

## Supporting Information

### **Electrolyte design for inorganic-rich solid-electrolyte interfaces to enable low-temperature Li metal batteries**

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## Experimental section

*Electrolyte and cathode preparation:* All solvents were dried with 4 Å molecular sieves (Sigma-Aldrich) and metallic Li to remove the moisture before use. The electrolyte was prepared by dissolving 1.6 M lithium bis(fluorosulfonyl)imide (LiFSI) and 2 wt.% lithium nitrate (LiNO<sub>3</sub>) additives in the solvent mixture of tetrahydrofuran (THF) and 2-methyltetrahydrofuran (MTHF) (1:1 by volume) in an argon gas-filled glove box (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm). The commercial electrolyte of 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,3-dioxolane/1,2-dimethoxyethane (DOL/DME, 1:1 by volume) purchased from DoDo Chem was used for comparison. LiFePO<sub>4</sub> (LFP) and LiNi<sub>0.85</sub>Co<sub>0.05</sub>Al<sub>0.1</sub>O<sub>2</sub> (NCA) cathodes were prepared by slurry coating on Al foils, comprising 80 wt.% active materials, 10 wt.% Super P (as conductive carbon) and 10 wt.% polyvinylidene (as binder). The obtained cathodes were dried at 80 °C overnight in vacuum, and then punched into 1.13 cm<sup>2</sup> disks.

*Characterizations:* Cycled Li anodes were obtained by disassembling coin-cells and then washed with DME in the glovebox to remove the residual electrolyte. SEM (FEI, Nova NanoSEM 450) was used to study the morphologies and elemental distribution of the electrodes cycled with different electrolytes. XPS (Kratos, AXIS-ULTRA DLD-600W) investigations were carried out to analyze the composition of the SEI layer on the Li electrode after stripping/plating for 100 h in Li||Li symmetric cells.

*Battery assembly and electrochemical measurements:* CR2025 coin cells and heat-sealed pouch cells were assembled by using the polyethylene (PE) separator in the glove box. Electrochemical stability windows were measured by cyclic voltammetry (CV,

−0.5 V to 2.5 V) and linear sweep voltammetry (LSV, 1 V to 6 V) conducted with a Li||Pt cell, at a scanning rate of 1 mV s<sup>−1</sup> on an electrochemical workstation (Gamry, Interface-1000E). The transference number of Li-ion ( $t_{Li^+}$ ) was evaluated by combining measurements of the electrochemical impedance spectroscopy (EIS, in the frequency range of 1 Hz to 1 MHz) and chronoamperometry (with a polarization voltage of 10 mV) using Li||Li symmetric cells. Ionic conductivities were measured by EIS in the frequency range of 1 Hz to 5 MHz with a sealed electrolytic cell. Li||Li symmetric cells were fabricated for the Li stripping/plating tests at 30 °C and −30 °C. The galvanostatic cycling tests of Li||LFP cells or Li||NCA cells were conducted with the LAND testing systems (LANHE, CT2001A) at 30 °C and −30 °C.

Table S1. Physical properties of solvents. <sup>1-3</sup>

Solvent	Melting point $T_m$ (°C)	Viscosity $\eta$ (cP)	Dielectric constant $\epsilon$
THF (tetrahydrofuran)	-109	0.46	7.6
MTHF (2-methyltetrahydrofuran)	-137	0.46	6.2
DOL (1,3-dioxolane)	-95	0.60	6.7
DME (1,2-dimethoxyethane)	-58	0.45	5.5

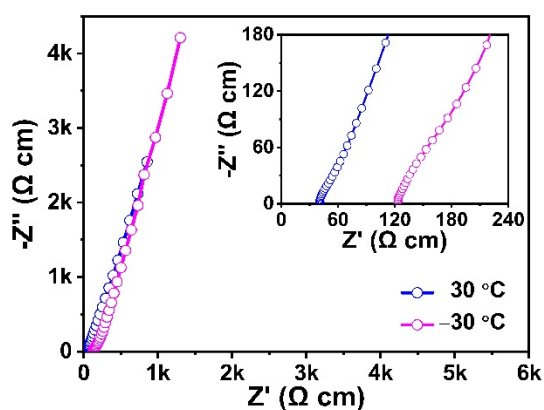


Fig. S1. EIS curves of the LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte at different temperatures.

