

Supplementary Information

Puzzle-like molecular assembly of non-flammable solid-state polymer electrolytes for safe and high-voltage lithium metal batteries

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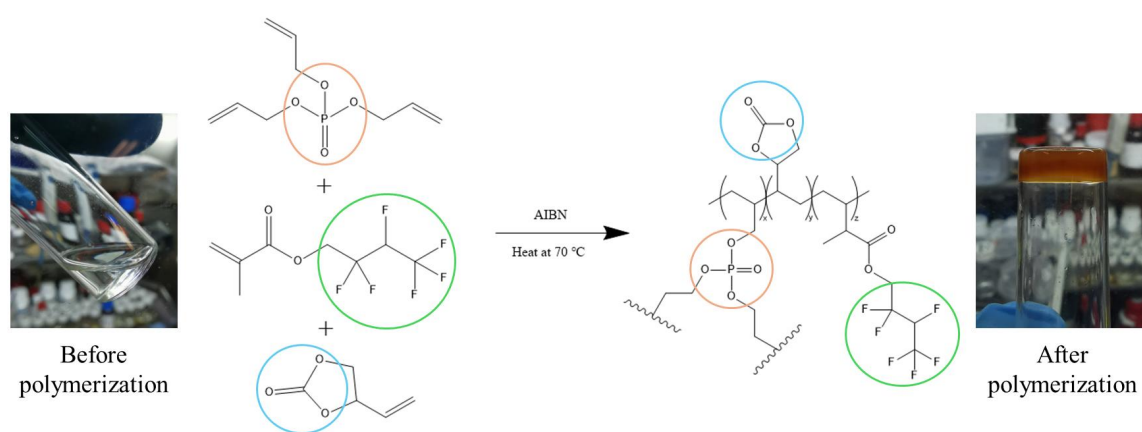


Figure S1. The synthesis of IWSWN-SPE.

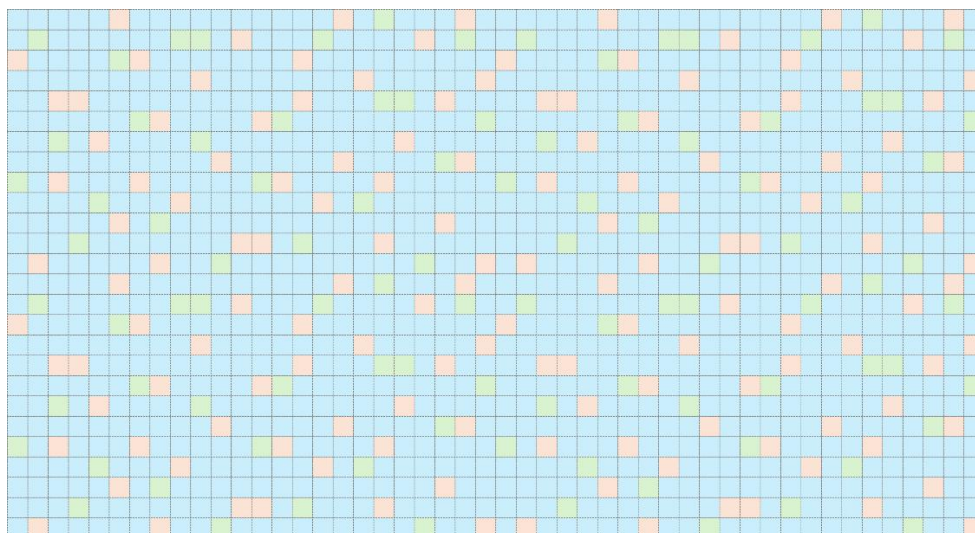


Figure S2. Schematic diagram of the product via puzzle-like assembly method (blue: VEC; orange: TAP; green: HFBMA).

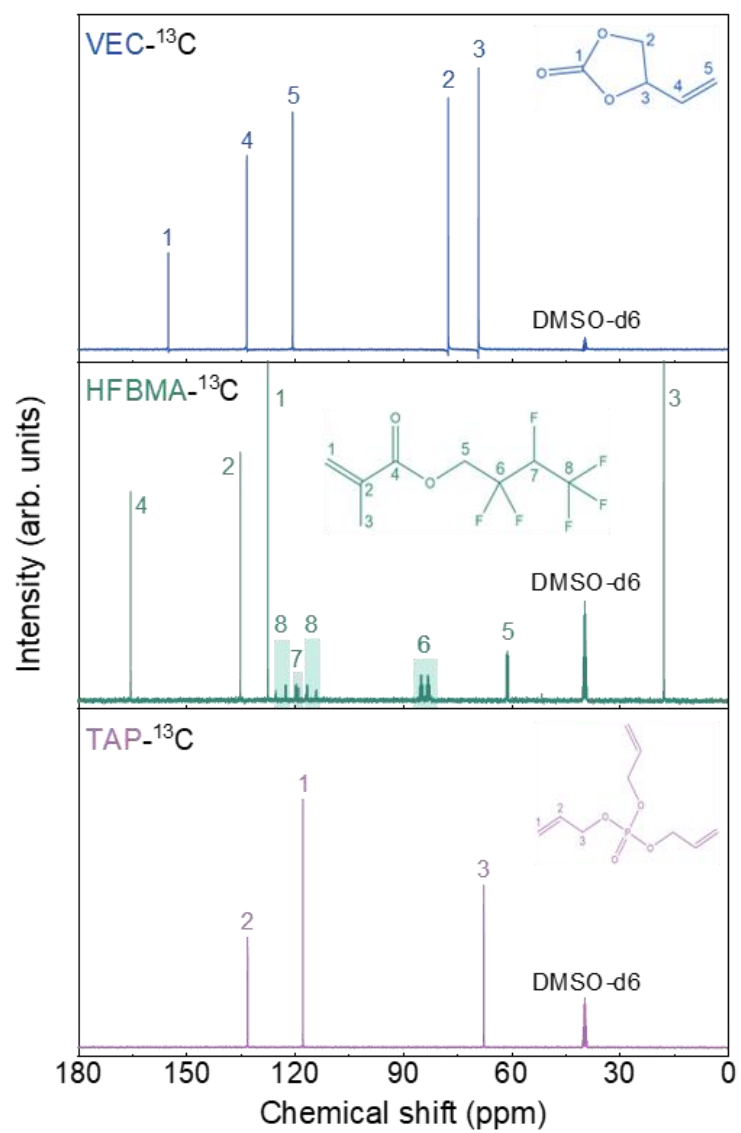


Figure S3. ^{13}C nuclear magnetic resonance results of VEC, HFBMA, and TAP.

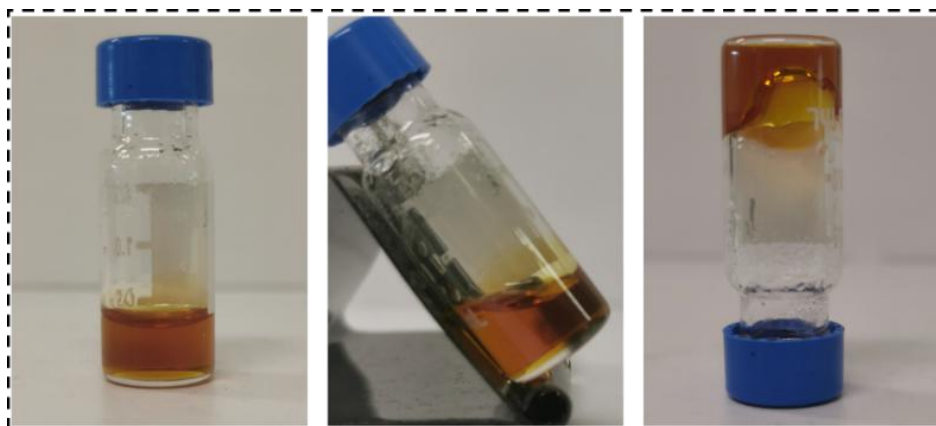


Figure S4. Digital photos of PVEC in different states obtained by in situ polymerization.

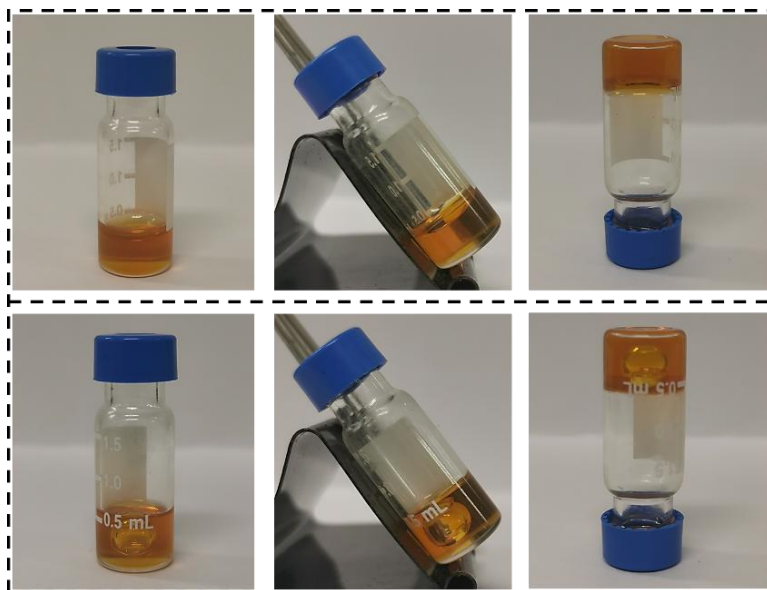


Figure S5. Digital photos of two kinds of IWSWN-SPE (the top row has no bubbles, and the bottom row contains one bubble) in different states obtained by in situ polymerization. The presence of bubbles in the polymer without any change in their positions suggests a dry state rather than a gel-like state.

