Deep eutectic solvent-based semi-interpenetrating polymer electrolyte for high-voltage stable lithium-metal batteries

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Experimental section

Electrochemical Characterization

Linear-sweep voltammetry was carried out using Li||SS symmetric cells from 2.5 to 5.2 V vs Li/Li^+ at a scan rate of 1 mV s^{-1}.

The ionic conductivity (σ) is calculated based on the equation:

$$\sigma = \frac{L}{RS} \tag{1}$$

where L (cm) is the thickness of the composites and separator, R (Ω) is the ohmic resistance and S (cm^2) is the contact area, respectively.

The t_{Li^+} was examined by combining AC impedance and direct-current (DC) polarization methods in a Li//Li symmetric cell, and the value can be calculated according to the Bruce-Vincent-Evans equation:[1, 2]

$$t_{Li^+} = \frac{Is(\Delta V - I_0 R_0)}{I_0(\Delta V - I_S R_S)} \tag{2}$$

where ΔV represents the applied DC polarization voltage with a value of 10 mV. I_0 and I_s are the direct current before and after polarization. R_0 and R_s represent the initial and final charge-transfer impedance of the polarization process.

The activation energies were calculated by fitting the conductivity data using the VFT equation:

$$\sigma = Aexp(-\frac{E_a}{k_b T}) \tag{3}$$

where E_a is the activation energy, A is the pre-exponential factor, k_b is the Boltzmann constant and T is the absolute temperature.

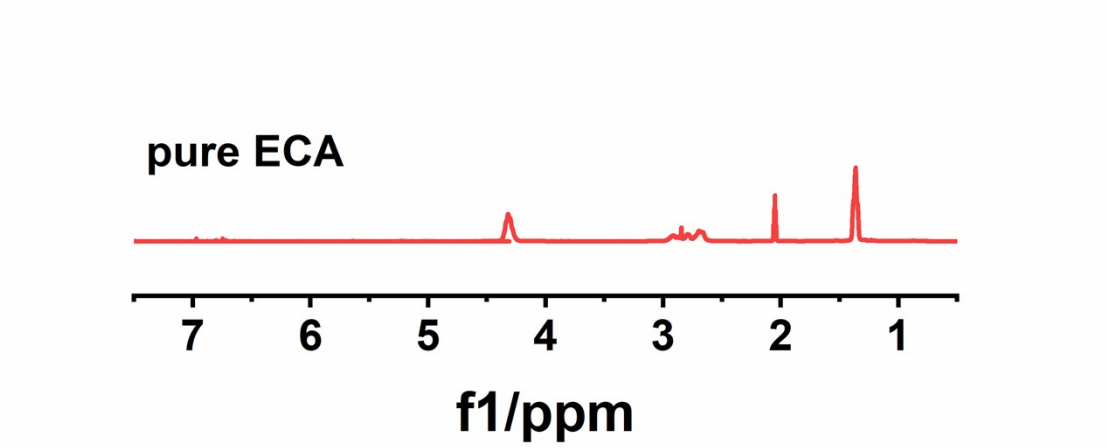

Figure S1. ^{1}H NMR spectra of pure ECA in deuterated acetone. When ECA was introduced in deuterated acetone, the C=C bonds disappeared, demonstrating the anionic polymerization caused by the trace amount of water.

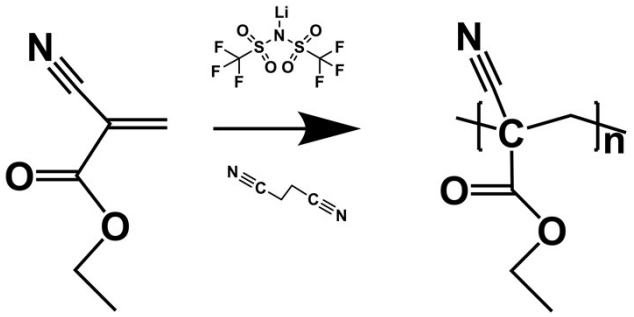

Figure S2. The polymerization process of ECA in DES.

