Supporting Information

Flexible solid-state electrolyte based on comb-like PEG-functionalized covalent organic frameworks for lithium metal batteries

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Materials

2,5-Bis(allyloxy)terephthalohydrazide (DHzDAll), 1,3,5-Benzenetricarboxaldehyde (Bt), Polyethylene Glycol Monomethyl Ether Methacrylate (PEGMA, $M_n = 475$ g mol⁻¹) were purchased from Bide Pharm, 1,4-dioxane and mesitylen, bis(trifluorome-thane)sulfonimide lithium salt were purchased used from Energy Chemical. Metal lithium foils with a thickness of 1.0 mm and a diameter of 16 mm, and lithium iron phosphate cathode with a thickness of ~16 µm were supplied by Guangdong Canrd New Energy Technology Co., Ltd., All solvents such as ethyl alcohol (AR, ≥99.5%) and tetrahydrofuran(AR, ≥ 99.5%) were purchased from Xi long Chemical Co., Ltd.

Synthesis

The preparation of Bt-COF:

2,5-Bis(allyloxy)terephthalohydrazide (23mg, 0.075 mmol) and 1,3,5-Benzenetricarboxaldehyde (8.1mg, 0.05mmol) were mixed in a 25mL Pyrex tube. A mixture of 1,4-dioxane and mesitylene (2.25 mL,1:2) was added into the tube and sonicated for 10 minutes. The mixture was then added with acetic acid (100 uL, 6 M), flash frozen at 77 K, and degassed under freeze-pump-thaw for three cycles. The tube

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was sealed and heated at 120 °C for three days. The solid obtained was exchanged with anhydrous THF (5 mL) 10 times and dried at 100 °C under vacuum for 8 hours to yield corresponding COFs (the yield of 88%).

The preparation of solid-state electrolytes:

The composite solid-state electrolytes (Bt-COF_{X%}-SPE) were prepared by an in situ polymerization with additional hot press curing. First of all, PEGMA and LiTFSI ([EO]/[Li] = 10:1), benzoyl peroxide (BPO,2wt%) were mixed and stirred at room temperature until the mixtures were transparent and uniform. After that, a different amount of Bt-COF powder was added into the solution and stirred for 24 hours to make the Bt-COF disperse evenly. Six types of Bt-COF_{x%}-SPE were synthesized by changing the weight ratio of PEGMA to Bt-COF (PEGMA: Bt-COF = 1:0, 200:1, 100:1, 50:1, 37.5:1 and 25:1, respectively); the obtained Bt-COF_{x%}-SPE was named Bt-COF_{0%}-SPE, Bt-COF_{0.5%}-SPE, Bt-COF_{1%}-SPE, Bt-COF_{2%}-SPE, Bt-COF_{3%}-SPE, and Bt-COF_{4%}-SPE respectively. Then the suspensions were poured into a Polytetrafluoroethylene mold and kept for 6 h at 60 °C under a hot press. Finally, the sample was dried at 60 °C under vacuum for 12 h. A uniform composite electrolyte film with a thickness of approximately 0.1mm was fabricated.

Characterization

PXRD patterns were collected on a Bruker D8 Advance diffractometer using Cu K α radiation ($\lambda = 1.5406$ Å) with a scanning rate of 5 ° min⁻¹ and a scanning range of 2–60°. Fourier Transform Infrared spectrum spectrum was measured on a Thermo Fisher Scientific with Universal ATR accessory between the ranges of 4000 to 550 cm⁻¹. Gas adsorption measurement N₂ adsorption measurements were performed on a BELSORP II mini, samples were activated at 120 °C for 12 h before the measurement. TGA was performed using a NETZSCH STA 449F5 under flowing N₂ with a 10 K min⁻¹ ramp rate from 30°C-800°C. SEM images were collected using a JSM-IT500HR system with an acceleration voltage of 10 kV. The elements distribution is detected by SEM EDS mapping of the four elements, C, N, F and O in the electrolyte membrane. The surface analyses of lithium surface from cycled Li/Li symmetrical cells were conducted by X-ray photoelectron spectroscopy (XPS, KRATOS ANALYTICAL LTD) under ultrahigh vacuum conditions.

The thermodynamic properties of PEGMA and Bt-COF_{2%}-SPE were analyzed by thermogravimetric analysis (TGA). The rate is characterized in the range of 25 °C to 800°C and TA Q20 analyzer was used for this purpose with a heat rate at 10 °C min⁻¹ under the N₂ atmosphere. Differential scanning calorimetry (DSC) was used to analyze the phase transition of Bt-COF_{0%}-SPE, Bt-COF_{2%}-SPE and Bt-COF_{4%}-SPE on TA DSC Q2000 differential scanning calorimeter. In the temperature range of -80 to 100 °C, two treatments are performed at a constant heating and cooling rate of 10 °C min⁻¹ under a continuous N₂ atmosphere, and finally the glass transition temperature (Tg) was obtained from the analysis of the secondary heating curve.

Electrochemical characterization measurement

Electrochemical impedance spectroscopy (EIS) measurements were measured using CHI660E electrochemical work-station. Tests were performed over a frequency range of 1 MHz to 0.01 Hz with an oscillating voltage of 10 mV. The resistance was determined as the extrapolated high-frequency intercept with the real x-axis of the Nyquist plot. The Ionic conductivity was calculated using the equation^{1,2} of

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

where L and S represent the thickness of the membrane and cross-sectional area, respectively, while R_b is the measured resistance.

