Supporting Information

Gradient Trilayer Solid-State Electrolyte with Excellent Interface Compatibility for High-Voltage Lithium Batteries

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1. Experimental Section

Preparation of the ultrathin gradient trilayer solid-state electrolyte (GTSSE):

To fabricate a gradient trilayer solid-state electrolyte, The polyvinylidene fluorideco-hexafluoropropylene (PVDF-HFP) (Mw=455,000, Sigma Aldrich) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) (99%, Aladdin) are successively added into polyethylene dimethylformamide (DMF), followed by magnetic stirring at 50 °C for 5 h to obtain the homogeneous electrolyte slurry. The weight ratio of PVDF-HFP, and LiTFSI was 3:1. The poly(ethylene glycol)-dimethyl ether (PEGDME) (Mn=2000, Sigma Aldrich), polyethylene oxide (PEO) (Mv = 10^6 g mol^{-1} Sigma Aldrich) and LiTFSI (EO/Li=12/1 molar ratio and PEGDME/PEO = 9:1 weight ratio) are dissolved in DMF and then stirred at 50 °C for 5 h to obtain the homogeneous electrolyte slurry. In the synthesis of an ultrathin gradient trilayer solid-state electrolyte (GTSSE), PVDF-HFP-Li salt slurry is evenly coated on the glass plate with a scraper, then the ultrathin porous membrane (5 µm polyethylene separator, CHONGQING YUTIANHUA CO., Ltd.) is laid flat on the glass plate, and the ultrathin porous membrane is half soaked and half surfaced on the slurry. the PEGDME-Li salt slurry is uniformly dropped on the surface of the ultrathin porous membrane to fill the remaining space. After dried in a vacuum oven at 80 °C for 24 h to remove the solvent. The amount of electrolyte slurry is precisely controlled to obtain the ultrathin gradient trilayer solid-state electrolyte (20 µm). All the preparation processes should be carried out in an Ar-filled glovebox with H_2O and O_2 contents below 0.1 ppm.

Preparation of the PVDF-HFP and PEGDME electrolyte:

As a comparison, PVDF-HFP electrolyte is fabricated by directly casting PVDF-HFP-Li salt slurry on the ultrathin porous membrane, which was entirely soaked. Similarly, PEGDME electrolyte is fabricated by dropping the PEGDME slurry on the 5µm ultrathin porous membrane. PVDF-HFP electrolyte and PEGDME electrolyte is synthesized by drop polymer-Li salt solution on ultrathin porous membrane and drying, which is similar to the method of preparing GTSSE.

Preparation of the PVDF-HFP, PEGDME, and PVDF-HFP/PEGDME membrane:

For X-ray diffraction (XRD) and stress-strain tests performance experiments, the PVDF-HFP membrane is fabricated by directly casting PVDF-HFP-Li salt slurry is evenly coated on the glass plate with a scraper. The PEGDME membrane is fabricated by dropping the PEGDME slurry on the glass plate with a scraper. The construction of PVDF-HFP/PEGDME membrane is the same as the above method. These three mentioned above were dried in a vacuum oven at 80°C for 24 hours to remove the solvent.

Preparation of the Composite Cathode:

The composite cathode is fabricated by a facile coating method, $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) powder, conductive additives (Super P), PVDF-HFP, PVDF and LiTFSI (70:10:10:6:4 by weight ratio) are ground in mortar and then mixed in NMP solvent with magnetic stirring for 3 hours, the composite slurry is coated on an aluminum current collector and vacuum dried at 70°C for 18 h. All the preparation processes should be carried out in an Ar-filled glovebox with H_2O and O_2

contents below 0.1 ppm The active material loading of cathode is about 2~3 mg cm^{-2}.
Similarly, the same weight ratio is applied to fabricated composite LiFePO$_4$ cathode
with a mass loading of 2~3 mg cm^{-2}.