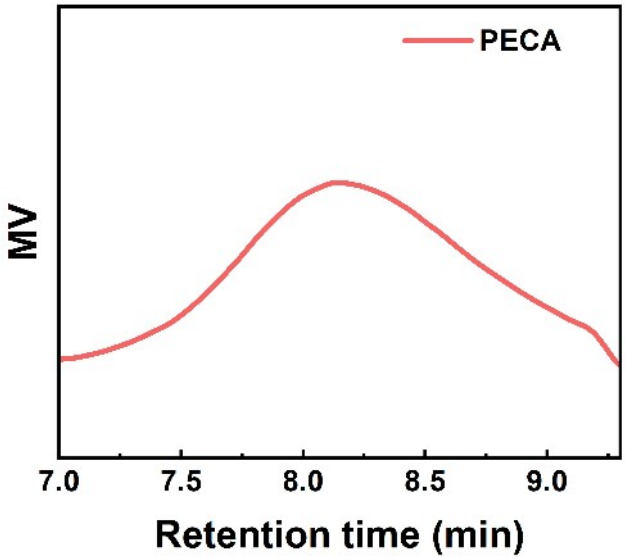

Figure S3. The comparative GPC curves of PECA obtained from DES-PECA.

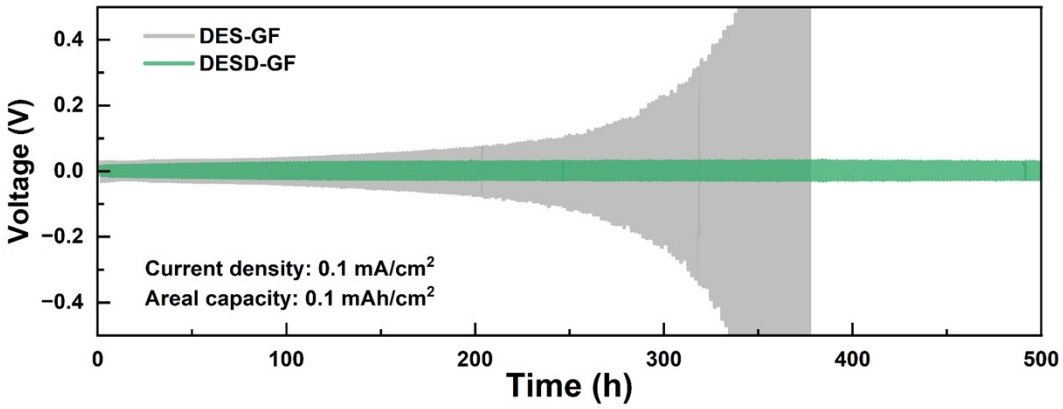

Figure S4. Cycling performance of Li/DES-GF/Li and Li/DESD-GF/Li symmetric cell at a current density of 0.1 mA cm^{-2} with a fixed capacity of 0.1 mAh cm^{-2}.

Figure S5. The digital image of the DESD electrolyte.

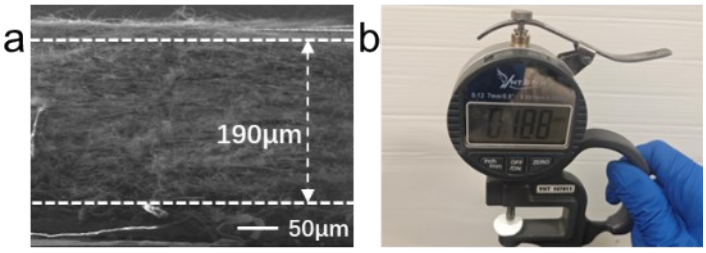

Figure S6. The thickness of glass fiber is measured by SEM (a) and micrometer (b).

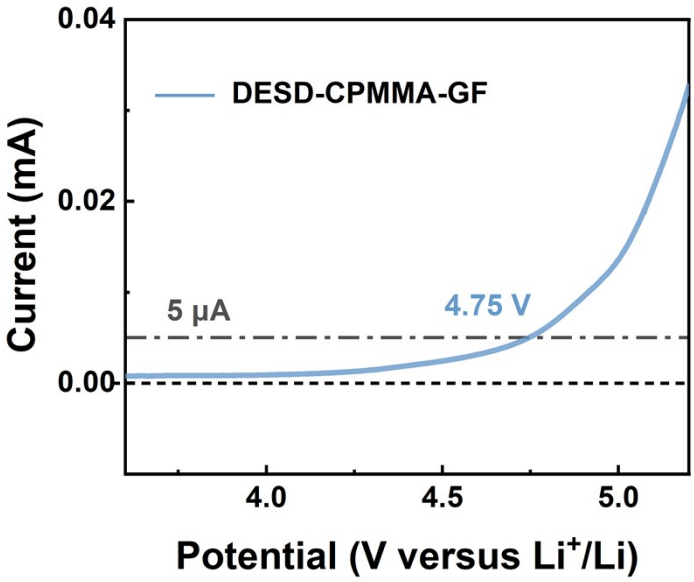

Figure S7. LSVs of the DESD-CPMMA-GF electrolyte at a scan rate of 0.1 mVs^{-1} from 3.6-5.2 V.