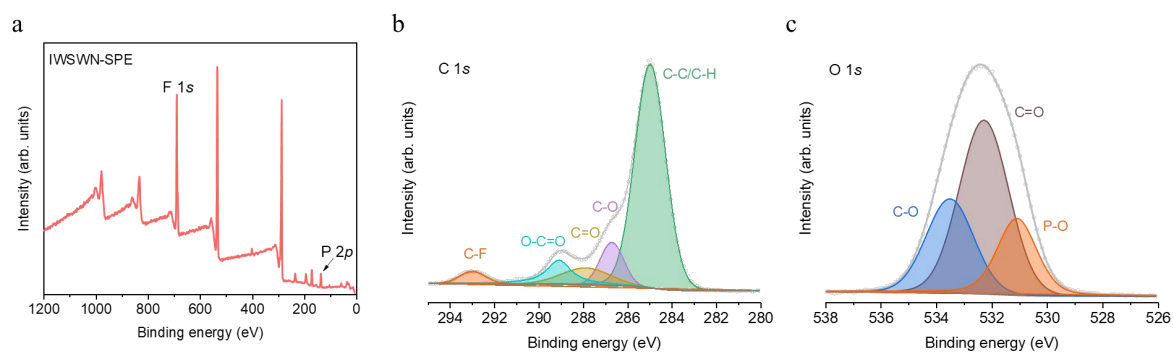


Figure S6. X-ray photoelectron spectroscopy (XPS) spectra of IWSWN-SPE. a) Full spectra of IWSWN-SPE. b) C 1s core level spectrum of IWSWN-SPE. c) O 1s core level spectrum of IWSWN-SPE.

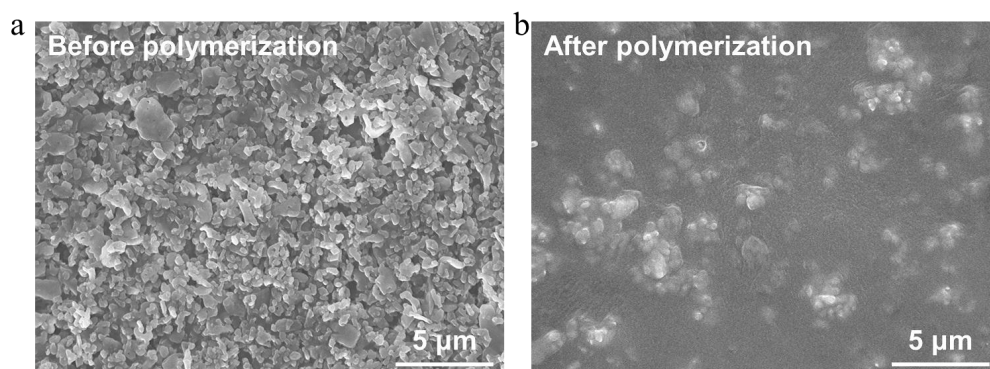


Figure S7. SEM images of ceramic (Al_2O_3)-coated polyethylene separator before (a) and after (b) polymerization.

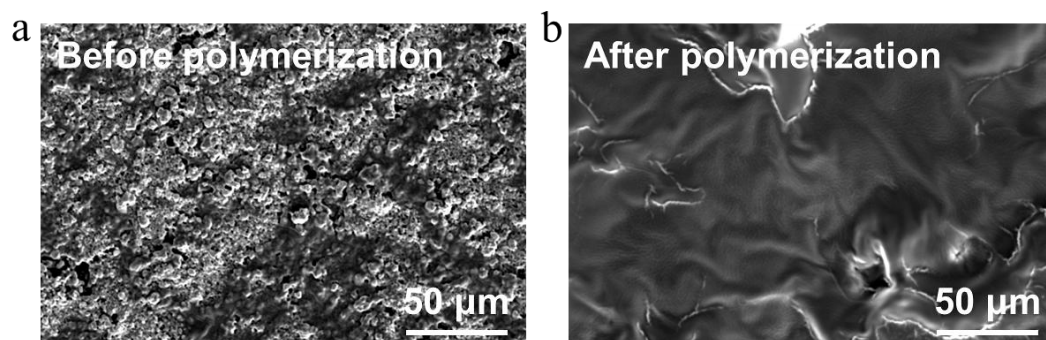


Figure S8. SEM images of the NCM622 positive electrode surface before (a) and after (b) polymerization.

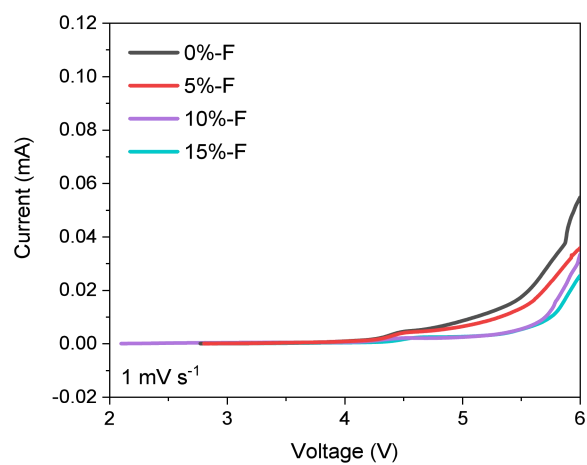


Figure S9. LSV test results for the SPE with different molar ratios of HFBMA (compared to VEC).

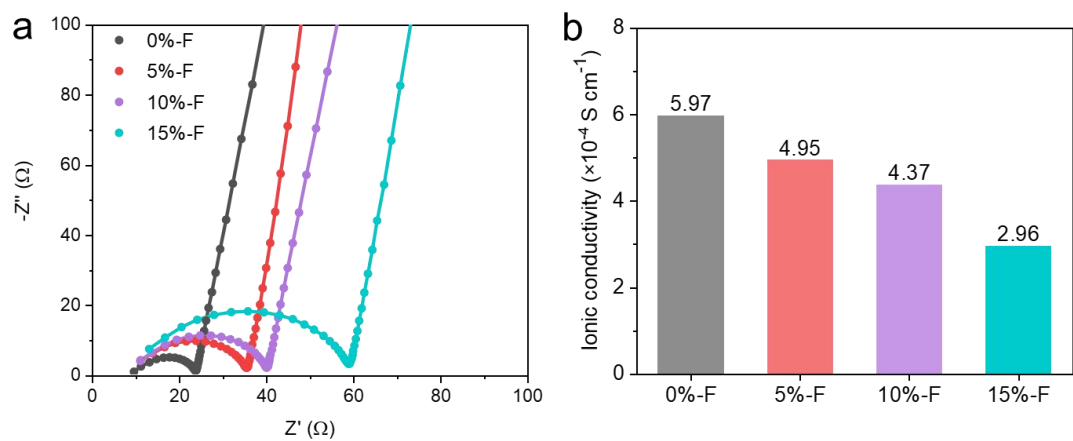


Figure S10. EIS results (a) and corresponding ionic conductivity (b) of the SPE with different molar ratios of HFBMA (compared to VEC).

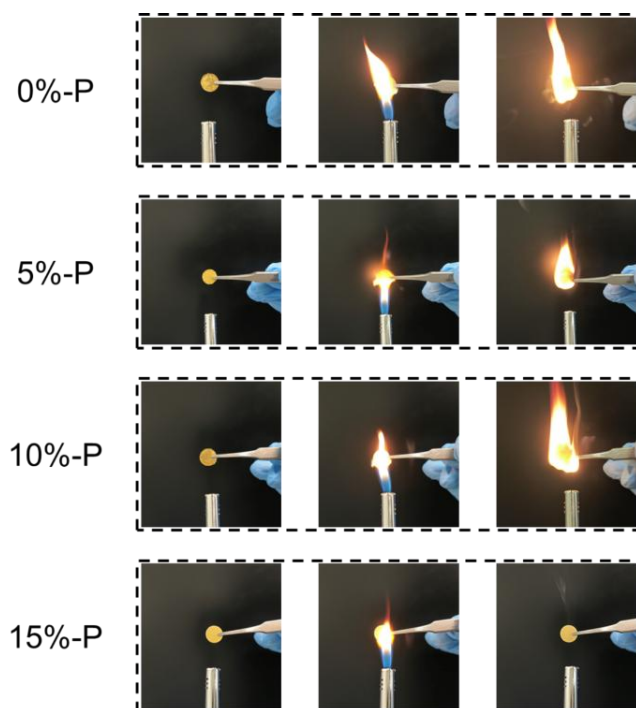


Figure S11. Burning tests of the SPE with different molar ratios of TAP (compared to VEC).