Materials Characterizations

XRD patterns were recorded using a D8 discover X-ray diffractometer with Cu
Kα radiation. The thermal stability was executed by thermogravimetric analysis
(TGA) using a NETZSCH STA 449F5 instrument over the temperature range
between 25 °C and 500 °C under Air flux at a heating rate of 10 °C min^{-1}. The
microstructure of the as-prepared SPEs were examined by scanning electron
microscope (JEOL-7100F) after gold spraying. Stress-Strain curves were tested by
Instron 5967. XPS analysis was performed using a VG MultiLab 2000.

Electrochemical Measurements:

Electrochemical impedance spectroscopy (EIS) was tested by assembling
blocking stainless steel|SSEs|stainless steel (SS)cell from 1 Hz to 10^6 Hz with an
amplitude of 10 mV via Autolab PGSTAT302N. The calculated using the Equation 1,
which L is S as the effective contacting area among SSE and SS, R presents the
resistance value of the bulk electrolyte, and L the thickness of the SSE.

$$\sigma = \frac{L}{S \cdot R} \tag{1}$$

Arrhenius were obtained by calculating ionic conductivity at a temperature range of
20-60 °C via Autolab PGSTAT302N. A is conductivity pre-exponential factor, Ea is
the activation energy, and T is the absolute temperature, R is the ideal gas constant.

$$\sigma(T) = A \exp\left(-\frac{Ea}{RT}\right) \tag{2}$$

The electrochemical stability window was tested by linear sweep voltammetry (LSV) on a lithium|SSEs|stainless steel cell from 0 to 6.5 V via Autolab PGSTAT302N at a scan rate of 10 mV s^{-1}. When it comes to the t_{Li+}(lithium ion transference number), the Li||Li symmetrical cells assembled with GTSSE was measured by chronoamperometry method, a polarization of 10 mV (ΔV) was applied to the cells for 5,000 seconds. The polarization currents of cell including initial (I_0) and steady-state (I_{ss}) were recorded. The interfacial resistances before (R_0) and after (R_{ss}) polarization were tested by alternating current impedance. Afterwards, t_{Li+} was calculated from Bruce-Vincent-Evans Equation 3:

$$t_{Li^+} = \frac{I_{SS}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{SS} R_{SS})} \tag{3}$$

The cycling stability of lithium|SSEs|lithium, and SSLB was conducted using a multichannel battery testing system (LAND CT2001A). The full cells were assembled with composite cathode, SSE, and lithium metal anodes via ordinal stacking. The cycle performance of Li||LFP cell is tested at 0.5 C between 2.8 and 4.0 V. The cycle performance of Li||NCM811 cell is tested at 0.5 C between 2.8 and 4.3 V. All the electrochemical properties of SSLBs and lithium compatibility at 50 °C. All of the cells were assembled with 2016 coin-type cells in glove box and tested at 50 °C.

Porosity Characterization:

The porosity was determined by the typical weighing method using absolute alcohol as the liquid. The wet weight of the ultrathin porous membranes was measured after wiping the excess absolute alcohol. The dry weight of the ultrathin porous membranes was measured after a vacuum drying process. The difference between dry weight and wet weight of the ultrathin porous membrane is the weight of absolute alcohol

absorbed by the ultrathin porous membrane. The porosity of the ultrathin porous membranes was calculated according to Equation 4

$$\text{porosity} = [(W_b/\rho_b)/(W_b/\rho_b + W_p/\rho_p)] \times 100\% \quad (4)$$

where W_b and W_p are the weights of the absolute alcohol and the dry ultrathin porous membrane and ρ_b and ρ_p are the densities of absolute alcohol (0.776 g·cm^{-3}) and the ultrathin porous membrane (0.95 g·cm^{-3}), respectively. The porosity of ultrathin porous membrane was tested and calculated to be 38%

2. Supporting Figures

Figure S1. Photograph as-prepared flexible GTSSE electrolyte with the thickness of