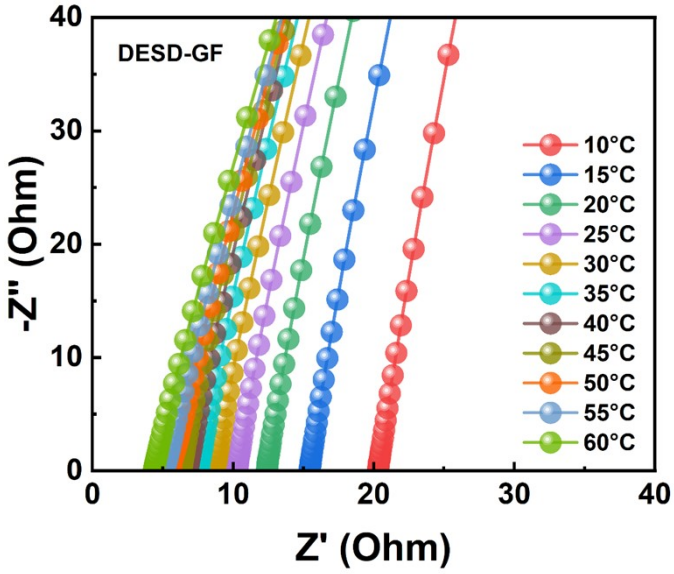

Figure S8. The EIS curves of DESD-GF electrolyte from 10 °C to 60 °C.

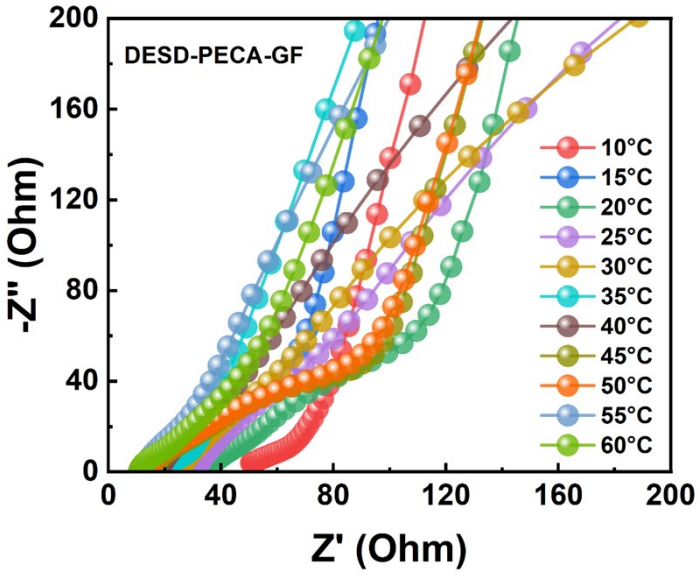

Figure S9. The EIS curves of the DESD-PECA-GF electrolyte recorded across the temperature range of 10 °C to 60 °C.

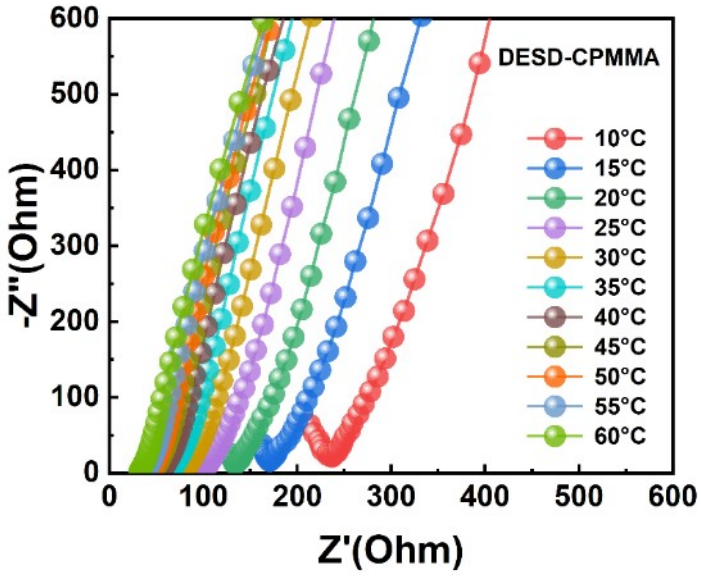

Figure S10. EIS curves of DESD-CPMMA-GF electrolyte from 10 °C to 60 °C.