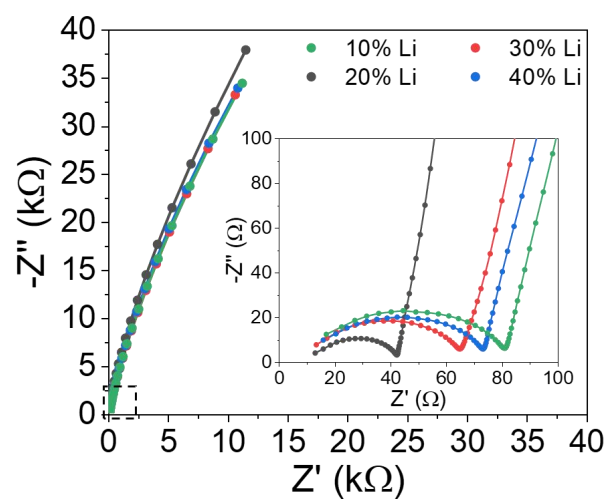


Figure S12. Electrochemical impedance spectra of IWSWN-SPE with different mass ratios of LiTFSI.

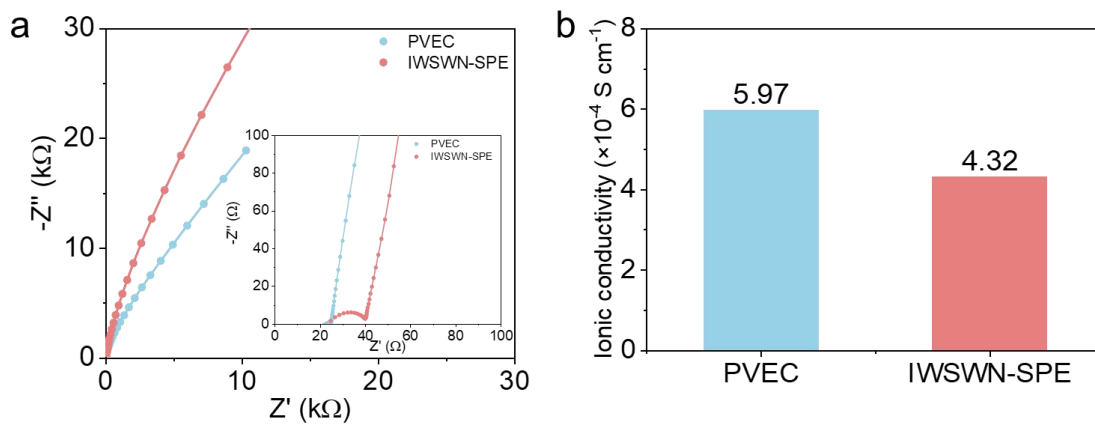


Figure S13. EIS tests (a) and corresponding ionic conductivity (b) of PVEC and IWSWN-SPE.

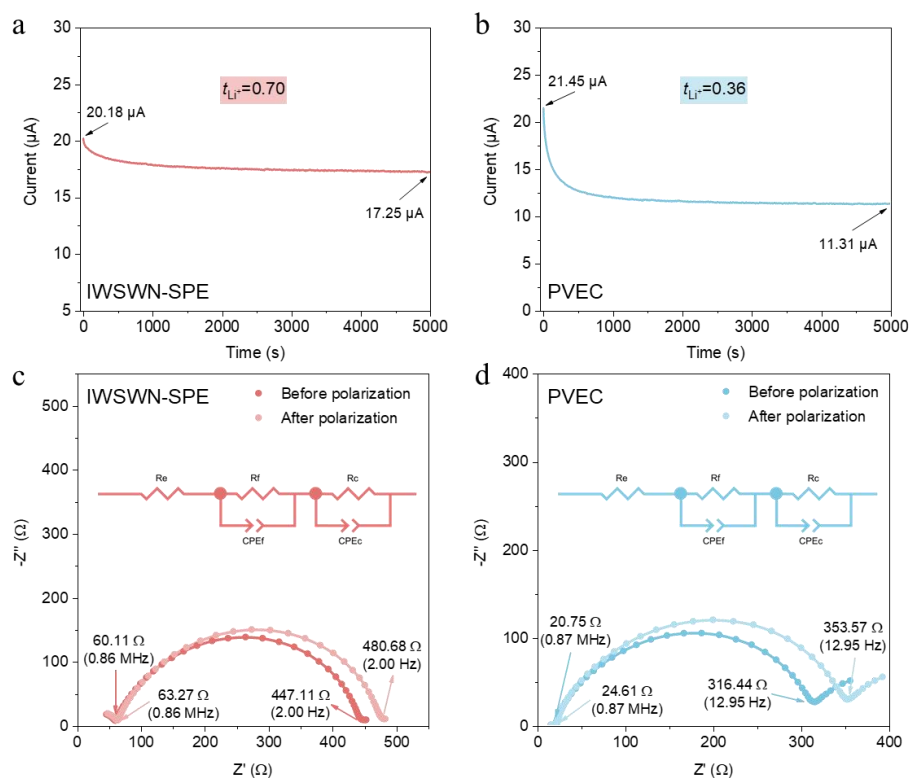


Figure S14. Li^+ transference number test results of IWSWN-SPE and PVEC. Polarization (POL) results (a, b) and electrochemical impedance spectra results before and after the POL (c, d) of IWSWN-SPE and PVEC.

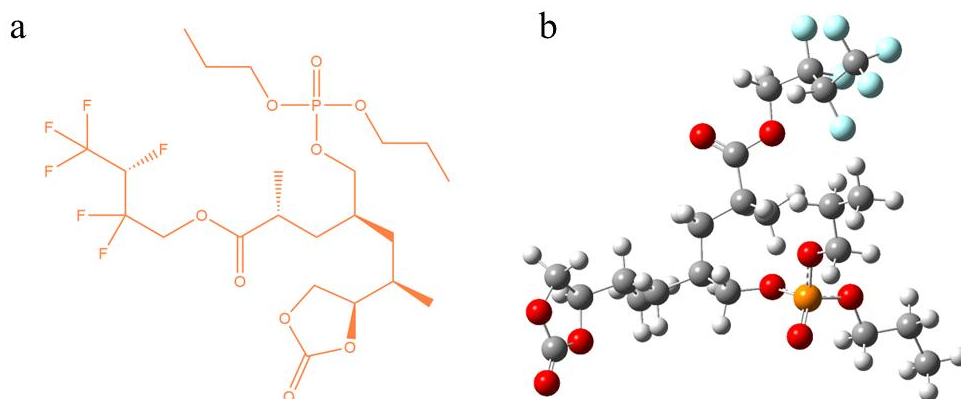


Figure S15. Schematic diagrams of the structure of the IWSWN-SPE unit. a) Structural formula. b) Ball-and-stick models. (O: red; P: orange; C: grey; H: white; F: aqua green).

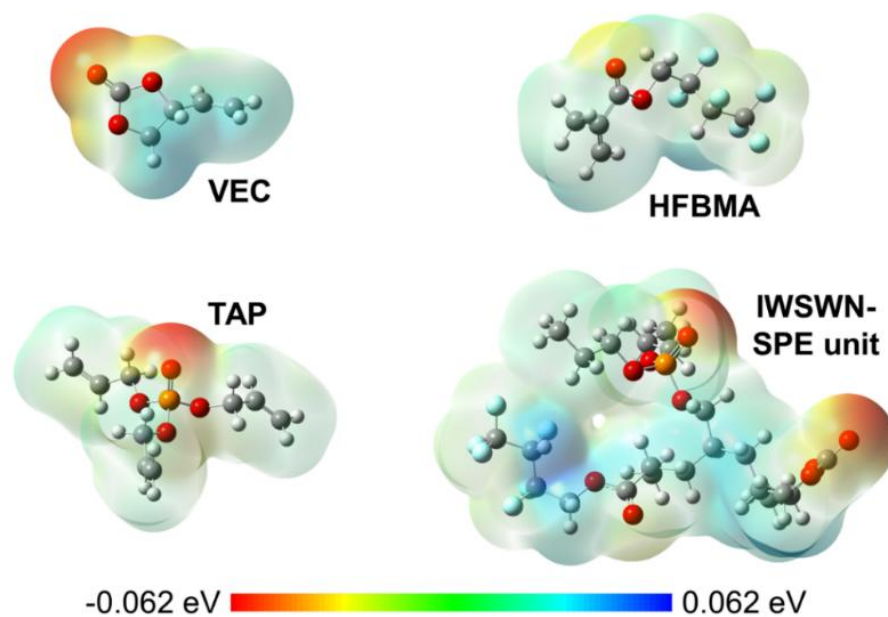


Figure S16. Simulations on electron cloud density distribution of VEC, HFBMA, TAP, and IWSWN-SPE unit. (O: red; P: orange; C: grey; H: white; F: aqua green).