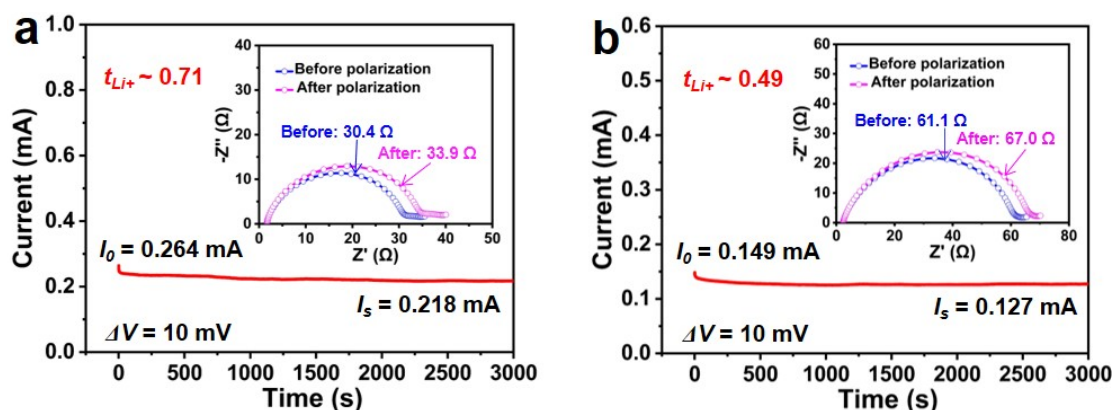


Fig. S2. Chronoamperometry profiles of electrolytes at 30 °C, insets are the Nyquist plots before and after chronoamperometry: (a) LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte, (b) LiTFSI DOL/DME electrolyte.

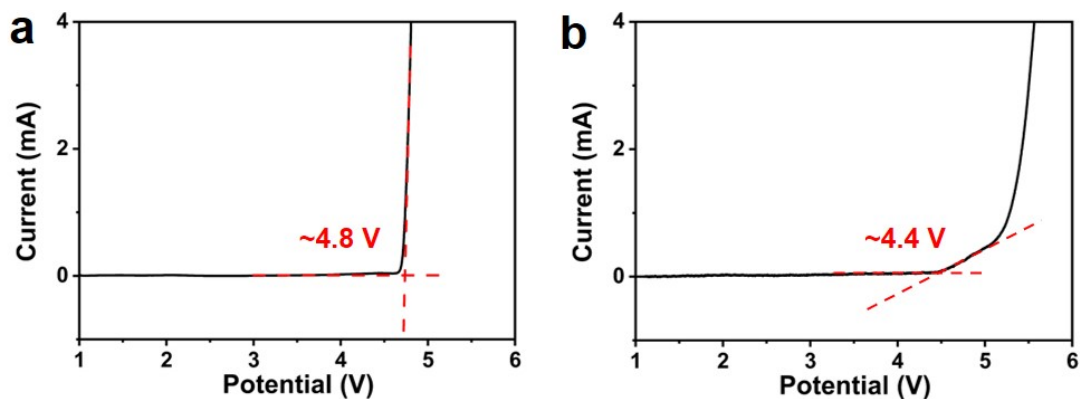


Fig. S3. LSV curves of different electrolytes: (a) LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte, (b) LiTFSI DOL/DME electrolyte.

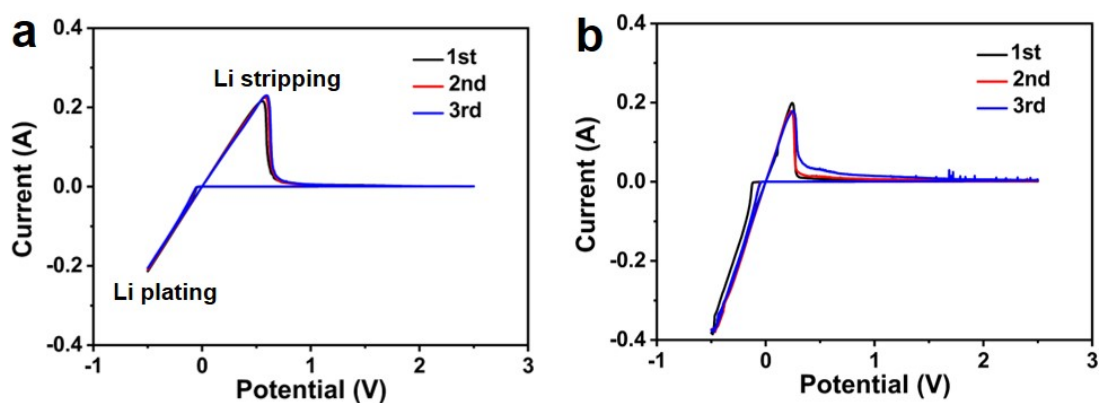


Fig. S4. CV curves of different electrolytes: (a) LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte, (b) LiTFSI DOL/DME electrolyte.