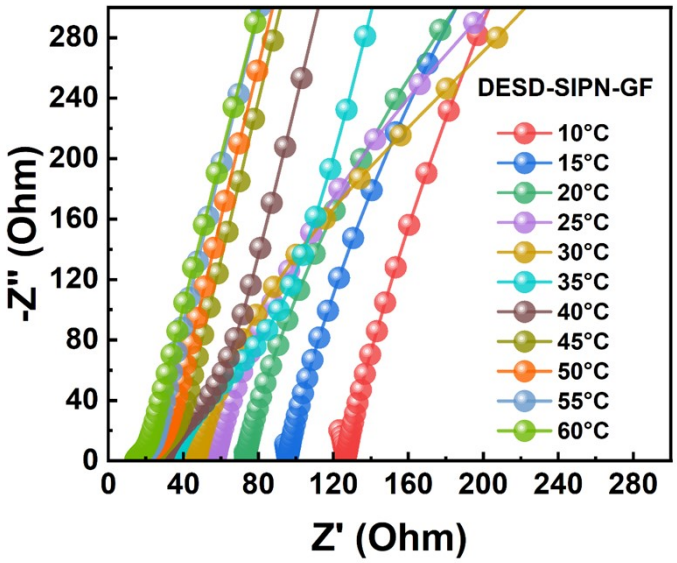

Figure S11. EIS curves of DESD-SIPN-GF electrolyte from 10 °C to 60 °C.

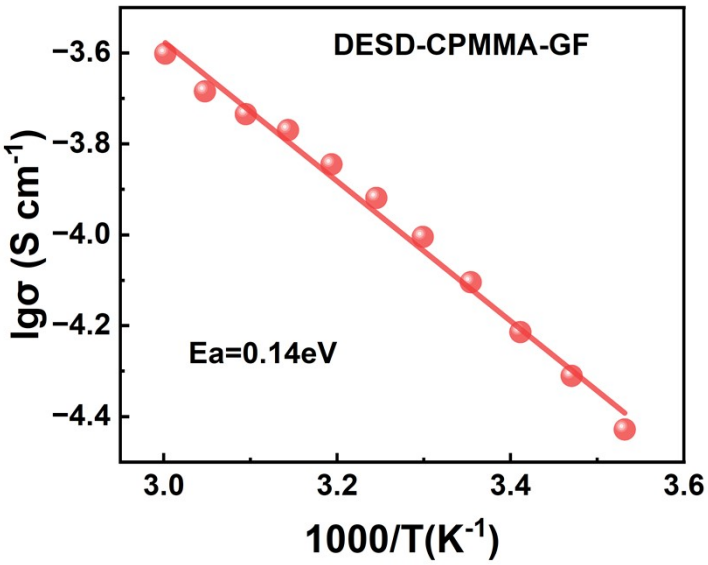

Figure S12. Ionic conductivities of the DESD-CPMMA-GF electrolyte as a function of temperature.

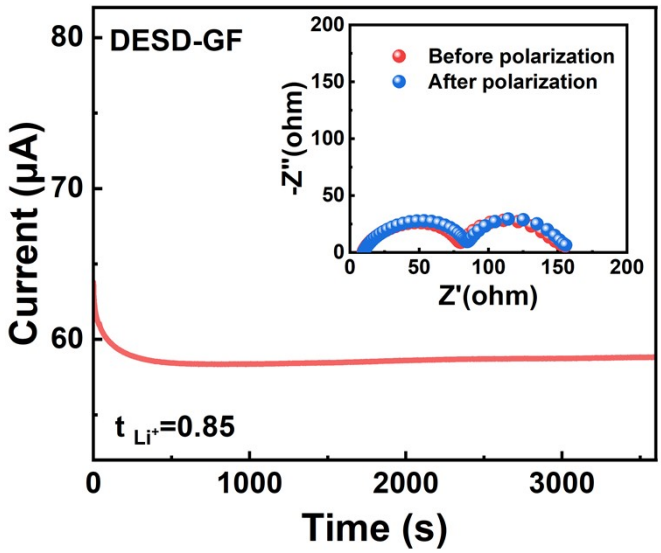

Figure S13. Chronoamperometry profile of Li/DESD-GF/Li symmetric cell under a polarization voltage of 10 mV. The inset is corresponding electrochemical impedance spectroscopy (EIS) spectra before and after polarization.