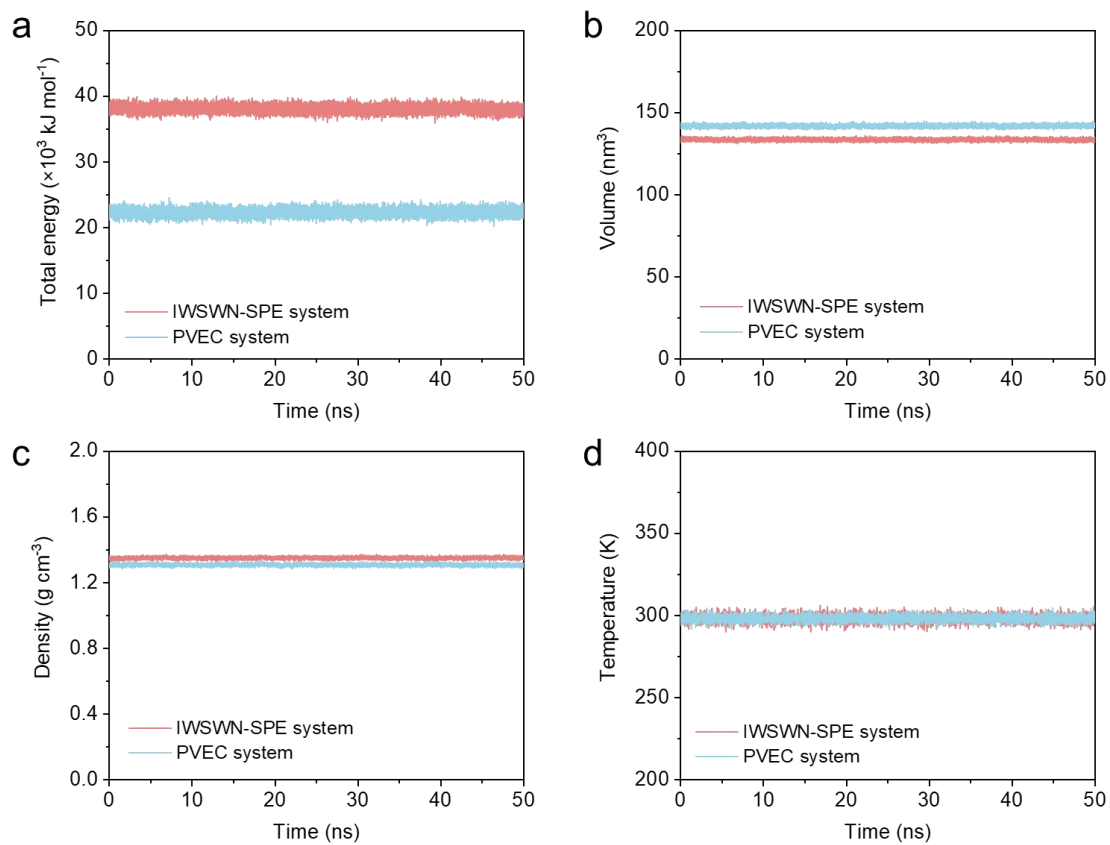


Figure S17. Graph showing the variation of parameters during the 50 ns equilibration process of MD calculations (a, total energy; b, volume; c, density; d, temperature).

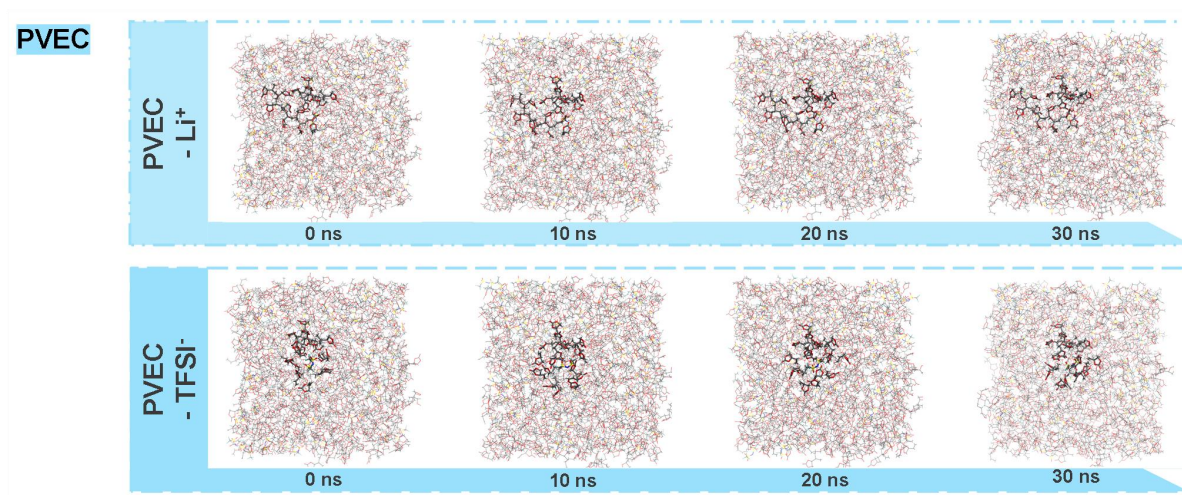


Figure S18. Environmental evolutions centred on a Li⁺ and a TFSI⁻ within the simulation model of PVEC systems.

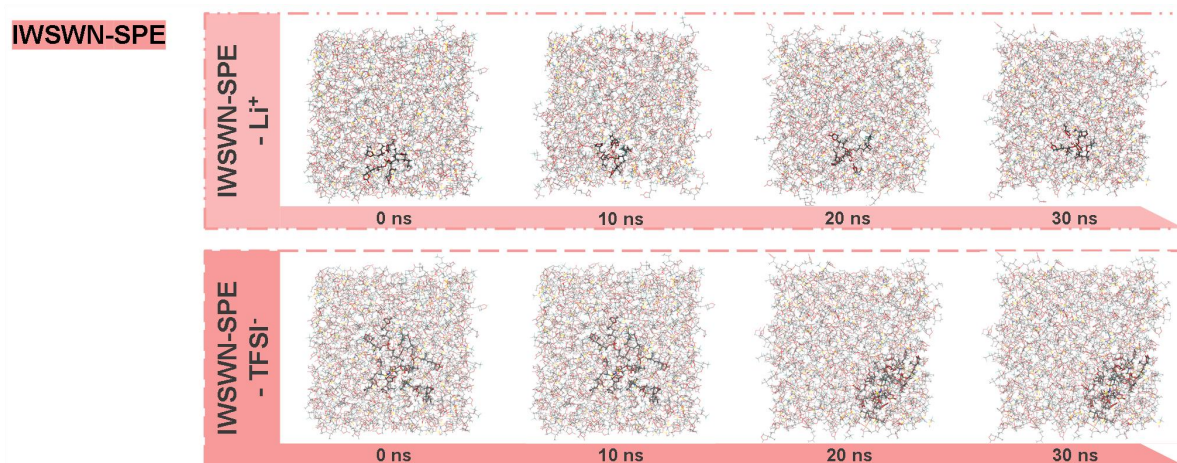


Figure S19. Environmental evolutions centred on a Li⁺ and a TFSI⁻ within the simulation model of IWSWN-SPE systems.

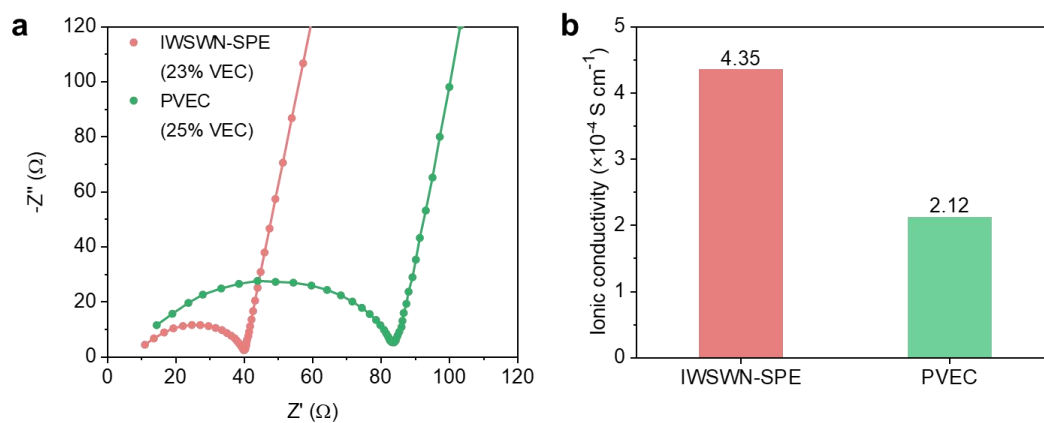


Figure S20. EIS curves (a) and calculated ionic conductivity results (b) of IWSWN-SPE and PVEC with similar weight ratios of VEC.

