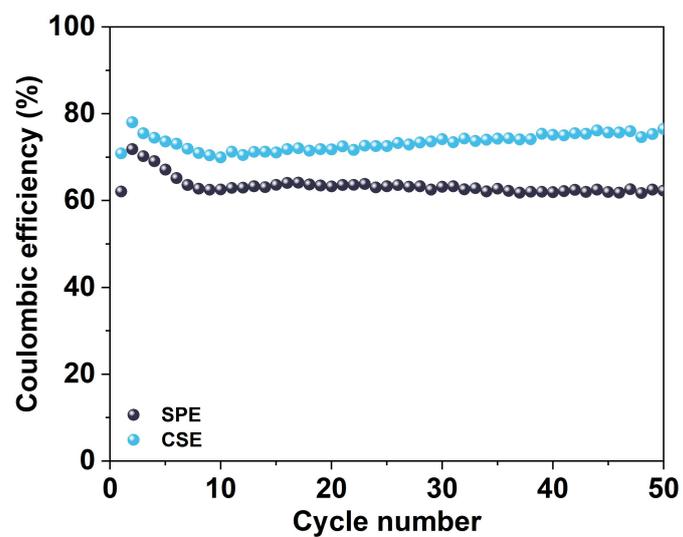


Figure S8. The Li-Cu asymmetric cells based on SPE and CSE electrolytes

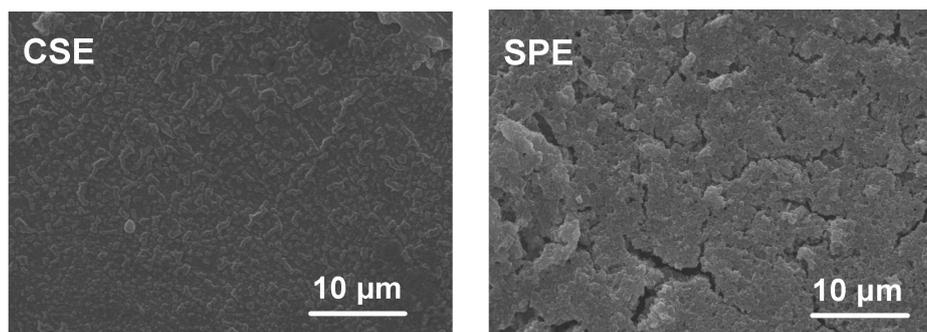


Figure S9. SEM images of the Li anode after cycling tests with CSE and SPE electrolytes

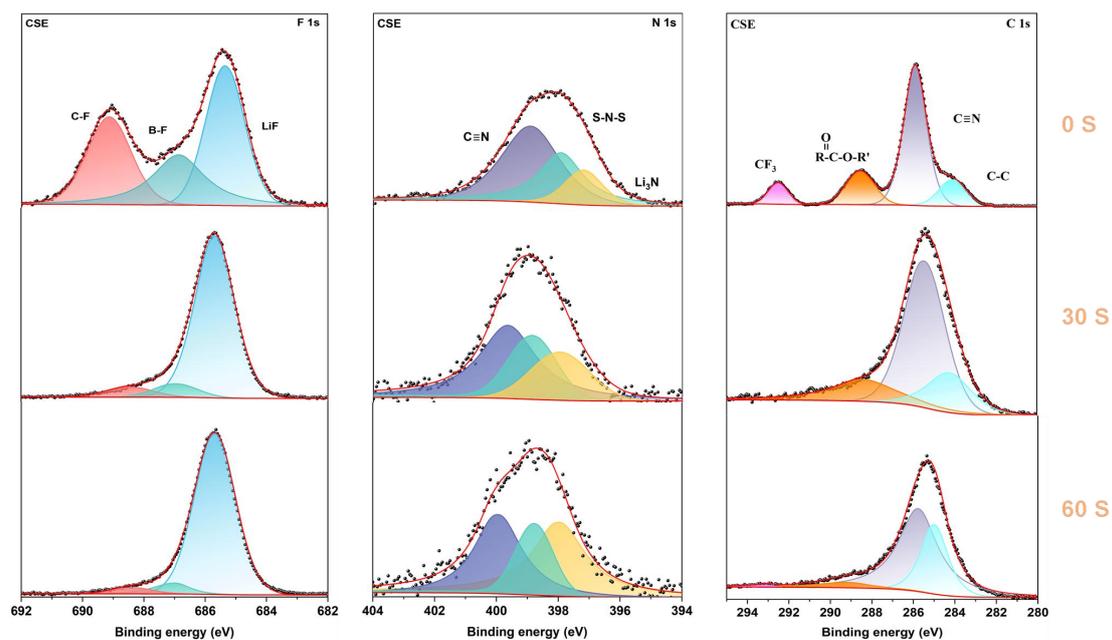


Figure S10. F 1s, N 1s and C 1s XPS depth profiles of Li anode surface after 50 cycles in Li/Li symmetric cells with CSE.