20 μm.
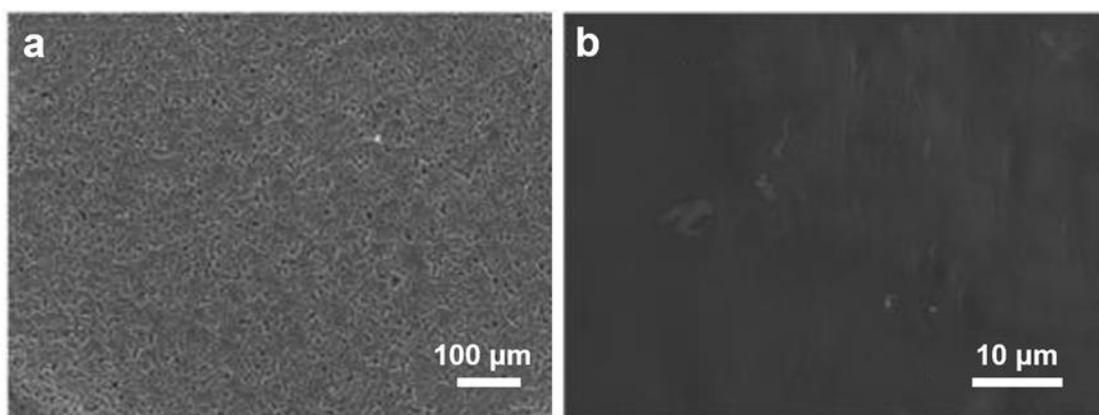
Figure S2. SEM images of the surface of a) PVDF-HFP and b) PEGDME in GTSSE.
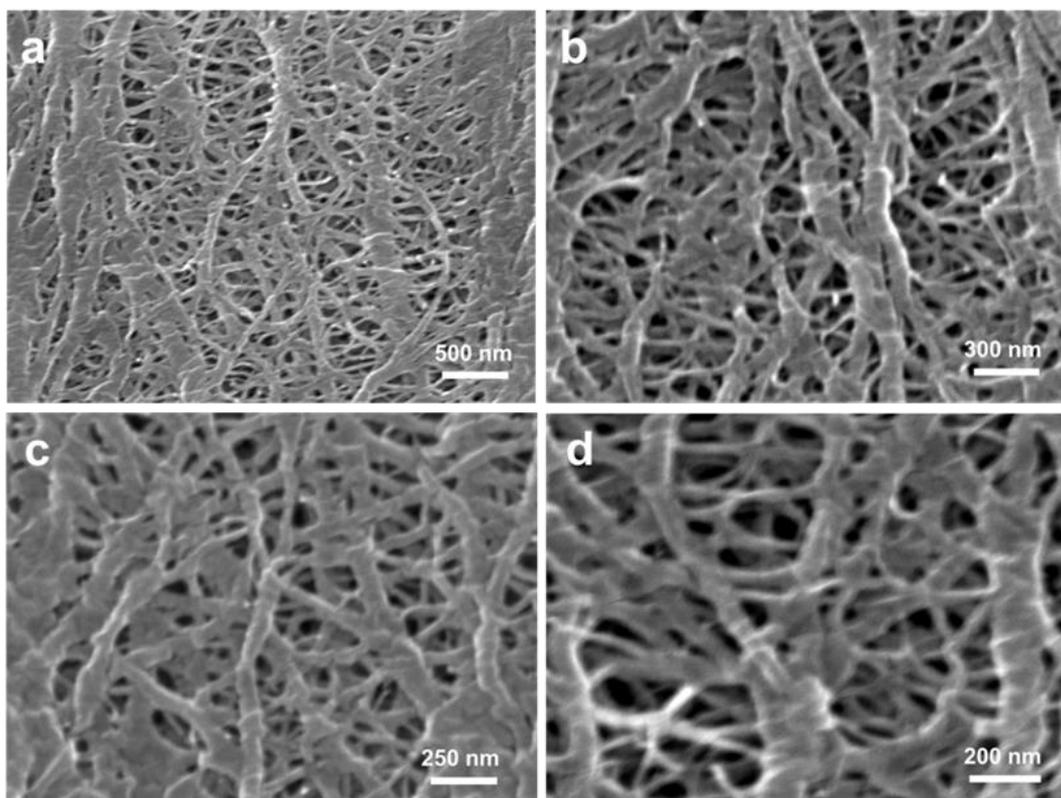
Figure S2. SEM images of the surface of the ultrathin porous membrane.