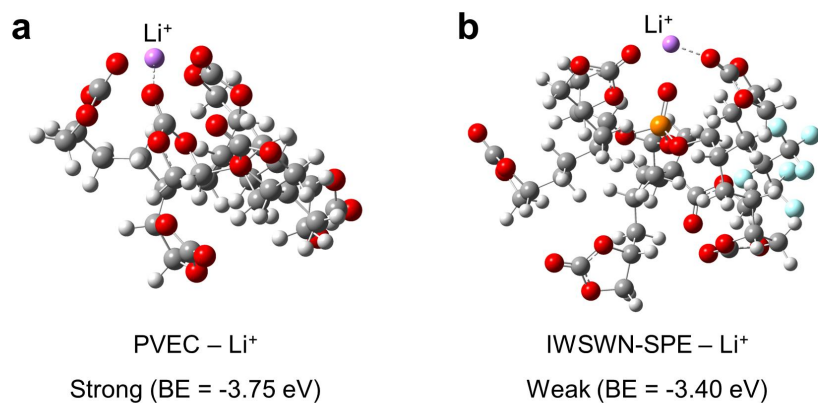


Figure S21. Binding energies between Li⁺ and PVEC (a) and IWSWN-SPE (b). (Li: purple; O: red; P: orange; C: grey; H: white; F: aqua green).

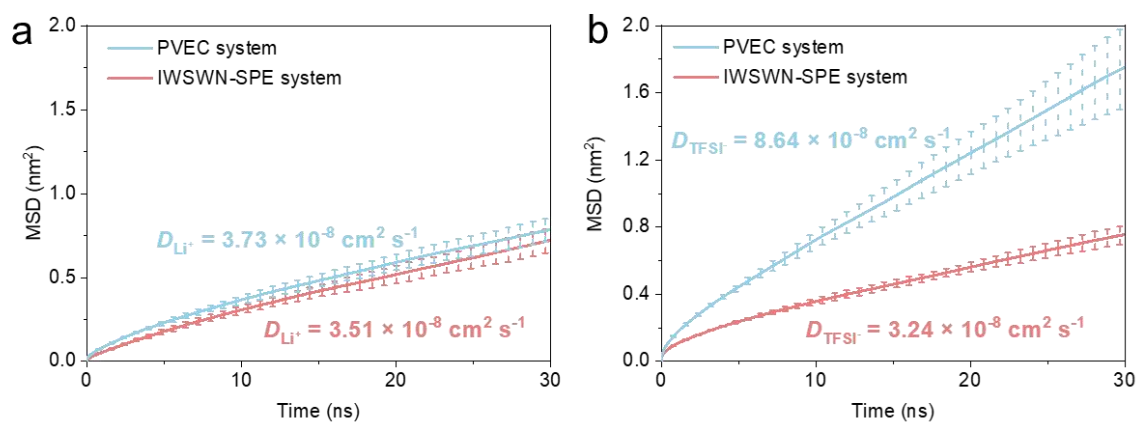
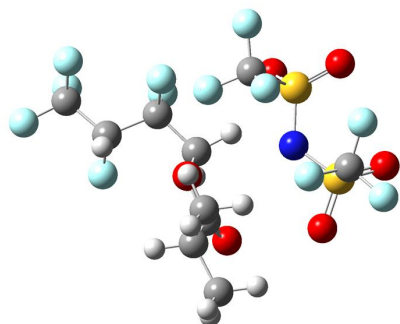


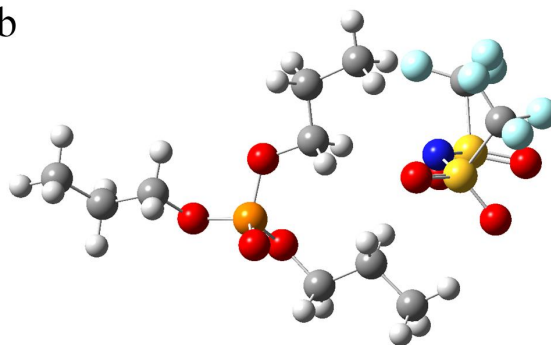
Figure S22. The mean and variance of MSD curves of Li⁺ (a) and TFSI⁻ (b) in the PVEC and IWSWN-SPE systems at 298.15 K.

a

HFBMA - TFSI⁻

BE = -0.31 eV

b

TAP - TFSI⁻

BE = -0.30 eV

Figure S23. Calculated results of the binding energy of (a) HFBMA-TFSI⁻ and (b) TAP-TFSI⁻. (O: red; S: yellow; N: blue; P: orange; C: grey; H: white; F: aqua green).

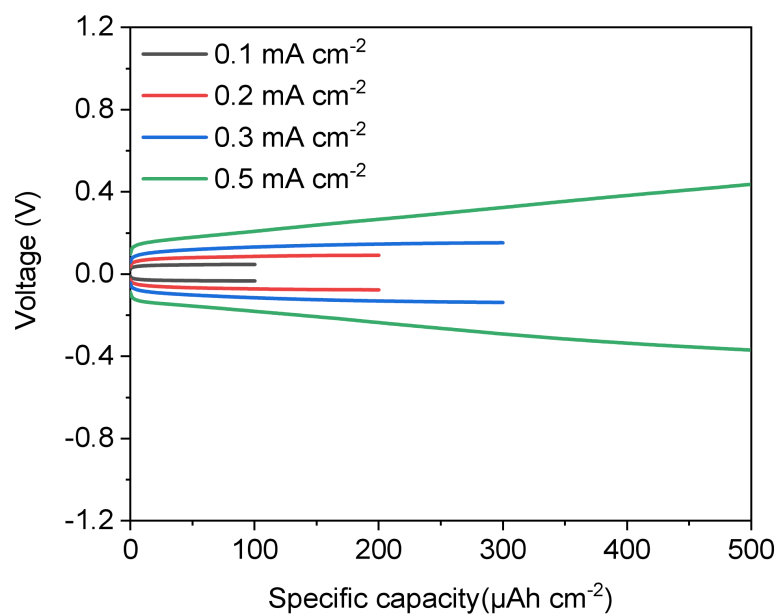


Figure S24. The charge/discharge voltage profiles of Li|IWSWN-SPE|Li cell at different current densities.

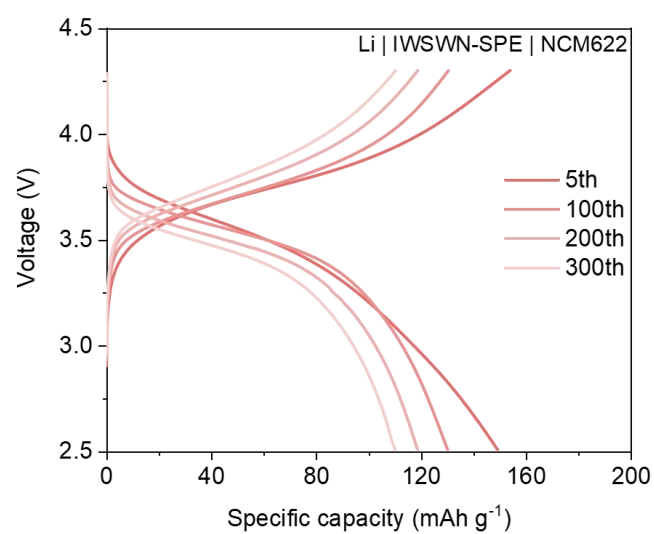


Figure S25. The charge/discharge voltage profiles of the Li|IWSWN-SPE|NCM622 cell.

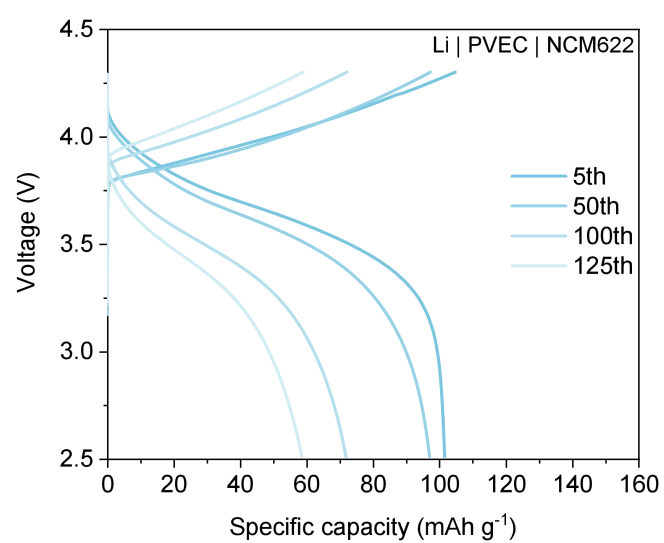


Figure S26. The charge/discharge voltage profiles of the Li|PVEC|NCM622 cell.

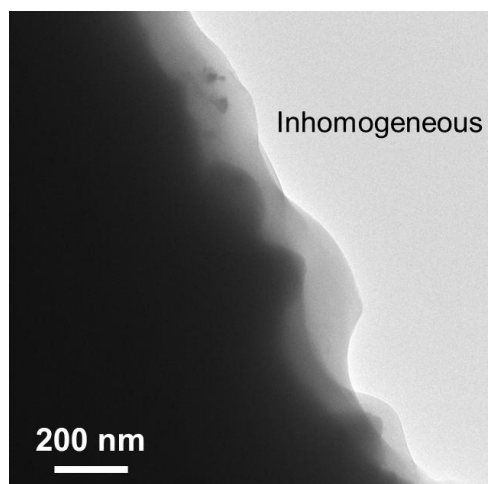


Figure S27. Cryo-TEM image of deposited Li in the cell with the PVEC.

