Electronic supplementary information

A lithium carboxylate grafted dendrite-free polymer electrolyte for all-solid-state lithium-ion battery

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1. Experimental section

1.1. Materials

Polyethylene glycol (PEG, Mw=2000g mol^{-1}), N,N-Dimethylformamide (DMF, 99.8%), Dibutyltin dilaurateand (DBTL, 99.8%), 1,4 butanediol (BDO, 99.8%), Dimethylol Propionic Acid (DMPA, 98.0%), Lithium hydroxide (LiOH,98.0%), N-Methyl pyrrolidone (NMP, 99.0%) and diphenylmethane diisocyanate (MDI, 98.0%) were purchased from Macklin. Lithium bis(trifluoromethane sulfonimide) (LiTFSI, 99.0%) was purchased from Aladdin. $LiFePO_4$, PVDF, and acetylene black were purchased from Kejing star technology Shenzhen. The liquid electrolyte (1:1 mixture of ethylene carbonate EC and dimethyl carbonate DMC containing 1 M LiPF6.) was purchased from CAPCHEM Shenzhen, and the separator (Celgard 2325 PP/PE/PP separator) was purchased from Celgard. PEG2000 need to be dried in a vacuum oven at 120°C for 24 hours before the experiment. The water contained in the DMF was removed by molecular sieves (4A). The LiTFSI, LiDMPA and LiOH need to be stored in an argon-filled glove box.

1.2. Synthesis

1.2.1. Synthesis of lithium 2,2-dimethylolpropionate (LiDMPA).

0.01 mol of 2,2-dimethylolpropionic acid and 0.01 mol of lithium hydroxide were dissolved together in 10 mL of distilled water, stirred for 4 hours at 60°C. After the reaction completed, the solution needs to be dried in a vacuum oven at 120 °C for 24 hours to remove water. The product was white crystal. It needs to be put into the Argon-filled glove box (O_2<0.1 ppm, H_2O<0.1 ppm).

1.2. 2. Synthesis of PEG-MDI/LiDMPA/LiTFSI solid state electrolytes (SPE1).

The synthesis method is completed by a two-step method, the first step is the polymerization process, and the second part is the chain extension process. 0.004 mol of PEG2000 and 0.008 mol of MDI were dissolved in 40 mL DMF in a three-necked flask. Then added 20 μL DBTL into the above mixture, adjusted the oil bath temperature to 80 °C and stirred for 2 hours. Later, further added LiDMPA and stirred for 2 hours. Finally added 0.013 mol of LiTFSI (EO:Li approximately equal to 18) and stirred for 6 hours. Then the solution was uniformly coated on a Teflon model and dried in a vacuum oven at 60 °C for 48 hours to remove the DMF solvent. Those dried SPE membranes were stored in an argon-filled glove box and marked as SPE1.

1.2.3. Synthesis of PEG-MDI/BDO/LiTFSI solid state electrolytes SPEx for comparison

The synthesis method of SPEx is similar to that of SPE1. The difference is that replacing the same amount of substance LiDMPA with1,4 butanediol. The synthesized electrolyte membranes are stored in an argon-filled glove box.

1.2.4. Assembling of $LiFePO_4$/SPE/Li batteries.

The cathode was prepared by mixing $LiFePO_4$, Super P carbon, and PVDF solution in NMP, with a weight ratio of 80:10:10, and stirred for 24 h at 300 rpm, then evenly spread on aluminium foil. The electrode sheet needed to be placed in a vacuum oven at 60 °C for 12 h to remove the NMP solvent. The coin cells (2032 type) were assembled by placing SPE membranes between the lithium metal anode and $LiFePO_4$ cathode. The thickness of the dry $LiFePO_4$ cathodes was about 110 μm with the mass loading of about 2 mg/cm^2. The thickness of SPE in the all-solid-state $LiFePO_4$/SPE/Li batteries was about 0.2-0.4 mm. And the areal loading of the SPE electrolyte was about 100-120 mg/cm^2.

1.2.5. Assembling of $LiFePO_4$ /liquid electrolyte+ separator/Li batteries.

The Assembling method of $LiFePO_4$/liquid electrolyte+separator/Li batteries is similar to that of $LiFePO_4$/SPE/Li batteries. The difference is that replacing the SPE with separator and liquid electrolyte. The amount of liquid electrolyte used herein was about 40-60 μL.