Figure S3. Photograph of ultrathin porous membrane with the thickness of 5 μm.
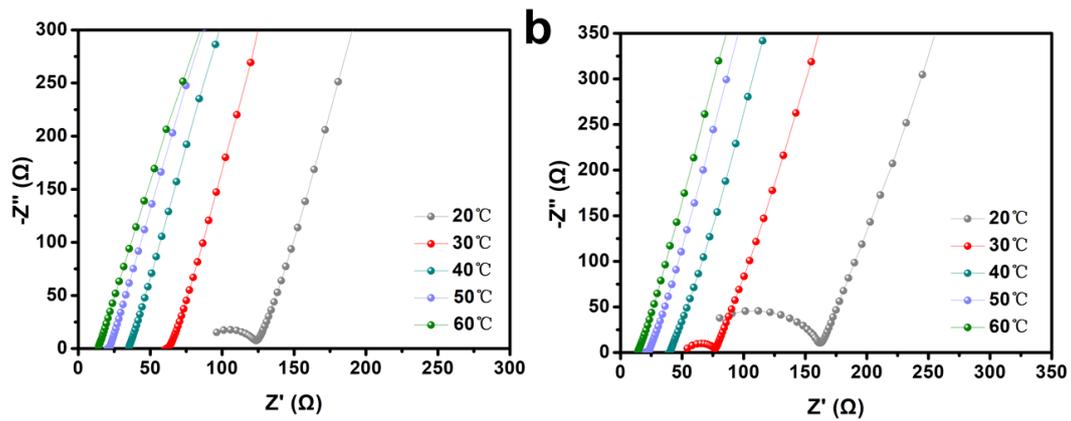
Figure S5. Alternate current impedance plots of a) PVDF-HFP and b) PEGDME electrolytes at different temperatures.
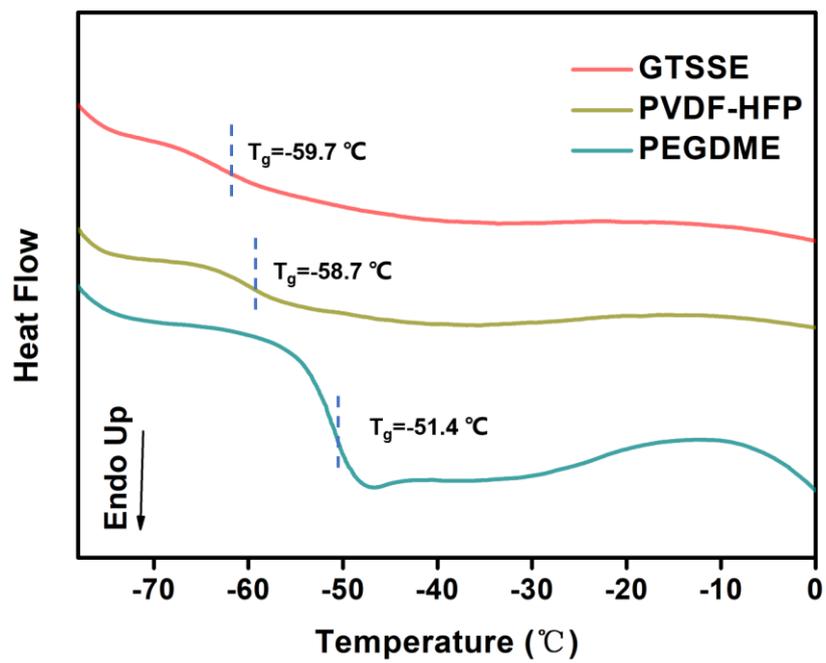
Figure S6. DSC curves of PEGDME, PVDF-HFP and GTSSE electrolytes.
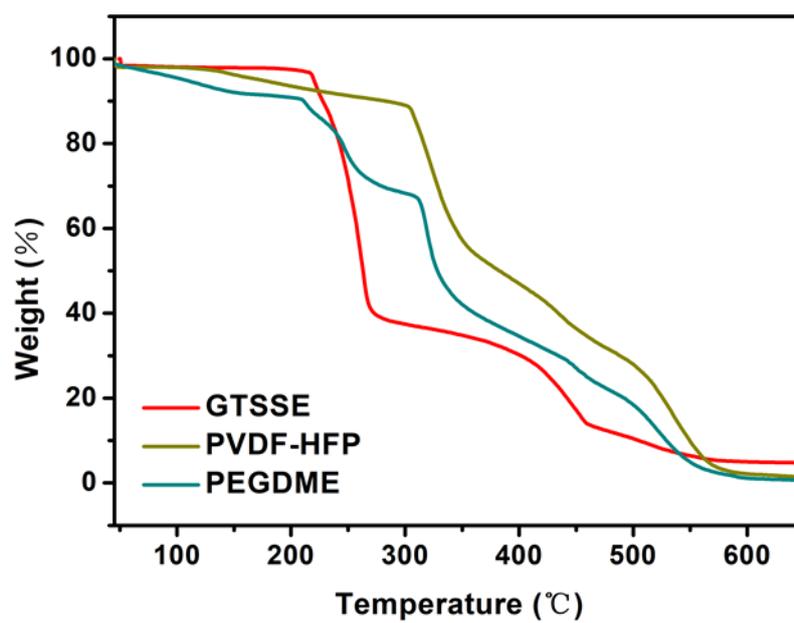
Figure S7. Thermogravimetric analysis of PEGDME, PVDF-HFP, and GTSSE.