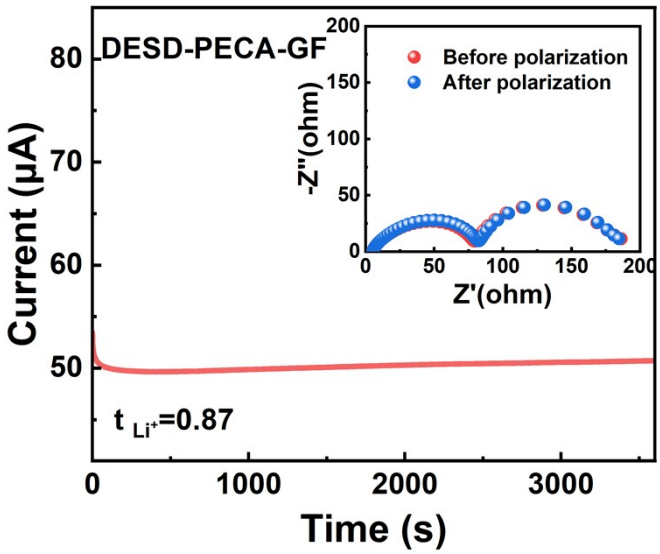

Figure S14. Chronoamperometry profile of Li/DESD-PECA-GF/Li symmetric cell under a polarization voltage of 10 mV. The inset is corresponding electrochemical impedance spectroscopy (EIS) spectra before and after polarization.

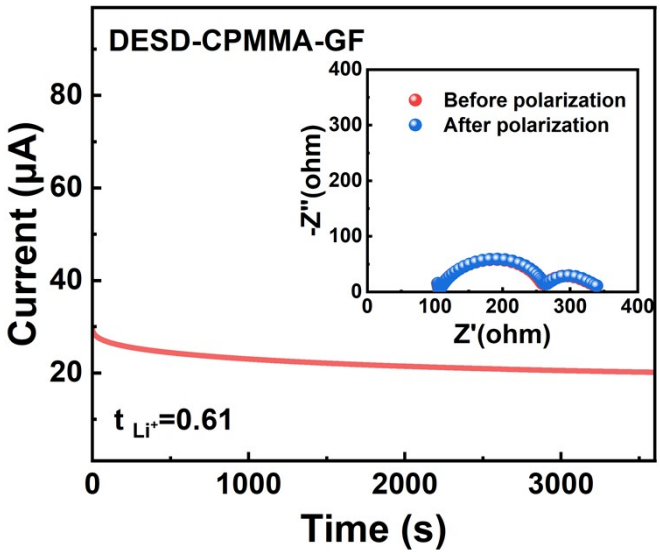

Figure S15. Chronoamperometry profile of Li/DESD-CPMMA-GF/Li symmetric cells under a polarization voltage of 10 mV. The inset is corresponding electrochemical impedance spectroscopy (EIS) spectra before and after polarization.

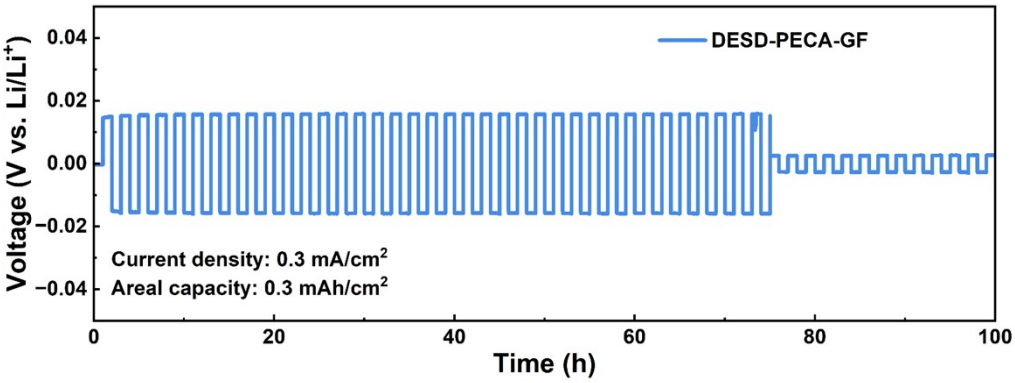

Figure S16. The enlarged Figure 3d of Li/DESD-PECA-GF/Li symmetric cell at 0.3 mA cm^{-2} with a fixed capacity of 0.3 mA h cm^{-2}.