1.3. Characterization

1.3.1. Characterization measurements

The X-ray diffraction (XRD) patterns of the SPEs were obtained in an Empyrean diffractometer using Cu K radiation and performed at the scan rate of 0.05 °/s from 10 ° to 90 °. The Attenuated Total Reflectance Fourier Transform Spectroscopy (ATR-FTIR) are performed using Perkin Elmer Spectrum One Version B. All the Electrolyte films are scanned in the range of 4000-400 cm^{-1} with the resolution of 4 cm^{-1} and need to scan 40 times. Field emission scanning electron microscope (FESEM, MJSM-7800F & TEAM Octane Plus) was utilized to characterize the morphology. All samples are observed under vacuum and anhydrous conditions. The Differential Scanning Calorimeter (DSC, DSC-200F3) was utilized to characterize the glass transition temperature. The experimental test temperature range is -50-50 °C with a heating rate of 5 K/min. Thermogravimetric analysis (TGA, STA409PC) are performed in a temperature range 25-600 °C in a nitrogen atmosphere, the heating rate is 5 K/min.

1.3.2 Electrochemical measurements

Electrochemical analysis tests are performed on a Solarton electrochemical workstation. The method used in the conductivity test is A.C impedance, with a frequency range from 0.1-100 KHz. Assembled stainless steel/SPE/stainless steel cells were tested at different temperatures (25 -80 °C). The Ionic conductivity can be calculated by the following equation (1).