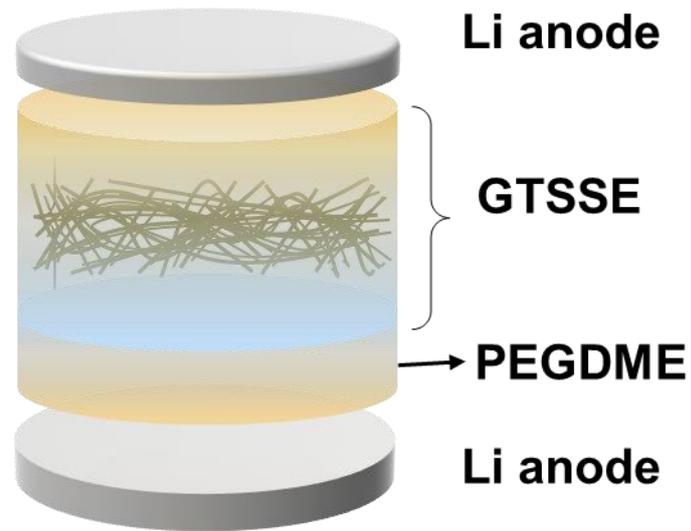
Figure S8. Schematic of the Li|GTSSE|Li cell for lithium plating/stripping experiments.
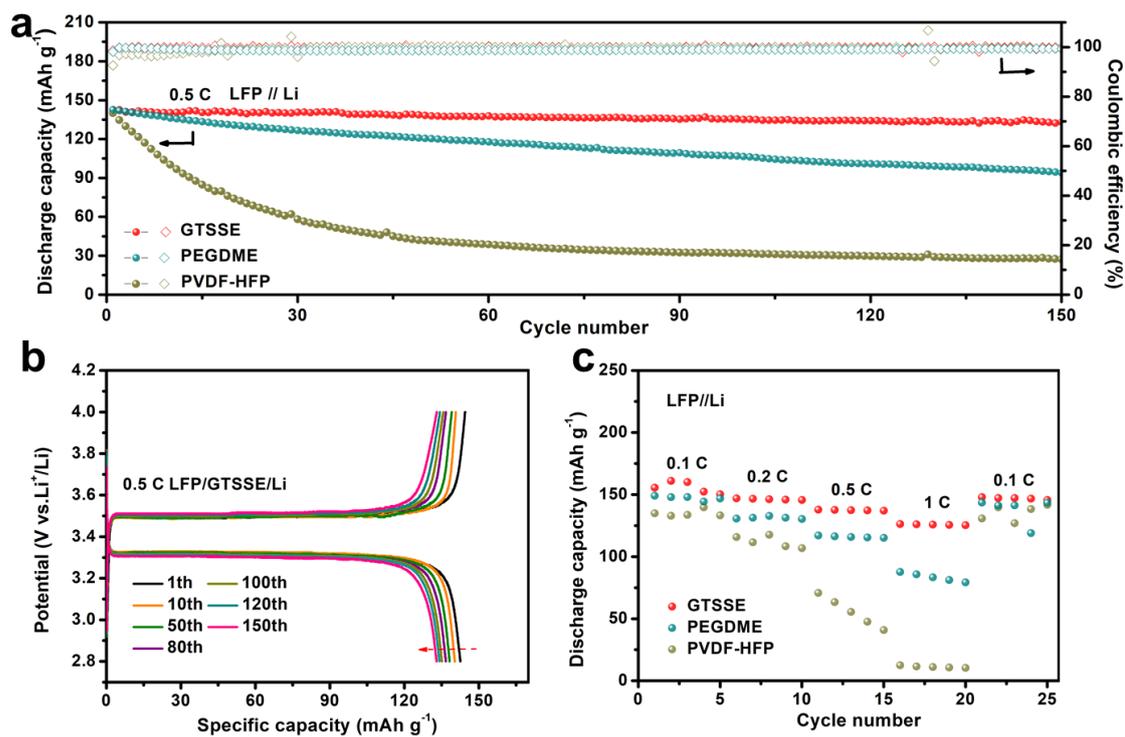
Figure S9. LFP‖Li full batteries with gradient trilayer solid-state electrolyte. a) Discharge specific capacity and Coulombic efficiency of the LFP|PVDF-HFP|Li, LFP|PEGDME|Li, and LFP|GTSSE|Li batteries at 0.5 C, together with the typical