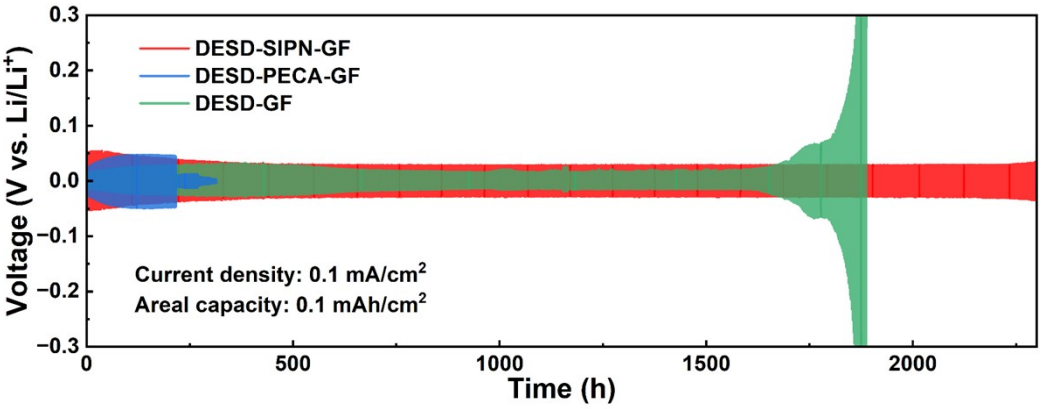

Figure S17. Cycling performance of symmetric cells at the current density of 0.1 mA cm^{-2} with capacity of 0.1 mAh cm^{-2}.

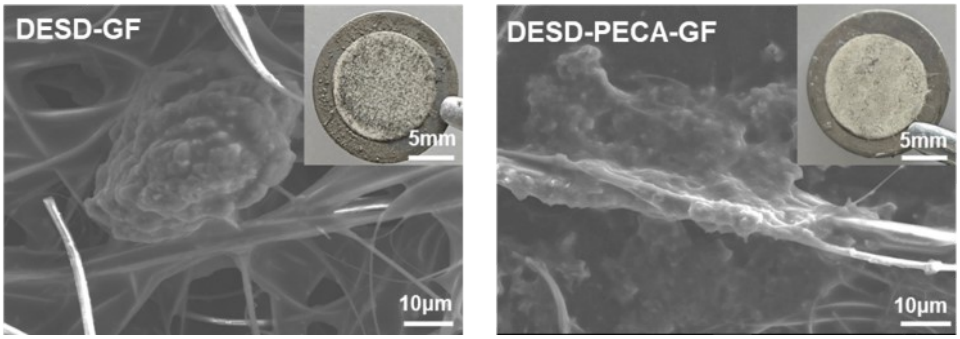

Figure S18. The SEM images of the morphologies of Li foils cycled in Li/DESD-GF/Li and Li/DESD-PECA-GF/Li symmetric cells after 200 h at 0.3 mA cm^{-2}. The inset is the photograph of the cycled Li foils.