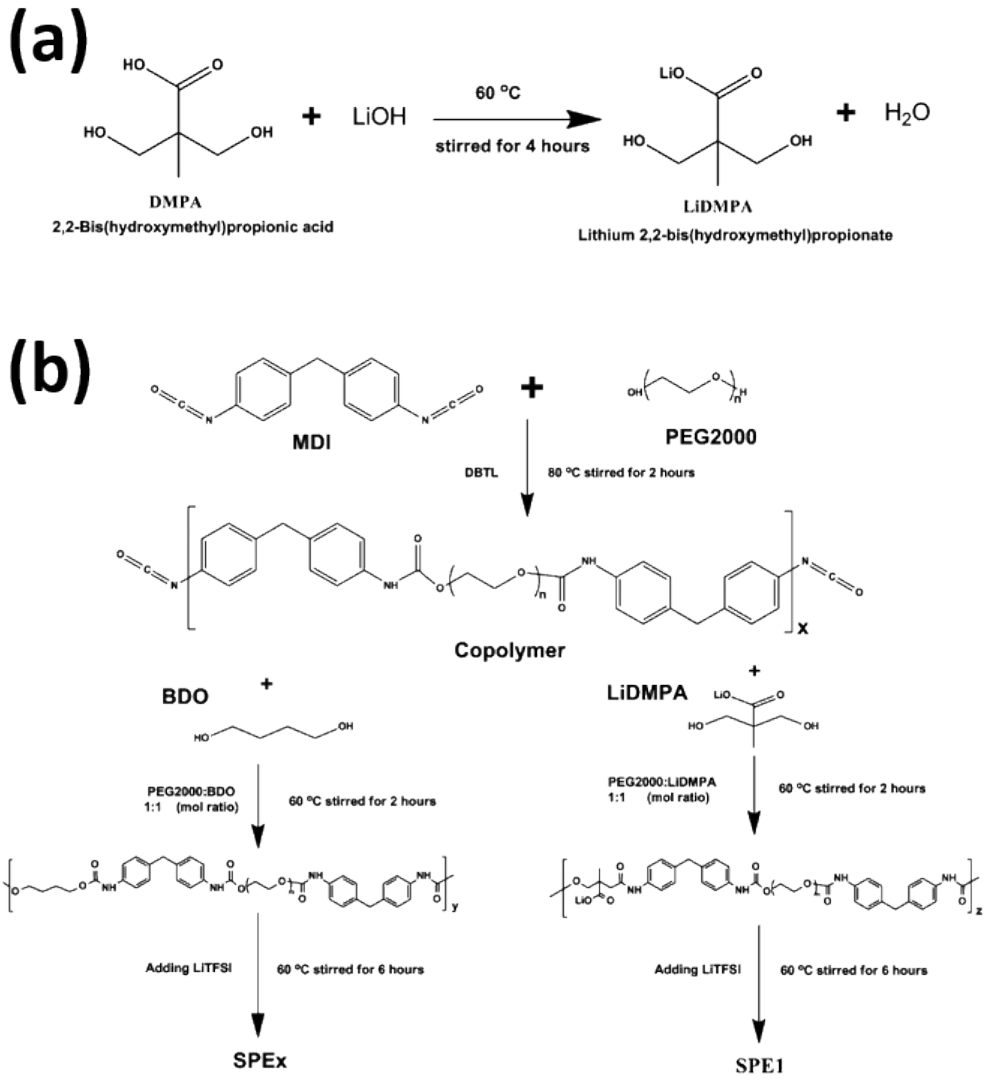
$$\sigma = \frac{L}{R \times S}$$

Where σ (S cm^{-1}) is the conductivity and L (cm) is the thickness of SPE films and S (cm^2) is the area of the film. R (Ω) is the resistance of the block (stainless steel/SPE/Stainless steel). The lithium ion transfer number (t_{Li^+}) is obtained through chonoamperometry (CA) and A.C impedance spectroscopy, which can be calculated by the following equation (2).

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

Where the I_{SS} and I_0 are the steady and initial current, respectively. R_0 and R_{SS} are the initial and steady block resistance, respectively. Δ*V* is the polarization voltage. The electrochemical stability windows of the SPEs were determined by linear sweep performed on Li/SPE/Stainless steel cells at 60 °C. The linear sweep voltammograms (LSV) were measured from 0 V to 7 V (vs. Li^+/Li) at a scan rate of 1 mV S^{-1}. Cyclic voltammograms (CV) were measured between -1 V and 3 V (vs. Li^+/Li) at a scan rate of 0.5 mV S^{-1}. The polarization tests of Li/SPE/Li cells and charge-discharge cycles of solid-state $LiFePO_4$/SPE/Li cells were performed on a LAND charge/discharge instrument (Wuhan LAND Testing Equipment Co, Ltd).

2. result and discussion



Scheme S1. Synthesis procedures of (a) LiDMPA, (b) SPE1 and SPEx.

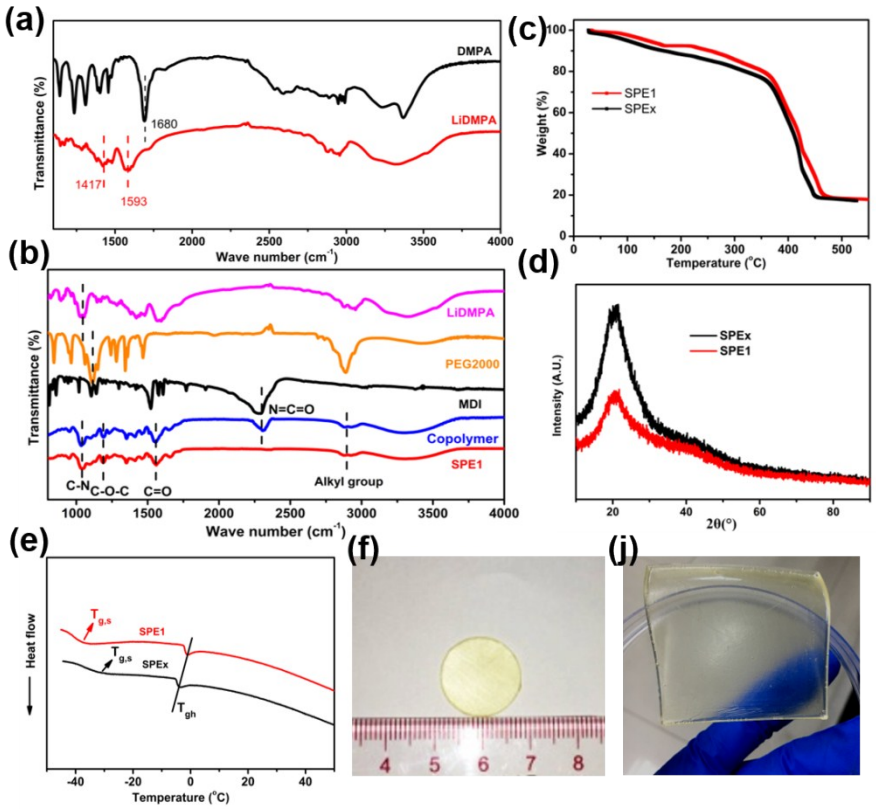


Fig S1. (a) FTIR spectra of LiDMPA and DMPA. (b) FTIR spectra of LiDMPA, PEG2000, MDI, Copolymer and SPE1. (c) TG curves of the SPE1 and SPEx films. (d) XRD patterns of SPE1 and SPEx films. (e) DSC curves of the SPE1 and SPEx films. (f, j) Photos of the SPE1 electrolyte film.