voltage profiles of b) the GTSSE. c) Rate capability of LFP|SSEs|Li batteries at different current densities.
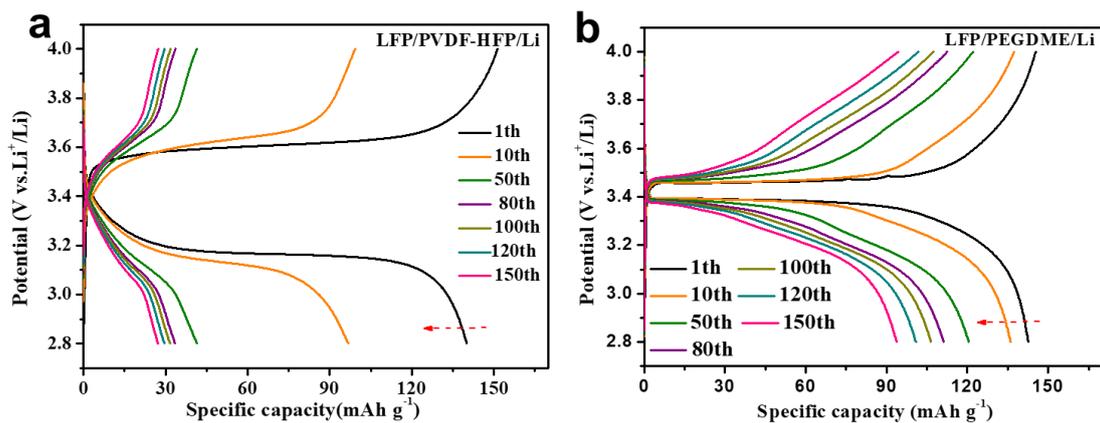
Figure S10. Typical voltage profiles of a) LFP|PVDF-HFP|Li and b) LFP|PEGDME|Li batteries at 0.5 C.
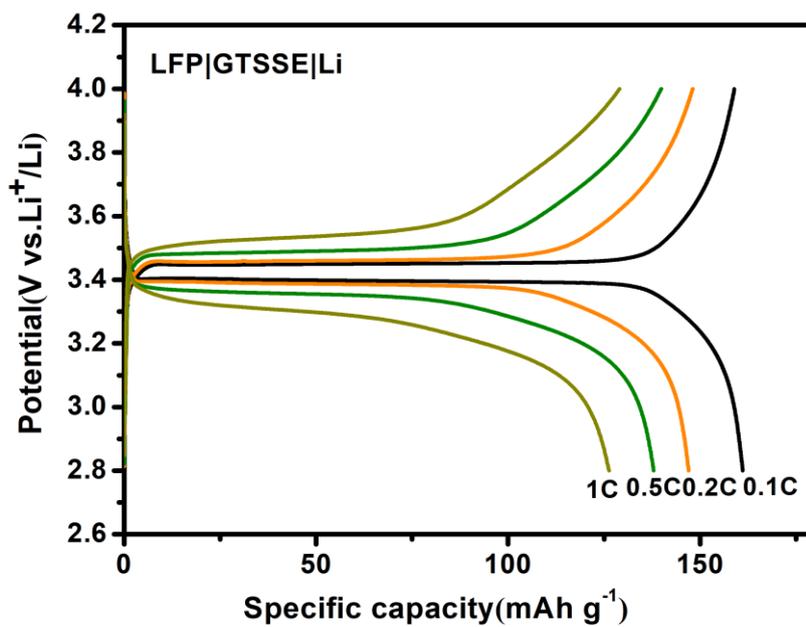
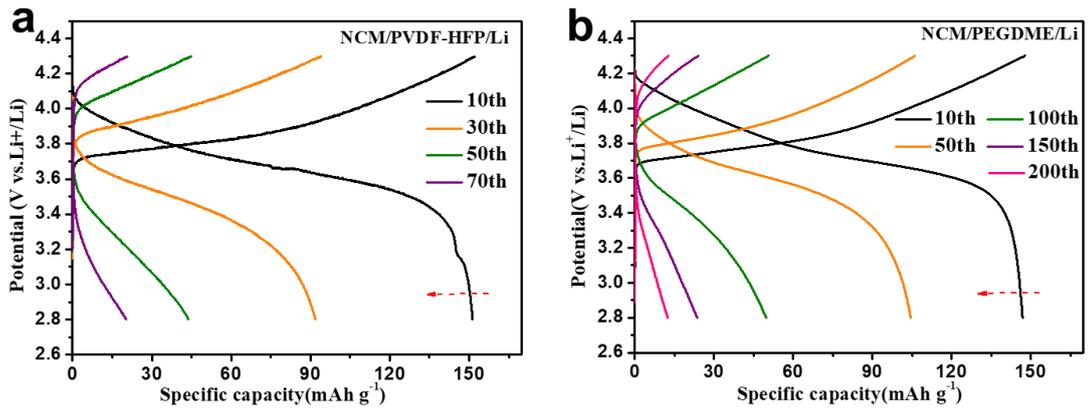**Figure S11.** Charge and discharge capacities of LFP|GTSSE|Li battery at different densities.