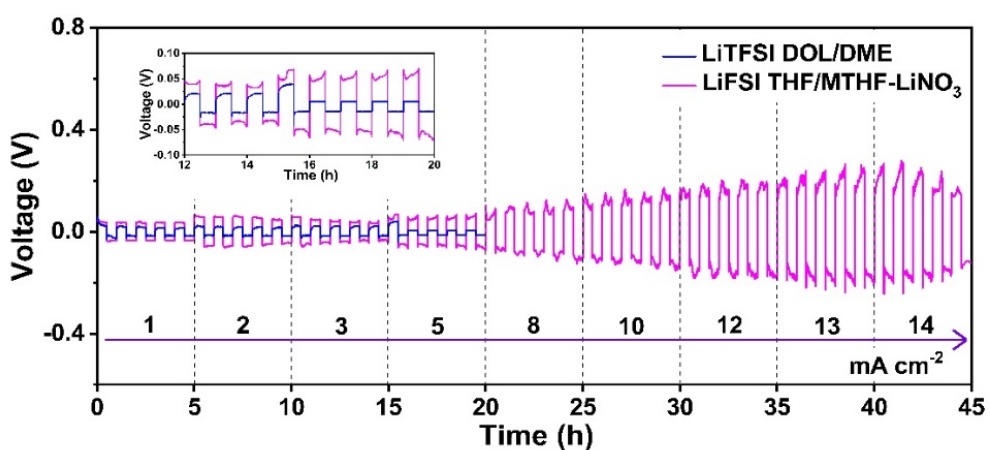


Fig. S5. Cycling stability demonstrated by Li plating/stripping in symmetric Li||Li cells using step-increasing current density from 1 to 14 mA cm<sup>-2</sup> at 30 °C. Inset: Detailed voltage curves between 12 to 20 h.

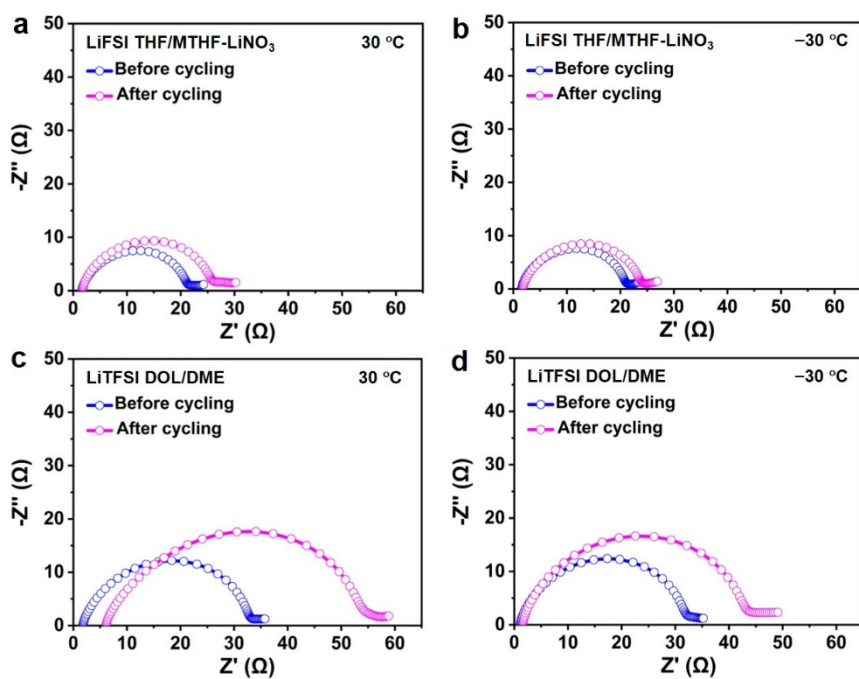


Fig. S6. EIS plots of Li||Li symmetric cells before and after cycling for 200 h with the LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte (a) at 30 °C and (b) -30 °C, and the LiTFSI DOL/DME electrolyte (c) at 30 °C and (d) -30 °C.