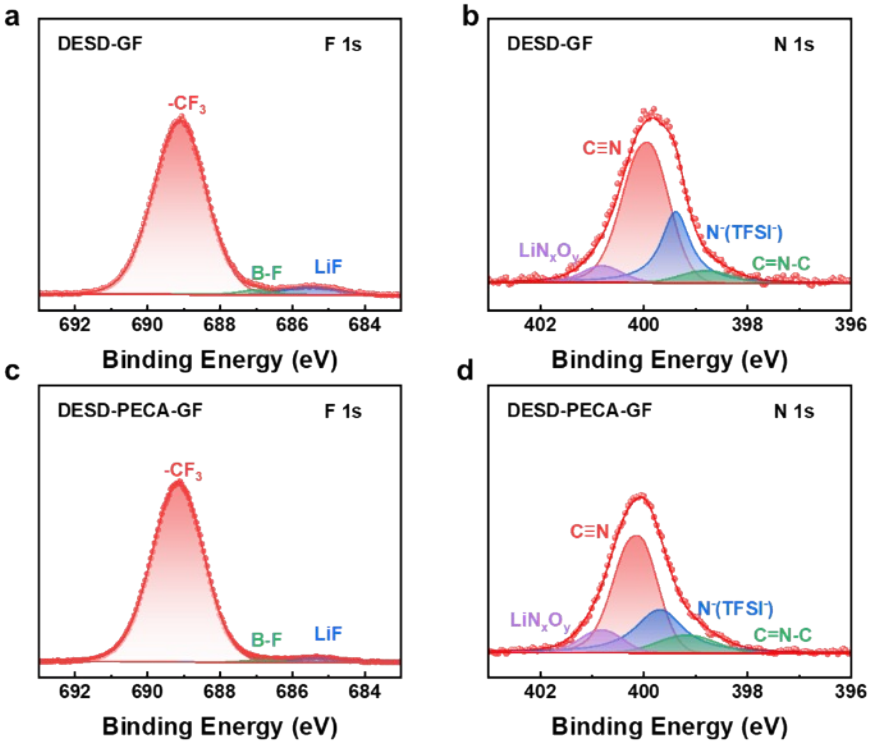

Figure S19. XPS spectra of Li/DESD-GF/Li and Li/DESD-PECA-GF/Li symmetric cells: F 1s spectra of (a)Li/DESD-GF/Li and (c) Li/DESD-PECA-GF/Li; N 1s spectra of (b) Li/DESD-GF/Li and (d) Li/DESD-PECA-GF/Li.

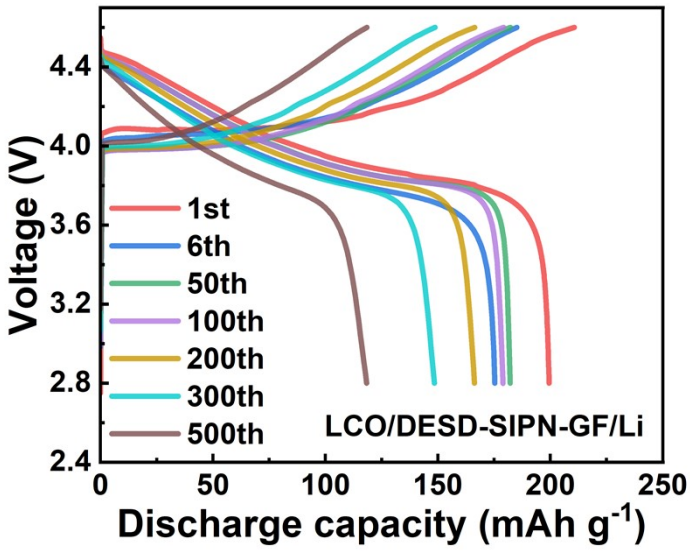

Figure S20. Charge-discharge voltage profiles of LCO/DESD-SIPN-GF/Li full cell at 1 C and 4.6 V.

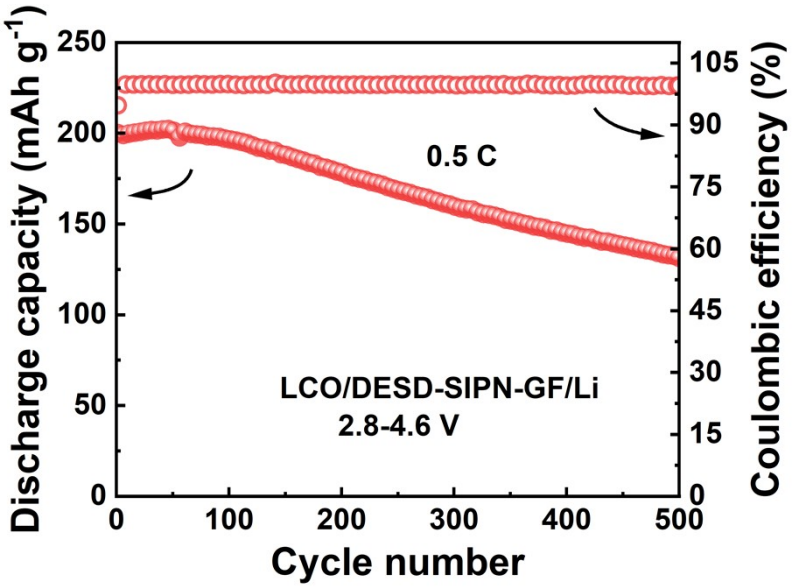

Figure S21. Electrochemical performance of LCO/DESD-SIPN-GF/Li full cell at a current density of 0.5 C and 4.6V.