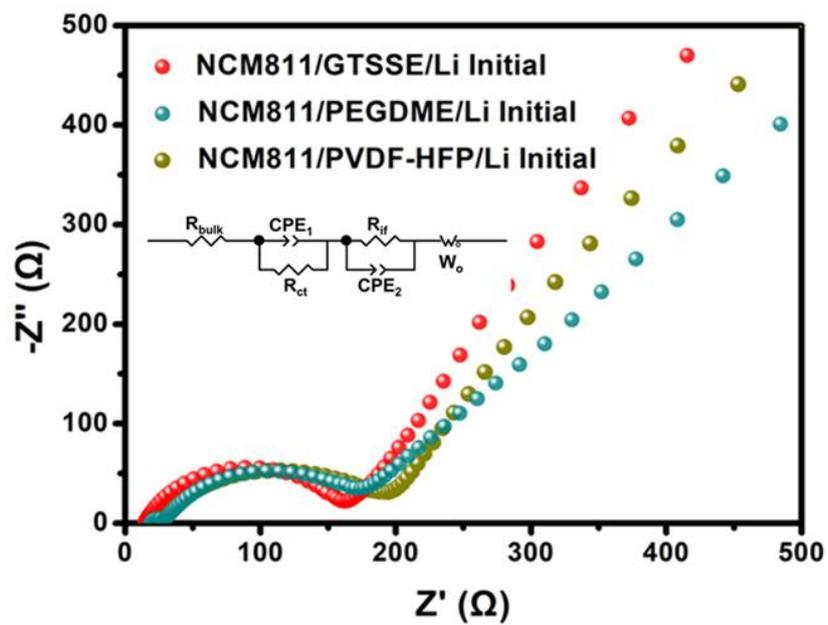**Figure S12.** Typical voltage profiles of a) NCM811|PVDF-HFP|Li and b) NCM811|PEGDME|Li batteries at 0.5 C.

