Supplementary Information

Corona-shaped two-dimensional polyaramid derivatives for poly(ethylene oxide)-based all-solid-state lithium batteries

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Experimental methods

Materials

1,3,5-benzenetricarboxylic chloride (TMC), melamine (MA), N-methyl-2-pyrrolidone (NMP), pyridine, HO-PEG-OCH₃ (Mw=350, 550, 750, 1000 g mol⁻¹), N,N-dimethylformamide (DMF), PEO (Mv=600,000 g mol⁻¹) and lithium bis(trifluoromethanesulphonyl)imide (LiTFSI) were purchased from Adamas. Lithium disc, LiFePO₄ (LFP) powder, LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) powder, Super P, poly(vinylidene fluoride) (PVDF) were purchased from Canrd.

Synthesis of 2DPA-PEGs

1.5 mmol TMC and equivalent MA were added into 8.5 ml NMP and 1.5 ml pyridine. After stirring 24 h at room temperature in argon-filled glovebox, the reaction system became a gel. Another 10 ml NMP was added and the gel was smashed via vigorously stirring, followed by adding 2 equivalent HO-PEG-OCH₃. The mixture was stirred for another 48 h at 60 °C. The products were collected by centrifugation and purified via dialysis.

Preparation of SPEs

2DPA-PEG and PEO were blended at certain ratios, (0, 5, 10, 20, 30, and 40 wt% 2DPA-PEG to total polymer weight), followed by 26.6 wt% LiTFSI (the weight of LiTFSI to overall solid weight), were dissolved in DMF. The solution was casted onto a mold, heated to 80 °C and vacuum dried for 6 h.

Material characterization

¹H NMR (600Hz, Bruker AVANCE NEO) and Fourier-Transform Infrared Spectroscopy (FTIR, 4000-500 cm⁻¹, Nicolet 6700) were used to identify the chemical structure of materials. Gel Permeation Chromatography (GPC, Agilent) was used to analyze the molecular distribution of 2DPA-PEGs. The molecular images of 2DPA-PEGs were collected by High-resolution Atomic Force Microscopy (AFM) (Cypher VRS1250, Oxford) on mica with the probe of Multi75-G by Budgetsensors. The crystallization behavior was evaluated by Differential Scanning Calorimetry (DSC, TA DSC250) from -80 to 80 °C at 10 °C min⁻¹ and X-ray Diffraction (XRD, Rigaku Smartlab 9KW) from 5 to 50° at 5° min⁻¹. Dynamic Mechanical Analysis (DMA, TA DMA850) was used to characterize the mechanical properties from 25 to 50 °C in 5 °C min⁻¹ at 10 Hz. Tensile test was conducted at the rate of 10 mm min⁻¹. Thermal stability was tested via Thermal Gravimetric Analysis (TGA, PE) from 50 to 800 °C in 20 °C min⁻¹ at N₂. Microscale Combustion Calorimeter (MCC, FTT) was used to investigate the combustion behavior of SPEs at 1 °C s⁻¹ in the gas stream of 20% O₂ and 80% N₂. Scanning Electron Microscopy (SEM, ZEISS Gemin 560) was used to detect the morphology.

Battery assembly and electrochemical characterization

The electrochemical properties were measured via Gamry Interface 1010 and Neware battery test system. Ionic conductivity (σ) was estimated from electrochemical impedance spectroscopy (EIS) of stainless steel (SS)|SPE|SS from 10⁶ to 10⁰ Hz by the equation of $\sigma = l/(R \times S)$, where l is the thickness of SPE, R is the resistance, S is the area. The activation energy (E_a) of ion conduction was calculated by the equation of $\ln (\sigma) = -E_a/(k \times T) + ln^{[m]}(\sigma_0)$, where k, T, and σ_0 is the is Boltzmann constant, temperature, and pre-expotienal factor, respectively. Linear scanning voltammetry (LSV) was used to examine the electrochemical window at 0.5 mV s⁻¹. Lithium transference number (${}^{L_l}{}^{+}$) was measured via chronoamperometry by the equation of $t_{Ll} + = I_s R_{bs} (\Delta V - I_0 R_{l0})/I_0 R_{b0} (\Delta V - I_s R_{ls})$, where ΔV is the applied potential (10 mV), R_b and R_l are the bulk and passivation layer resistance, I is the current (the subscripts 0 and s refers the initial and steady state respectively). Symmetric cells of Li|SPE|Li were cycled at 0.05 mA⁻¹ to examine lithium stripping/plating at 50 °C. LFP and NCM811 cathodes were prepared by slurry casting (weight ratio of active material:PVDF:super P=8:1:1, dispersed in NMP), heated to 80 °C and vacuum-