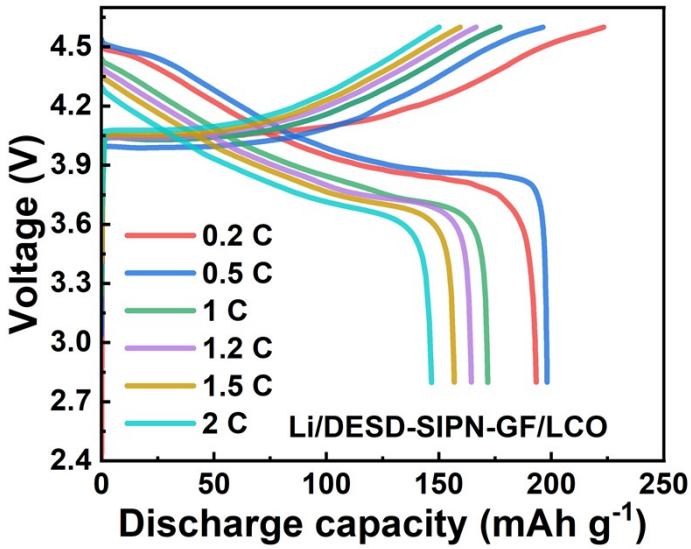

Figure S22. Galvanostatic charge/discharge voltage profiles of LCO/DESD-SIPN-GF/Li at different current density and 4.6 V.

Table S1. The GPC results of PECA.

Product	M_n	M_w	PDI
PECA	10905	21310	1.95

Table S2. The detailed values of the current, impedance and voltage for calculating the t_{Li+} of DESD-GF, DESD-PECA-GF, DESD-CPMMA-GF and DESD-SIPN-GF.

Electrolyte		I_0 (mA)	I_s (mA)	R_0 (Ω)	R_s(Ω)	ΔV (V)	t_{Li+}
DESD-GF	#1	0.06378	0.05883	76.78	75.78	10	0.85
	#2	0.05930	0.05670	83.46	77.65	10	0.86
DESD-PECA-GF	#1	0.05346	0.05073	109.9	108	10	0.87
	#2	0.06044	0.05821	86.46	82.29	10	0.88
DESD-CPMMA-GF	#1	0.02949	0.02017	91.45	92.13	10	0.61
	#2	0.02745	0.01963	99.18	96.22	10	0.64
DESD-SIPN-GF	#1	0.03789	0.03461	127.3	124.8	10	0.83
	#2	0.03840	0.03460	122	117	10	0.80

Table S3. The details of the polymer electrolyte from previous literatures cited in the Figure 5e**,** and the comparative electrochemical performance of those electrolytes with current work (DESD-SIPN-GF).

Electrolyte (Ref)	Separator	Rate (C)	Cycle number (cycles)	Voltage range (V)	Capacity retention
This work	Glass fiber	1C	500	2.8-4.3	79%
		1C	400	2.8-4.5	71%
		2C	600	2.8-4.7	60%
SPCE-LE [ref.49]	Cellulose membrane	0.3C	100	3.0-4.2	77.7%
PEO [ref.50]	PE separator	0.5C	300	2.8-4.3	10%
dmlSPE [ref.48]	Glass fiber	0.2C	400	2.8–4.3	67%
SPE [ref.48]	Glass fiber	0.2C	69	2.8–4.3	21%
QSPE2 [ref.47]	Glass fiber	0.2C	400	3–4.3	19%
PDDA-TFSI [ref.42] DFMA-co-MMA	Glass fiber	0.5C	300	2.7-4.3	71.9%
70PSA [ref.45]	PP separator	0.5C	200	2.8-4.5	71%
PVDF [ref.43]	PP separator	0.2C	100	2.5-4.5	51%
PI [ref.43]	PP separator	0.2C	100	2.5-4.5	54%
p-BA [ref.44]	Glass fiber	1C	200	3.0-4.7	40%
p-ICA [ref.44]	Glass fiber	1C	200	3.0-4.7	25%
LiFSI-EMC/FEC [ref.46]	PE separator	0.5C	300	3.0–4.7	67%

Notes and references

1. D. Zhang, Y. Liu, Z. Sun, Z. Liu, X. Xu, L. Xi, S. Ji, M. Zhu and J. Liu, Angew. Chem. Int. Ed., 2023, **62**, e202310006.
2. D. Zhang, Y. Liu, S. Yang, J. Zhu, H. Hong, S. Li, Q. Xiong, Z. Huang, S. Wang, J. Liu and C. Zhi, Adv. Mater. 2024, **36**, 2401549.