Figure S13. Nyquist plots before cycling for NCM811|PVDF-HFP|Li, NCM811|PEGDME|Li batteries and NCM811|GTSSE|Li batteries. (The inset is the equivalent circuit.)
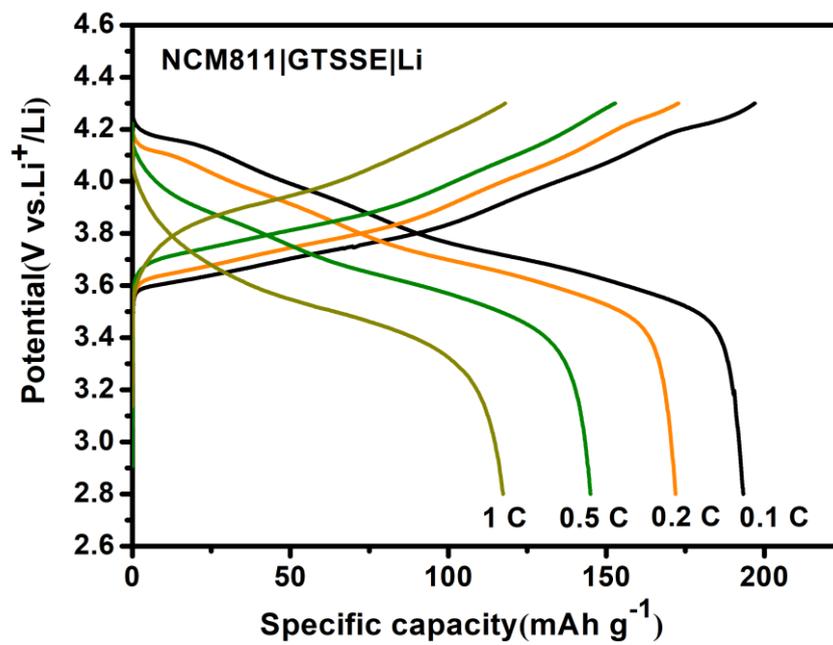
Figure S14. Charge and discharge capacities of NCM811|GTSSE|Li battery at different densities.
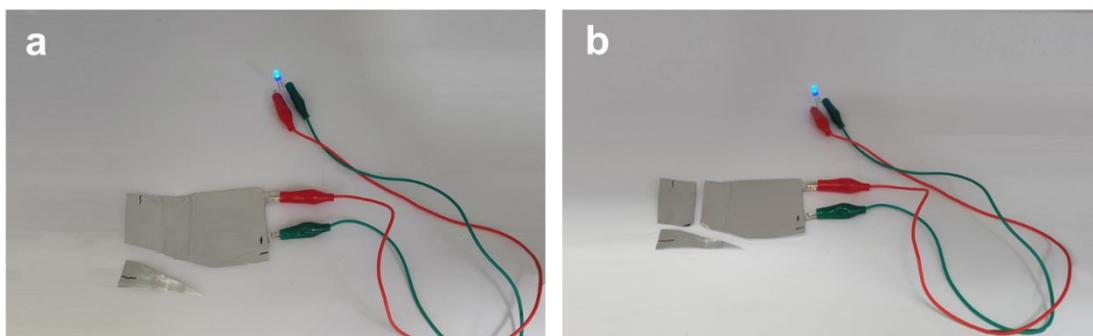
Figure S15. Photographs of the flexible NCM811|GTSSE|Li pouch cell lighting up LED lamps under destructive conditions at room temperature.