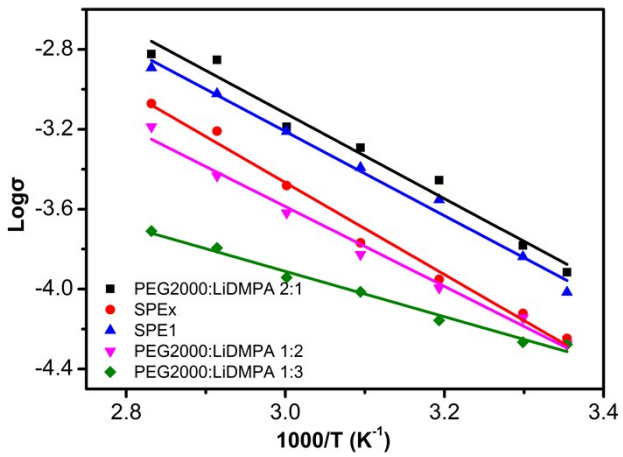


Fig S2. Temperature dependence of ionic conductivity for SPEs with different mol ratios of PEG2000 and LiDMPA.

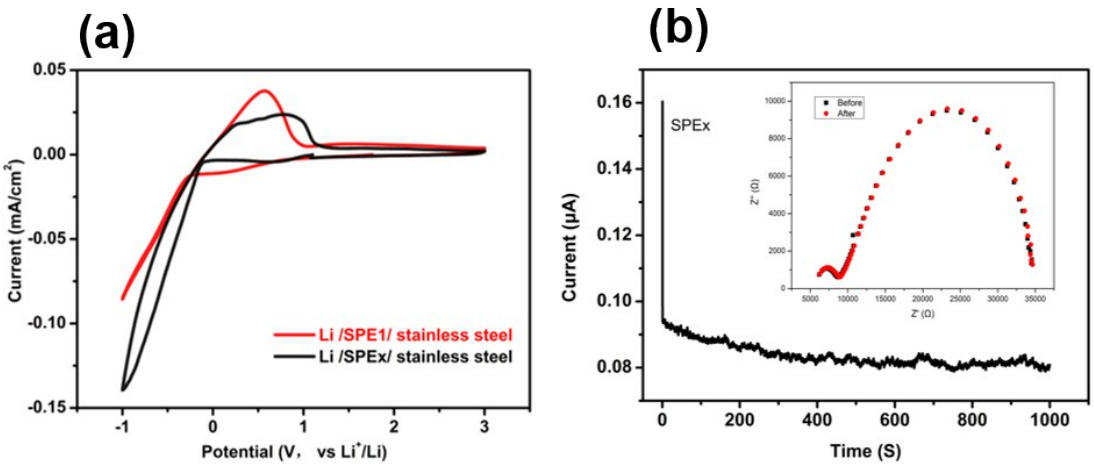


Fig S3. (a) CV curves of SPE1 and SPEX at 60 °C, (b) Variation of current with time and the impedance spectra of SPEx.

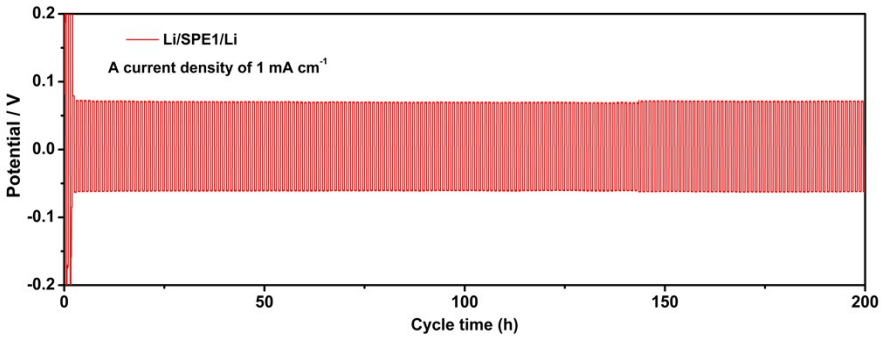


Fig S4. The long-term lithium plating/stripping test of Li/SPE1/Li cells.