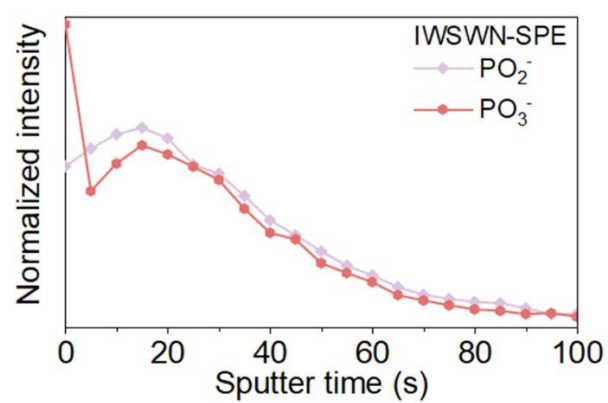


Figure S28. Depth profiles of PO_2^- and PO_3^- species from the LMAs in cycled Li||Li cell with the IWSWN-SPE.

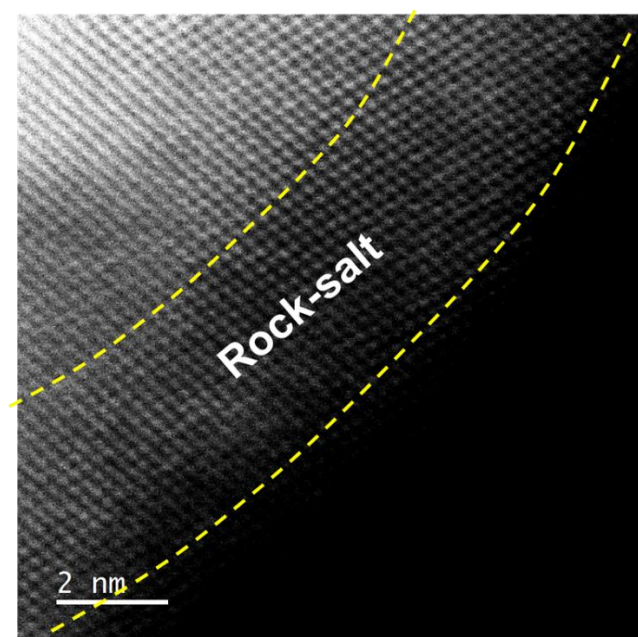


Figure S29. High-resolution TEM image for NCM622 particles cycled with PVEC.

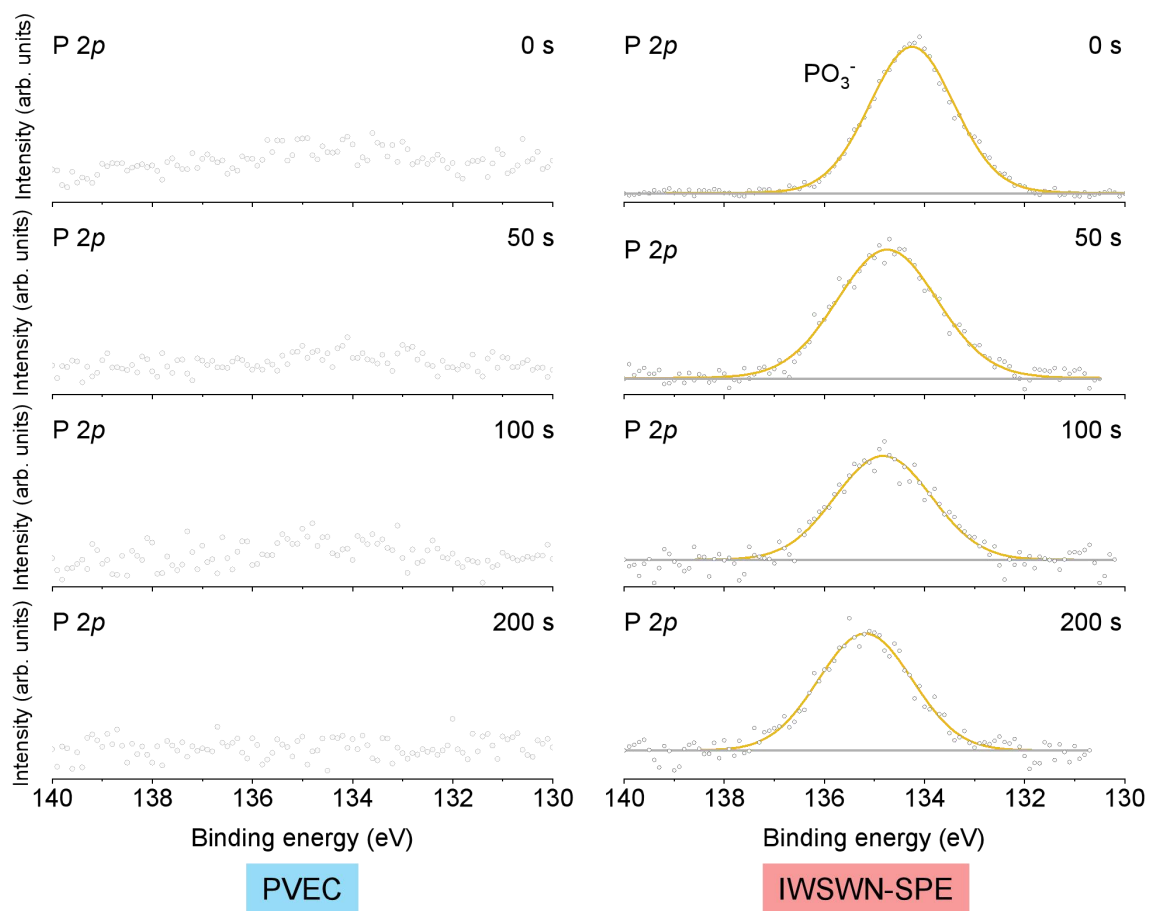


Figure S30. P 2*p* depth sputtering XPS spectra of the cycled NCM622 positive electrodes in the PVEC and IWSWN-SPE.

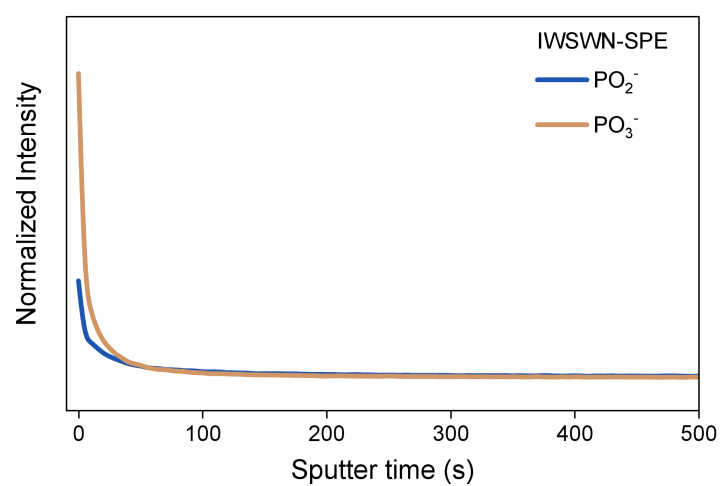


Figure S31. Depth profiles of PO_2^- and PO_3^- species from the NCM622 positive electrode in cycled $\text{Li}||\text{NCM622}$ cell with the IWSWN-SPE.

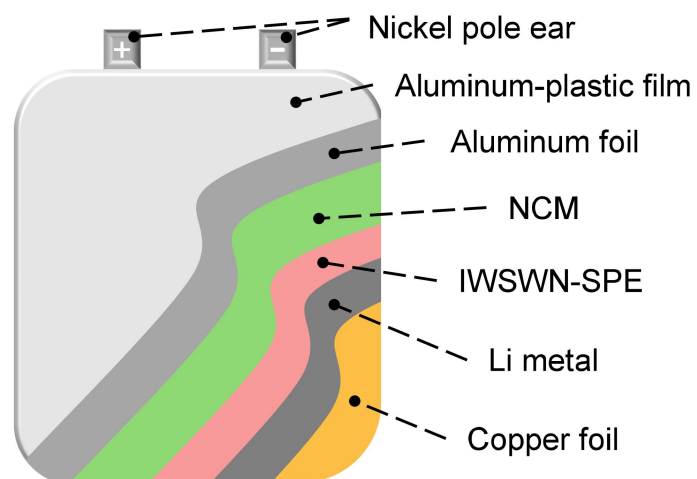


Figure S32. Schematic of the pouch cell structure.