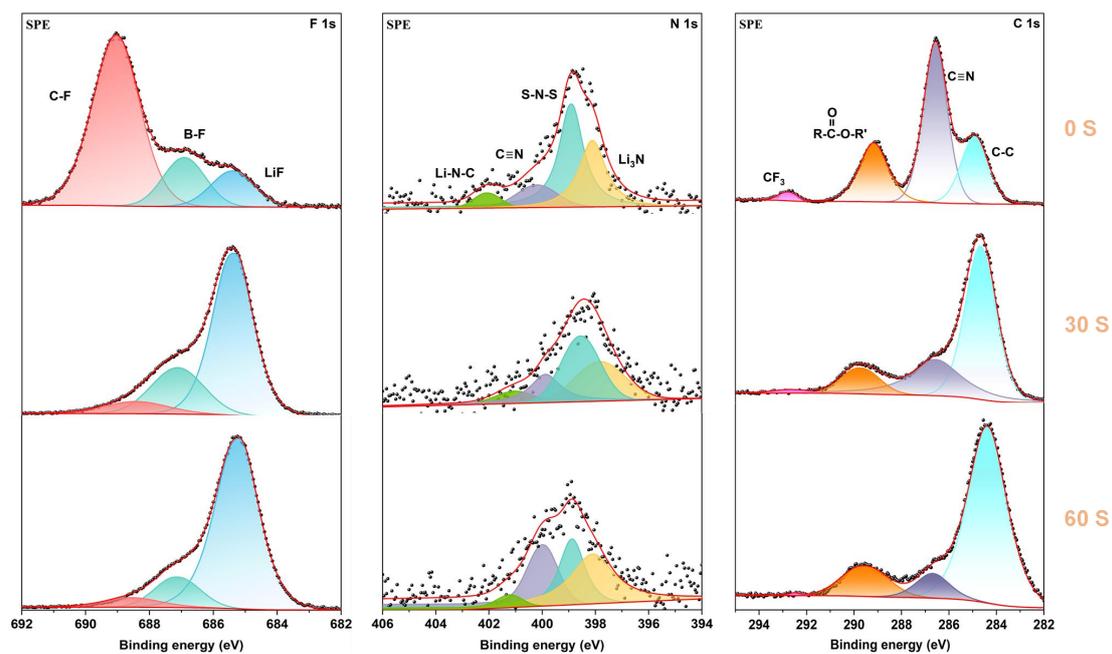


Figure S11. F 1s, N 1s and C 1s XPS depth profiles of Li anode surface after 50 cycles in Li/Li symmetric cells with SPE.

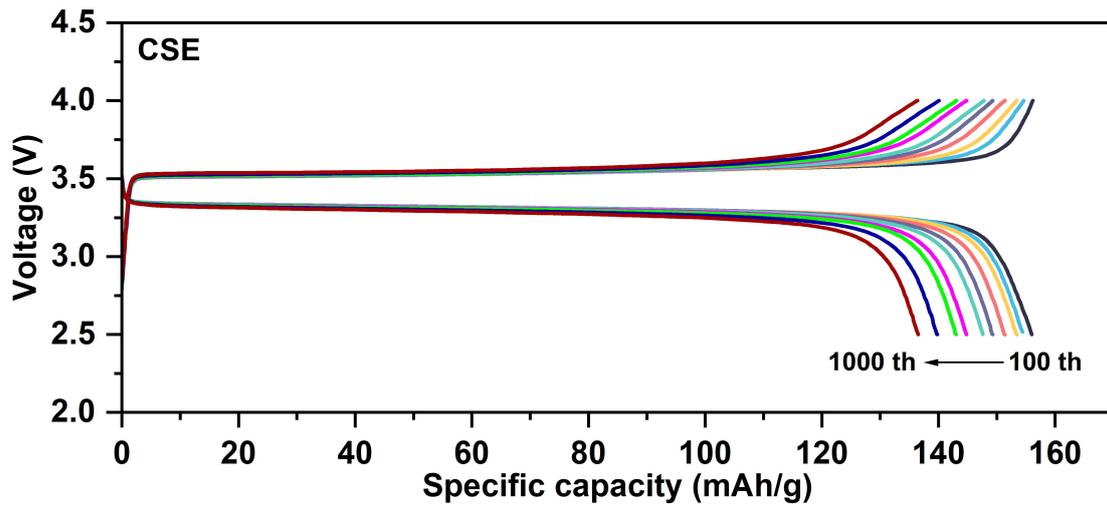


Figure S12. The charge and discharge voltage profiles of LiFePO₄/CSE/Li after different cycles.