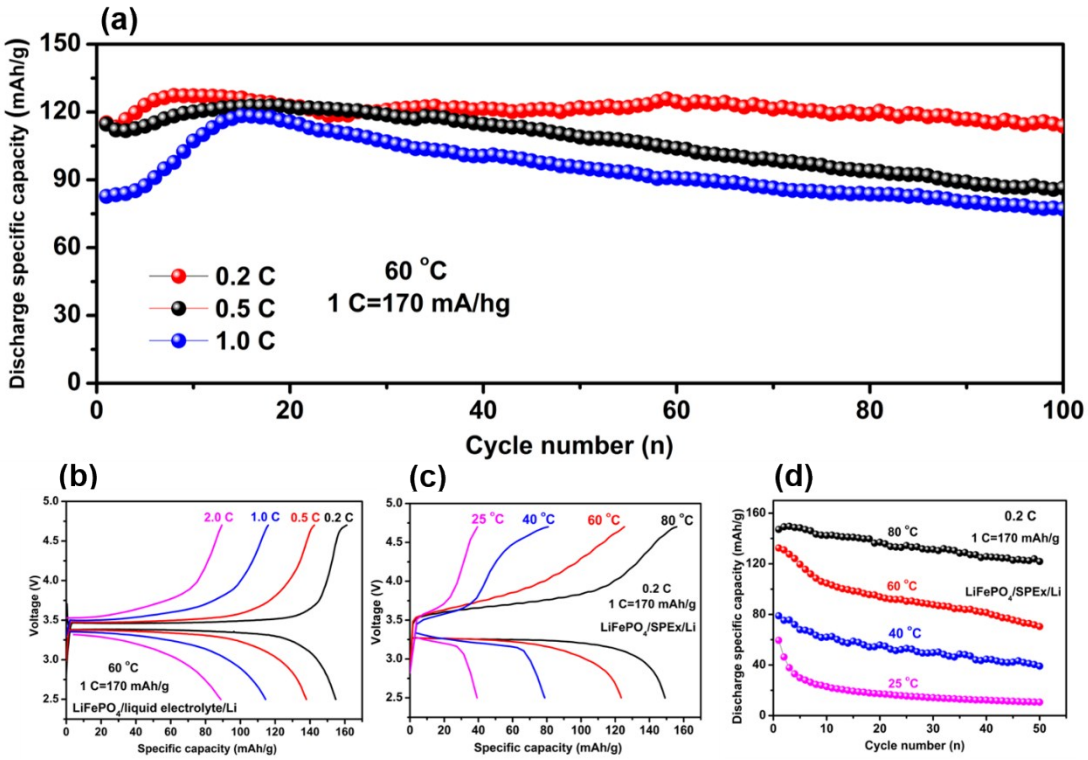


Fig S5. (a) The capacity retentions of $LiFePO_4$/SPE1/Li cells at different rates. (b) Charge and discharge profiles of the $LiFePO_4$/liquid electrolyte/Li batteries at different rates. (c) Charge and discharge profiles of the $LiFePO_4$/SPEx/Li batteries at different temperatures. (d) The capacity retentions of $LiFePO_4$/SPEx/Li cells at different temperatures.