The electrochemical stability window of the polymer electrolyte is determined by linear sweep voltammetry (LSV) at a sweep rate of 10 mV S⁻¹ from 1.0 to 7.0 V. Li| Bt-COF_{2%}-SPE |SS batteries were assembled by sandwiching all solid polymer electrolyte between lithium metal and stainless steel as the reference/counter electrode and working electrode in a glove box. It mainly measures the oxidation resistance of materials within a certain voltage range.

Lithium ion (Li⁺) transference number was tested by a constant voltage polarization method. Electrolytes were pressed into pellets. The pellet was sandwiched between two lithium metal foils to assemble into a lithium-symmetric cell. Transference number measurement was carried out with the CHI660E working station. A constant bias voltage of 10 mV was imposed on the electrolyte pellet. The transference number was calculated by equation^{3–5} of

$$t_{Li}^{+} = \frac{I_{ss}(\Delta V - I_{00}R_{00})}{I_{ss}(\Delta V - I_{ss}R_{ss})}$$

Where ΔV is the polarization voltage applied, I_0 and R_0 represent the initial current and interfacial resistance correspondingly, and I_{ss} and R_{ss} are the steady state current and interfacial resistance, respectively. The electrochemical compatibility of solid polymer electrolyte membrane was estimated by monitoring the response of voltage with longterm lithium deposition/striping cycles on the Neware battery system at room temperature. In each cycle, the Li/Li symmetric cell was charged for 1 h and discharged for 1 h at 0.1 mA cm⁻² in the temperature of 60 °C. The galvanostatic charge/discharge tests for LilBt-COF_{x%}-SPEILi CR2032-type coin cells were performed on a multichannel battery test system (Neware Battery Testing System) at 60 °C. The typical active mass loading was 1.2 mg cm⁻², and the voltage range was 2.5-4.2V.



Fig. S1 The optimized structure of Bt-COF in Materials studios, AA-stacking model (left) , AB-stacking model (right).



Fig. S2 EDS mapping of Bt-COF $_{0\%}$ -SPE and Bt-COF $_{4\%}$ -SPE film for carbon (C), oxygen (O), fluorine (F) and nitrogen (N) element.



Fig. S3 Ion conductivity profiles with different standing times for LilBt-COF_{2%}-SPE|Li samples at 60 °C.



Fig. S4 LiBt-COF_{0%}-SPELi symmetric cells, the EIS before and after

the polarization (inset)

c/a=0.1143)								
Atom	x/a	y/b	z/c					
C1	1.55169	0.01464	-0.51620					
C2	1.53702	0.05128	-0.51620					
C3	1.48580	0.03652	-0.51620					
C4	1.57541	0.10501	-0.51620					
N5	1.56313	0.13964	-0.51620					
N6	1.60063	0.19042	-0.51620					
C7	1.58805	0.22942	-0.51620					
08	1.54395	0.21852	-0.51620					
С9	1.62823	0.28259	-0.51620					
C10	1.67887	0.29517	-0.51620					
011	0.57306	1.60336	0.48380					
C12	0.62431	1.61538	0.48380					
C13	0.65763	1.67106	0.48380					
C14	0.70733	1.69097	0.48380					
H15	1.47378	0.06620	-0.51620					
H16	1.61708	0.11690	-0.51619					
H17	1.64093	0.20096	-0.51620					
H18	1.68911	0.26419	-0.51620					
H19	0.63206	1.59887	0.21811					
H20	0.63205	1.59886	0.74947					
H21	0.64050	1.69658	0.48380					
H22	0.72564	1.67532	0.28520					
H23	0.73166	1.72371	0.68239					

Table S1 Atomistic coordinates for vdW-DF2 optimized unit cell parameters for Bt- COF (space group P6, a=b=30.6649 Å c=3.5036 Å

Element(%) Materials	С	0	Ν	F	S
Bt-COF _{0%} -SPE	61.8	26.34	2.34	5.96	3.56
Bt-COF _{2%} -SPE	60.24	25.76	4.57	5.71	3.72
Bt-COF _{4%} -SPE	59.49	25.96	5.80	5.65	3.10

Table S2 Bt-COF_{x%}-SPE(X=0, 2 and 4) content of each element by EDS

Materials	Ionic conductivity (S cm ⁻¹)	Transferenc e number	E _a (e V)	Electrochemi cal window (V)	Refer ence
PDM/V-COF (1%)	5.00 *10 ⁻⁵ (RT)	0.45	/	5.0	S1 ⁶
TCPP-08 CPE PEG-	2.34*10 ⁻⁵ (RT)	0.23	0.10	5.0	S2 ⁷
Li ⁺ @EBCOF- ClO ₄	1.93*10 ⁻⁵ (RT)	0.17	0.21	/	S3 ⁸
COF-PEO-6-Li	6.25*10 ⁻¹⁰ (30°C)	/	/	5.2 (100°C)	S4 ⁹
COF-PEG-B6-Li	3.4 *10 ⁻⁶ (60°C)	0.30(100°C)	0.6	4.0 (100°C)	S5 ¹⁰
PEG-Li ⁺ @COF-M	2.2*10 ⁻⁵ (20°C)	/	0.46	5.0 (100°C)	S611
(PEO)18LiClO ₄ /T pPa-SO ₃ Li(0.75)	3.40*10 ⁻⁴ (60°C)	0.3(60°C)	/	4.5 (60°C)	S7 ¹²
PEG- Li@NKCOF-11	1.36 *10 ⁻⁵ (30°C)	0.95	0.18	5.5	S8 ¹³
3D-COF-PEG6-Li	3.70 *10 ⁻⁶ (100°C)	0.22(100°C)	0.49	4 .0(100°C)	S9 ¹⁴
Bt-COF _{2%} -SPE	5.30×10 ⁻⁵ (RT)	0.47	0.20	4.5	this work

Table S3 PEG/PEO related COF-based polymer electrolytes

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