pumping dried overnight. The active loading was 1.0-1.8 mg cm⁻². Electrochemical floating experiment was applied to evaluate the high voltage stability of Li|SPE|NCM81. Batteries of Li|SPE|LFP were assembled to test in the cut-off voltage from 2.5 to 4.2 V in different charge/discharge rates at 50 °C.

Fourier Transform Infrared (FTIR) Spectroscopy of 2DP-PEGs



Figure S1. The FTIR spectra of 2DPA-PEGs with different PEG chains.

¹H NMR spectra of 2DPA-PEGs



igure S2. (a) The reaction scheme of different pathways. (b) The ¹H NMR spectra of 2DPA-PEGs in DMSO-d6 and their integration of characteristic peaks.

In Figure S2 and S3, the peaks at around $\delta = 4.5$ ppm belong to -CH₂- in the targetproduct 2DPA-PEGs, indicating the success in synthesis. The weak bulge peaks at $\delta =$ 13-14 ppm are associated to the carboxyl acid produced via the side reaction between residual acyl chloride and moisture after quenching with PEGs. According to the integration ratio, the conversion rate to 2DPA-PEGs is over 90.48%.



Figure S3. The ¹H NMR spectra of 2DPA-PEGs in DMSO-d6. (a) 2DPA-PEG350, (b)

2DPA-PEG550, (c) 2DPA-PEG750, (d) 2DPA-PEG1000.

High-resolution Atomic Force Microscopy (AFM) test



Figure S4. The molecular images of 2DPA-PEG1000 (a-c) and their thickness (1-3), respectively.

The molecules of 2DPA-PEGs are equipped with two-dimensional features as a distinct height that is close to 0.348 ± 0.018 nm and a diameter that around 20~30 nm (measured as half-peak width, which is about two orders of magnitude higher than its height). This high diameter-to-height ratio enables the high specific surface area of 2DPA-PEGs molecules.

Gel Permeation Chromatography (GPC) test



Figure S5. The peak signals of (a) PEGs and (b) 2DPA-PEGs by GPC. Polymers were dissolved in DMF for testing.

The 2DPA-PEGs exhibit increased dispersity with longer grafting PEG chain length, which may be attributed to the reactivity difference of PEG chains in kinetics. The solution transformed into gel state at the end of condensation of 2DPA platelets. The gel was smashed into suspension and treated with quenching agents. The steric hindrance effect becomes predominant in this quenching process as the chain length increases from PEG350 to PEG1000. In each type of PEGs, the relatively lower molecular weight compositions are attached to 2DPA faster than the higher molecular weight compositions. In addition, the 2 equilibriums of PEGs, which are used to improve conversion rates, result in some 2DPA-PEGs grafting with the shorter PEGs in majority. This phenomenon would be magnified when PEGs in high Mw are used.

X-ray Diffraction (XRD) test



Figure S6. The XRD spectra of 2DPA-PEGs powders from 5 to 50°.

In previous work by Zeng et al,² 2DPA powders are amorphous without any detective orientations. After attaching PEG short chains to the 2DPA core, the derivates remain similar spectra with no crystallizations or orientations.

Images of 2DPA-PEG, PEO, and LiTFSI solutions



Figure S7. The solution of (a) LiTFI (left) and 2DPA-PEGs/LiTFSI (right) in DMF,(b) PEO/LiTFSI (left) and 2DPA-PEGs/PEO/LiTFSI (right) in DMF.



Surface SEM images of SPEs

Figure S8. The SEM images of electrolyte surfaces of (a-c) 30-2DPA-SE and (d-f) PEO/LiTFSI.

The surface of 30-2DPA-SE is denser than PEO/LiTFSI with fewer cracks which would benefit surface contact with electrodes and improve the ion transport at the interface of electrolyte/electrode.

Ionic conductivity measurement



Figure S9. The ionic conductivities of 2DPA-PEGs/LiTFSI at room temperature.