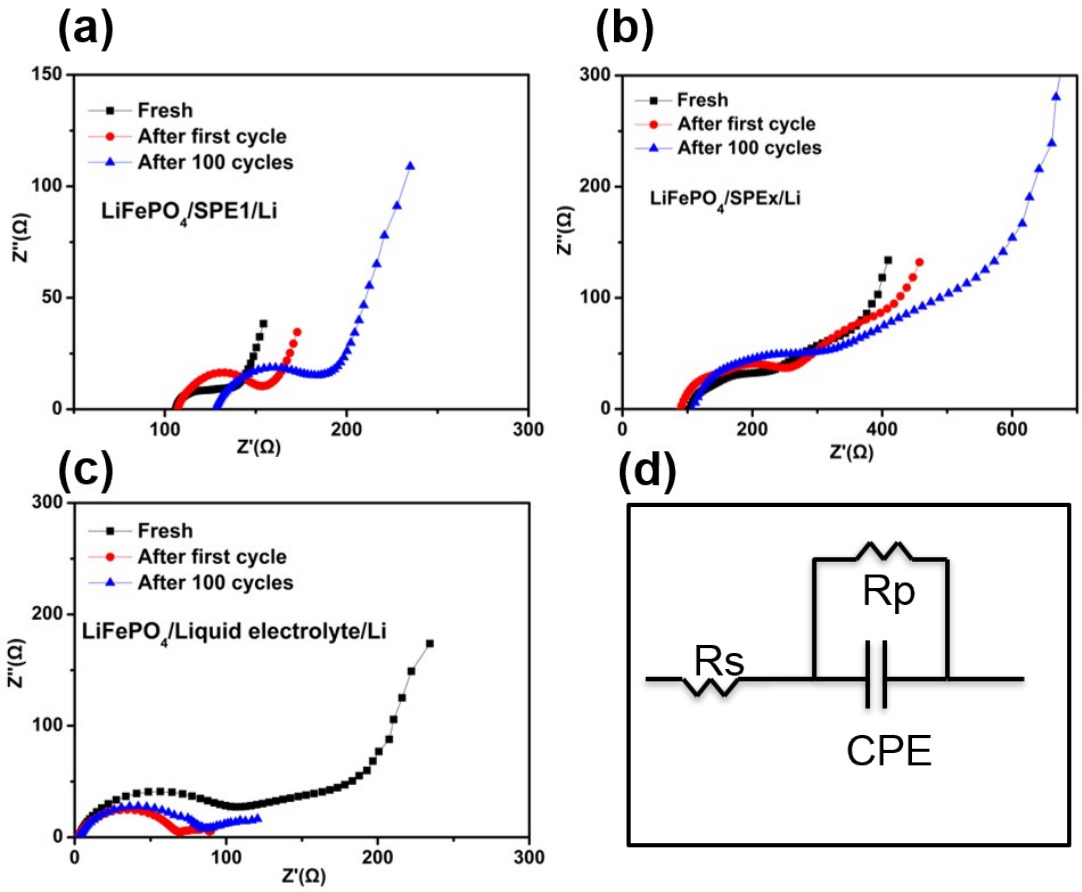


Fig S6. (a-c) The impedance results of $LiFePO_4$/SPE1/Li, $LiFePO_4$/SPEX/Li, and $LiFePO_4$/liquid electrolyte/Li cells at different cycles, (d) the equivalent circuit of all-solid-state $LiFePO_4$/SPE/Li batteries.

Table S1. Fitting result of different cells.

$LiFePO_4$/SPE1/Li	**R_S**	**R_P**
Fresh	105.50	56.80
After first cycle	100.00	62.58
After 100 cycles	125.50	76.07
$LiFePO_4$/ Liquid electrolyte/Li	R_S	R_P
Fresh	2.98	81.54
After first cycle	3.88	80.86
After 100 cycles	2.71	112.90
$LiFePO_4$/SPEx/Li	R_S	R_P
Fresh	94.51	200.20
After first cycle	77.85	231.40
After 100 cycles	91.88	310.50

Table S2. Comparison of some electrochemical performances of polymer electrolytes

Electrolyte composition	Ionic conductivity	Electrochemical stability window	Li^+ transfer number	Specific capacity/ Capacity retention/ C-rate	reference s
PU based Polymer Electrolytes	6.5×10^{-5} S/cm 25 °C	4 V		116mAh/g 80th 72.8% 0.1 C	1[1]
TPU/PEO blend polymer electrolytes	5.3×10^{-4} S/cm 60 °C	5 V		140 mAh/g 100th 95% 0.2 C	2[2]
Single Lithium-Ion Conducting Polymer Electrolytes	1.35×10^{-4} S/cm 90 °C	4 V	0.91		3[3]
(Si-PEG) film polymer electrolyte	1.2×10^{-4} S/cm 30 °C	5 V	0.62	139 mAh/g 500th 80% 0.5 C	4[4]
Poly(ethylenecarbonate) based Polymer Electrolytes	4.05×10^{-4} S/cm 55 °C	4.5 V	0.63	126 mAh/g 200th 93.4% 1.0 C	5[5]
PEO/LAGP hybrid polymer electrolytes	6.67×10^{-4} S/cm 60 °C	5.3 V	0.385	155 mAh/g 50th 90% 0.2 C	6[6]
$Li_{10}GeP_2S_{12}$/PEO hybrid polymer electrolyte	1.12×10^{-3} S/cm 80 °C	5.7 V	0.26	148 mAh/g 50th 92% 0.2 C	7[7]
PEO based polymer Electrolytes	1.4×10^{-4} S/cm 30 °C		0.51		8[8]
SPE1	9.6×10^{-5} S/cm 25 °C	5 V	0.72	159 mAh/g 50th 99.1% 80 °C 0.2 C 127 mAh/g 100th 98.7% 60 °C 0.2 C	This work

Notes and references

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