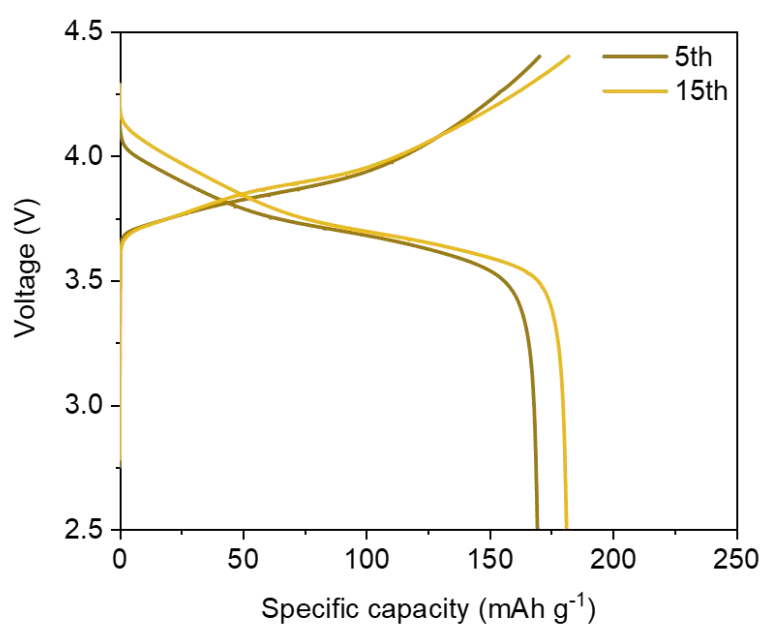


Figure S33. The charge/discharge voltage profiles of the Li (20 μm)|IWSWN-SPE|NCM622 pouch cell.

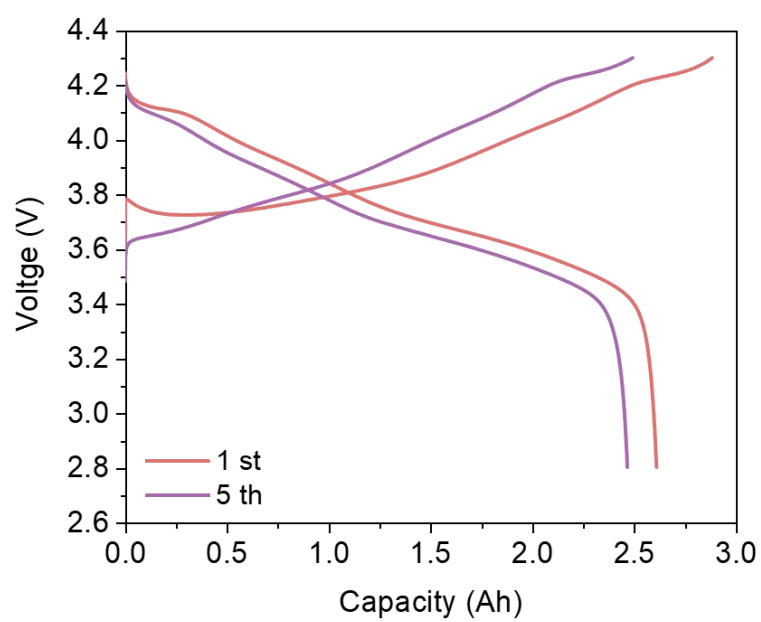


Figure S34. The charge/discharge voltage profiles of the solid-state 2.6-Ah Li|IWSWN-SPE|NCM811 pouch cell.

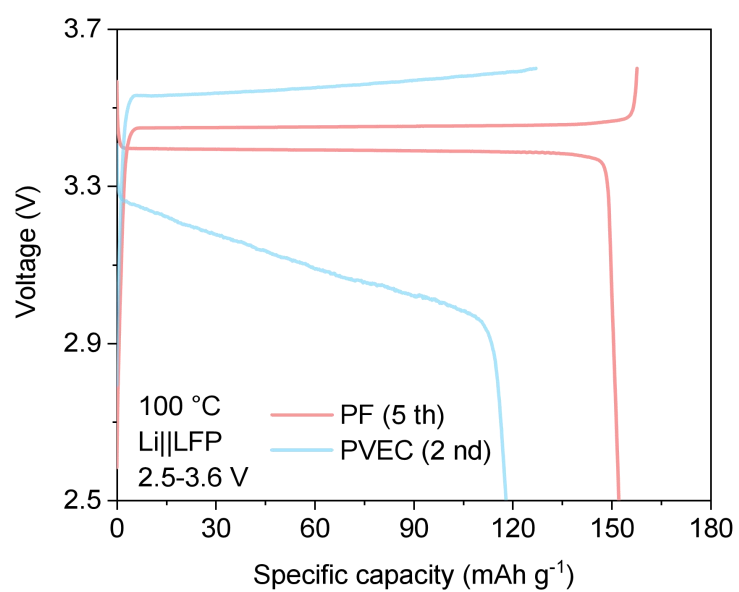


Figure S35. Comparison of the charge/discharge voltage profiles of Li||LFP cells with PVEC and IWSWN-SPE at 100 °C.



Figure S36. The nail penetration test of the 1.0-Ah Li|IWSWN-SPE|NCM811 pouch cell.

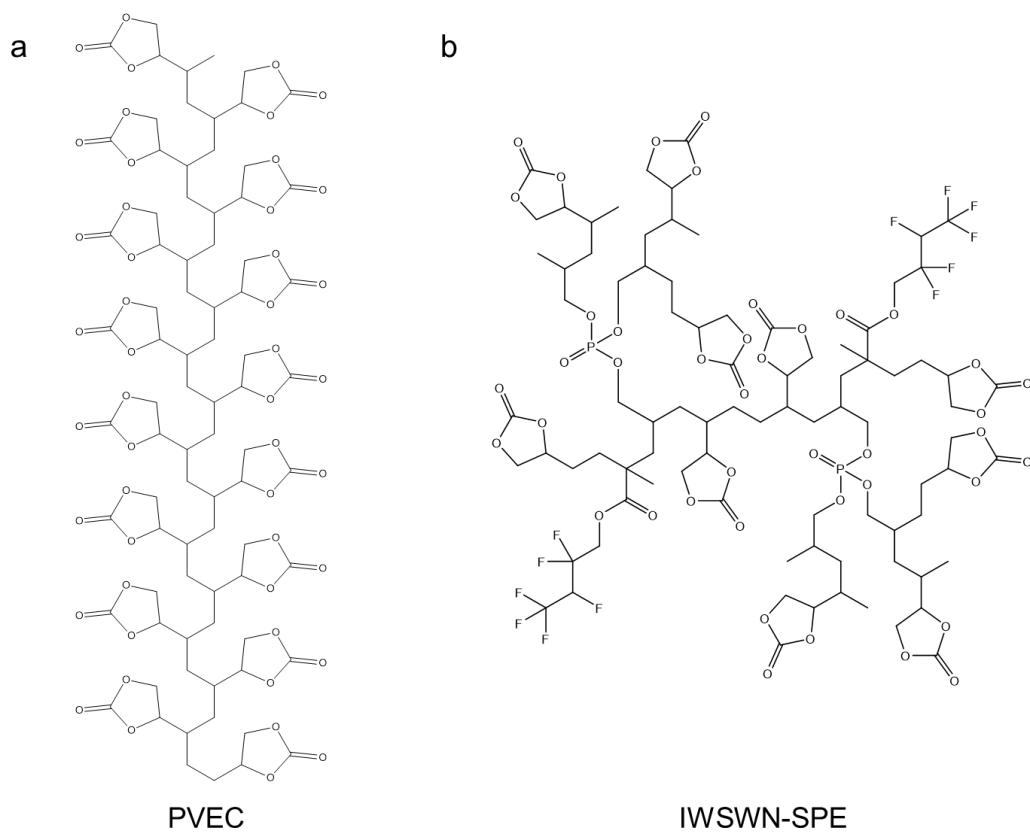


Figure S37. Schematic diagram of the molecular formulas of proposed PVEC (a) and IWSWN-SPE (b). In the PVEC system, the molar ratio of (VEC monomer : VEC unit in a single polymer chain : LiTFSI) is 12 : 8 : 1.5. In the IWSWN-SPE system, this ratio is 5 : 5 : 1.5.

Table S1. Li⁺ transference number comparison in various polymer-based electrolytes.

Literature	Electrolyte Type	Li ⁺ transference number
<i>Adv. Energy Mater.</i> 13 , 2202789 (2023).	SPE	0.3
<i>Nat. Commun.</i> 14 , 4617 (2023)	LPE	0.38
<i>Angew. Chem. Int. Ed. Engl.</i> 62 , e202306948 (2023)	SPE	0.39
<i>Adv. Sci.</i> 8 , 2003675 (2021)	SPE	0.4
<i>Nat. Commun.</i> 14 , 2301 (2023)	SPE	0.4
<i>Adv. Energy Mater.</i> 13 , 2203547 (2023)	SPE	0.42
<i>Adv. Energy Mater.</i> 12 , 2200967 (2022)	SPE	0.472
<i>Adv. Mater.</i> 33 , 2105329 (2021)	SPE	0.5
<i>Acs Energy Lett.</i> 7 , 2289-2296 (2022)	SPE	0.63
<i>Adv. Mater.</i> 35 , e2209402 (2023)	SPE	0.63
<i>Adv. Energy Mater.</i> 13 , 2203640 (2023)	SPE	0.65
<i>Angew. Chem. Int. Edit.</i> 62 , e202213606 (2023)	SPE	0.65
<i>Adv. Energy Mater.</i> 12 , 2102932 (2022)	QSPE	0.61
<i>Angew. Chem. Int. Edit.</i> 62 , e202310006 (2023)	QSPE	0.55
<i>Adv. Mater.</i> 35 , 2300998 (2023)	GPE	0.48
<i>Adv. Energy Mater.</i> 12 , 2200412 (2022)	QSPE	0.44
This work	SPE	0.70

Table S2. Details of comparisons in radar plots.