The 2DPA-PEGs powders were dissolved in DMF with LiTFSI, after casting and drying, the resulting electrolyte films were further assembled with stainless steels to perform EIS test. The ionic conductivities increase with longer PEG chains, suggesting that the flexible chains promote ion transport. However, all the 2DPA-PEGs/LiTFSI exhibit inferior ionic conductivity compared to 30-2DPA-SE, probably due to the lack of continuous ion transport paths. Compared to other works of PEO-based SPEs in Table S1, 30-2DPA-SE exhibits an outstanding lithium-ion transference number of 0.78 and a high room-temperature ionic conductivity of 4.39 \times 10⁻⁵ S cm⁻¹.

Table S1. Comparison of ionic conductivity and lithium-ion transference number ofPEO-based solid polymer electrolytes.

Sample	Ionic conductivity (S cm ⁻¹)	Lithium-ion transference number	Ref.
30-2DPA-SE	4.39 × 10 ⁻⁵ (RT)	0.78	This work
PEO/LiTFSI/PEGDE-g- LLZTO@PDA	$1.1 \times 10^{-4} (RT)$	0.34	3
PEO/LiTFSI/ZIF-67	1.51 × 10 ⁻⁵ (25 °C)	0.185	4

PEO/LiTFSI/Mg2B2O5	$1.53 \times 10^{-4} (40 \text{ °C})$	0.44	5
PEO/LiTFSI/BN-MPS	$1.05 \times 10^{-4} (\text{RT})$	0.49	6
PEO/LiTFSI/g-C ₃ N ₄	$1.7 \times 10^{-5} (30 \text{ °C})$	0.56	7
PEO/LiTFSI/Mxene	$2.2 \times 10^{-5} (25 \text{ °C})$	0.18	8
PEO/LiTFSI/Nickel-based MOF	1.66 × 10 ⁻⁵ (25 °C)	0.378	9
PEO/LiClO ₄ /SiO ₂	$1.1 \times 10^{-4} (30 \text{ °C})$	0.367	10
PEO/LiTFSI/SiO ₂	$1.89 \times 10^{-4} (60 \text{ °C})$	0.293	11

High-voltage stability



Figure S10. (a) Electrochemical floating experiment of Li|SPE|NCM811 full cells at 50 °C. (b) LSV curves of Li|SPE|SS at 0.5 mV s⁻¹, 50 °C.





Figure S11. The DSC curves of PEO/LiTFSI blended with 2DPA-PEGs, (a) 2DPA-PEG350, (b) 2DPA-PEG550, (c) 2DPA-PEG 750, (d) 2DPA-PEG1000.

Tensile test of SPEs



Figure S12. The tensile test of 30-2DPA-SE and PEO/LiTFSI.

Thermal Gravimetric Analysis (TGA) test



Figure S13. The TGA curves of 30-2DPA-SE and PEO/LiTFSI from 50 to 800 °C at 20 °C min⁻¹.

Microscale Combustion Calorimeter (MCC) test



Figure S14. The MCC results of 2DPA-PEG750, 30-2DPA-SE, PEO, and PEO/LiTFSI.

The peak heat release rate (HRR) and total heat release (THR) of PEO are 735.6 W g⁻¹ and 28.9 kJ g⁻¹, respectively. While the 2DPA-PEG750 exhibits superior flame retardancy by a reduced peak HRR of 300.8 W g⁻¹ and THR of 16.9 kJ g⁻¹. After blending to SPEs, the 30-2DPA-SE shows a reduced peak HRR and THR of 391.2 W g⁻¹ and 14.5 kJ g⁻¹ compared to the 475.3 W g⁻¹ and 17.41 kJ g⁻¹ of PEO/LiTFSI, indicating the addition of 2DPA-PEG750 slows down the combustion process of SPE.

Surface SEM images of lithium metal electrodes



Figure S15. The surface of lithium metal electrodes in (a-b) Li|30-2DPA-SE|Li after 1440 h and (c-d) Li|PEO/LiTFSI|Li after 279 h.

Electrochemical Impedance Spectroscopy (EIS) measurement



Figure S16. The EIS spectra of assembled (a) Li|Li and (b) Li|LFP at 50°C.



Figure S17. (a) The discharge capacity of Li|30-2DPA-SE|LFP at 0.2C, 50 °C. (b) the evolution of impedance during the cycles.

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