Literature	Electro-chemical window	σ /10⁻⁴ S cm⁻¹	Li⁺ transference number	Processability	Flame retardancy
<i>Adv. Energy Mater.</i> 12 , 2200967 (2022)	4.72	1.32	0.472	3	3
<i>Adv. Energy Mater.</i> 13 , 2203640 (2023)	5	5.5	0.65	1	3
<i>Nat. Commun.</i> 14 , 4617 (2023)	5.2	1.09	0.38	5	5
<i>Adv. Mater.</i> 35 , e2209402 (2023)	4.28	0.1	0.63	4	3
<i>Angew. Chem. Int. Ed. Engl.</i> 62 , e202306948 (2023)	4	1.2	0.35	4	3
This work	5.15	4.32	0.7	5	5

Table S3. Cycling performance comparison of different polymer-based LMBs.

Literature	Cut-off Voltage	Cathode cycles	Li Li cycles (cycle hour*mA cm⁻²)
<i>Adv. Energy Mater.</i> 12 , 2200967 (2022)	4.2	300	500*0.2
<i>Adv. Energy Mater.</i> 12 , 2102932 (2022)	4.3	200	2000*0.1
<i>Adv. Energy Mater.</i> 13 , 2203640 (2023)	4.3	150	1200*0.2
<i>Adv. Mater.</i> 35 , 2300998 (2023)	4.3	200	500*0.1
<i>Angew. Chem. Int. Ed. Engl.</i> 62 , e202213606 (2023)	4.2	400	480*0.3
<i>Nat. Commun.</i> 14 , 4617 (2023)	4.2	300	2250*0.1
<i>Adv. Mater.</i> 35 , e2209402 (2023)	4.3	100	4000*0.1
<i>Angew. Chem. Int. Ed. Engl.</i> 62 , e202306948 (2023)	3.8	420	600*0.1
<i>Angew. Chem. Int. Ed. Engl.</i> 62 , e202309613 (2023)	4.3	100	1100*0.1
<i>Adv. Funct. Mater.</i> 33 , 2209828 (2022)	4.3	150	1000*0.1
<i>Nat. Commun.</i> 13 , 4181 (2022)	4.3	100	3880*0.1
<i>Nano Energy</i> 98 , 107330 (2020)	4.4	100	800*0.5
<i>Adv. Funct. Mater.</i> 31 , 2101736 (2021)	3.7	60	1500*0.1
<i>Nano Energy</i> 73 , 104786 (2020)	4.3	200	600*0.1
<i>Adv. Sci.</i> 4 , 1600377 (2017)	4.3	150	600*0.1
This work	4.3	300	2600*0.2

Table S4. Positive electrode mass loading comparison in various polymer-based electrolytes.

Literature	Electrolyte Type	Mass loading of positive electrode (mg cm ⁻²)
<i>Nat. Commun.</i> 14 , 482 (2023)	SPE	1.5
<i>Nat. Commun.</i> 14 , 4617 (2023)	LPE	1.6
<i>Nano Energy</i> 98 , 107330 (2022)	SPE	2
<i>Adv. Mater.</i> 35 , e2209402 (2023)	SPE	2
<i>Angew. Chem. Int. Ed. Engl.</i> 62 , e202213606 (2023)	SPE	2
<i>Nat. Commun.</i> 13 , 4181 (2022)	SPE	4
<i>Adv. Sci.</i> 4 , 1600377 (2017)	SPE	5
<i>Adv. Funct. Mater.</i> 33 , 2209828 (2022)	SPE	5
<i>Angew. Chem. Int. Ed. Engl.</i> 62 , e202306948 (2023)	SPE	6
<i>Adv. Energy Mater.</i> 13 , 2203547 (2023)	SPE	7
<i>Nano Energy</i> 73 , 104786 (2020)	SPE	9.4
<i>Acs Energy Lett.</i> 7 , 2289-2296 (2022)	QSPE	0.98
<i>Adv. Energy Mater.</i> 12 , 2200967 (2022)	QSPE	7.6
<i>Adv. Mater.</i> 35 , 2300998 (2023)	GPE	2
<i>Angew. Chem. Int. Ed. Engl.</i> 62 , e202309613 (2023)	QSPE	2.5
<i>Adv. Energy Mater.</i> 13 , 2203640 (2023)	QSPE	4
This work	SPE	15.8

Table S5. Component details of the solid-state 2.6-Ah Li||NCM811 pouch cell.

Pouch cell overview		
NCM811	Specific capacity	205 mAh g ⁻¹
	Active material percentage	97 wt%
	Area weight of single layer	24.5 mg cm ⁻²
	Area capacity of single layer	5.0 mAh cm ⁻²
	Area	33 mm*62 mm
	Number of layers	13
Aluminium foil	Thickness	10 µm
Li metal anode	Thickness of single layer	70 µm
	Area	35 mm*64 mm
	Area weight	3.74 mg cm ⁻²
	Number of layers	14
Separator	Thickness	7*2 µm
	Area weight	0.73 mg cm ⁻²
Aluminium plastic film	Thickness	88 µm
	Surface density	15.4 mg cm ⁻²
Cell weight		28.2 g
Cell capacity		2.6 Ah
Specific Energy		349 Wh kg ⁻¹

Supplementary Note 1

The concept of puzzle-like molecular assembly

Regarding the concept of puzzle-like assembly, we use the analogy of assembling puzzles by interlocking puzzle pieces to illustrate how we design and synthesize the solid-state polymer electrolyte at the molecular level. Just as one can use various colored puzzles of similar shapes in daily life, these puzzles can be arranged randomly or arranged according to preference by the interlocking of the puzzle pieces.

Similarly, we employ this analogy to showcase how we utilize three monomers in free radical polymerization to synthesize the solid-state polymer electrolyte. In our work, we are not attempting to precisely control the self-assembly of the monomers through free radical polymerization. The monomers can polymerize with themselves or with other different monomers.

However, by uniformly mixing different monomers at the molecular level in the precursor solution, we can form a homogeneous SPE through free radical polymerization like assembling a puzzle, as illustrated in Figure S2 (Here, we use the interlocking between the puzzle pieces in a puzzle as a metaphor for how different polymer monomers interact and connect with each other through free radical polymerization). From a macroscopic perspective, the distribution of the three colored puzzles, representing the three monomers, appears uniform throughout the entire structure. However, upon closer examination, their arrangement is random, encompassing various possible combinations.

Supplementary Note 2

The ratio of HFBMA and TAP

Increasing fluoride content enhances the antioxidant capacity of the polymer electrolyte while potentially reducing ionic conductivity. The LSV and EIS results (Figures S9 and S10) demonstrate that increasing fluoride-based HFBMA molar ratio from 5% to 10% (compared to VEC) significantly boosts antioxidant capacity (low oxidation current), with a slight decrease in ionic conductivity from 0.495 to 0.437 mS cm⁻¹. However, further increasing fluoride-based HFBMA molar ratio to 15% (compared to VEC) shows a less pronounced enhancement in antioxidant capacity but a more significant decrease in conductivity to 0.296 mS cm⁻¹, a 32.3% reduction. Thus, the fluoride-based HFBMA molar ratio in the polymer electrolyte is optimized at 10% (compared to VEC) to achieve a balance between ion transport and antioxidant capacity. In experiments optimizing the fluorine-based HFBMA content, the molar ratio of phosphide-based TAP is 15% (compared to VEC) and the weight ratio of LiTFSI to the total monomer is 20 wt%.

Then, to evaluate the phosphide-based TAP content, combustion tests were conducted. As shown in Figure S11, a phosphide-based TAP molar ratio of 10% (compared to VEC) still allows the polymer electrolyte to burn while increasing the molar ratio to 15% (compared to VEC) imparts flame-retardant properties. Hence, a phosphide-based TAP molar ratio of 15% (compared to VEC) is deemed appropriate for achieving fire resistance. In experiments optimizing the phosphide-based TAP content, the molar ratio of fluorine-based HFBMA is 10% (compared to VEC) and the weight ratio of LiTFSI to the total monomer is 20 wt%.

In conclusion, the molar ratio of VEC to HFBMA to TAP is 1: 0.1: 0.15.

Supplementary Note 3

The Li⁺ and TFSI⁻ self-diffusion coefficients

From the three replicas, we extracted Li⁺ and TFSI⁻ self-diffusion coefficients (averaged over replicas with standard deviations) of two systems as follows:

PVEC:

$$D_{\text{Li}^+} = (3.73 \pm 0.47) \times 10^{-8} \text{ cm}^2\text{s}^{-1};$$

$$D_{\text{TFSI}^-} = (8.64 \pm 1.07) \times 10^{-8} \text{ cm}^2\text{s}^{-1}.$$

IWSWN-SPE:

$$D_{\text{Li}^+} = (3.51 \pm 0.34) \times 10^{-8} \text{ cm}^2\text{s}^{-1};$$

$$D_{\text{TFSI}^-} = (3.24 \pm 0.32) \times 10^{-8} \text{ cm}^2\text{s}^{-1}.$$