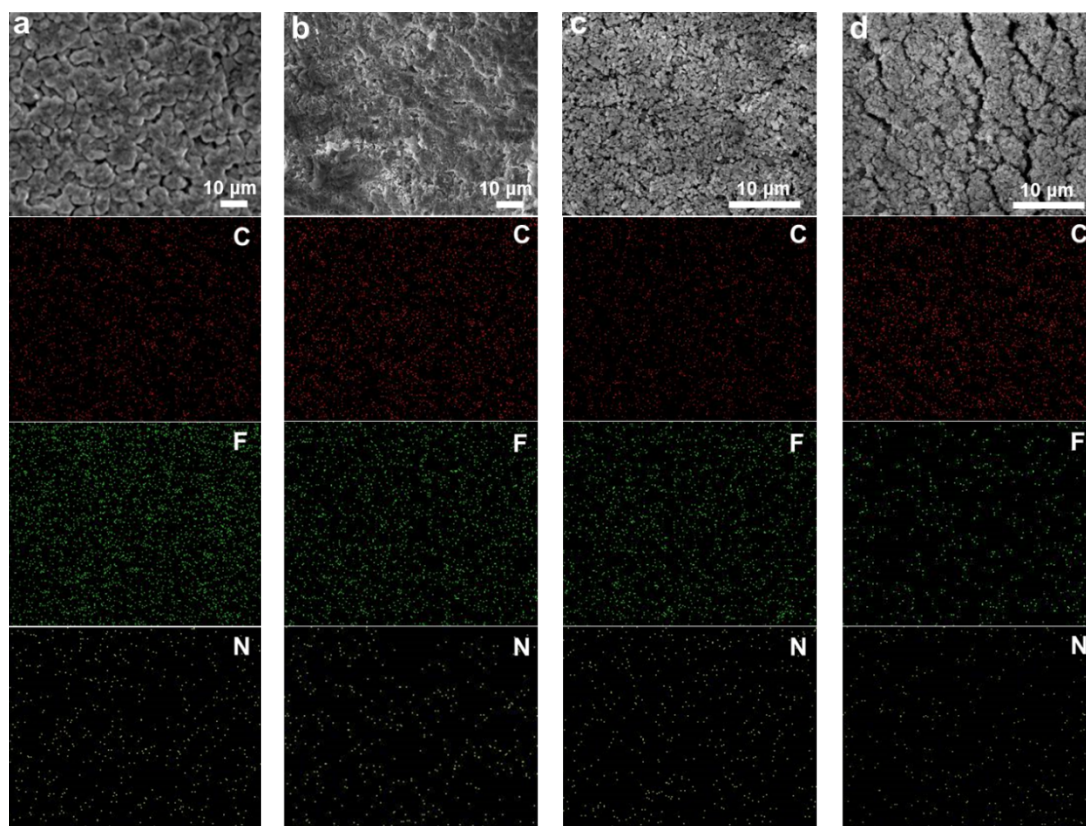


Fig. S7. SEM and EDS elemental mapping images of cycled Li metal anodes with LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte (a) at 30 °C and (c) -30 °C, and LiTFSI DOL/DME electrolyte (b) at 30 °C and (d) -30 °C.

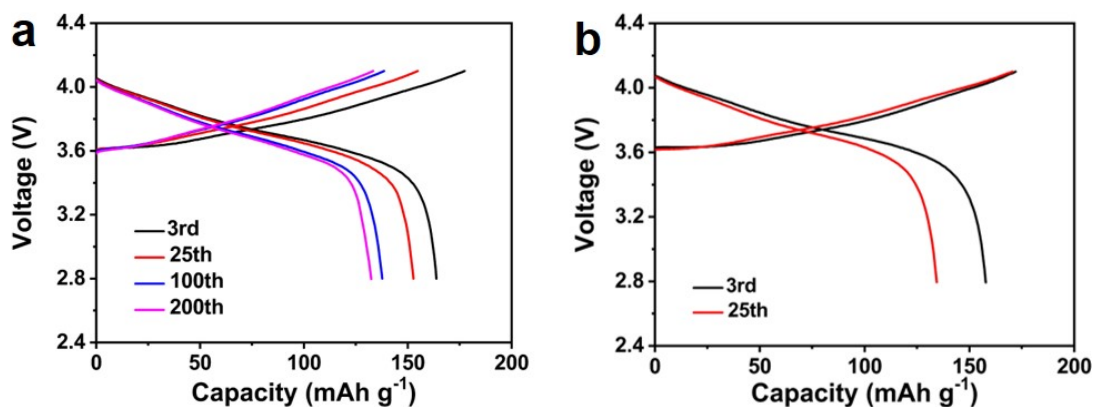


Fig. S8. Typical charge/discharge curves of Li||NCA cells with different electrolytes at 30 °C: (a) LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte, (b) LiTFSI DOL/DME electrolyte.

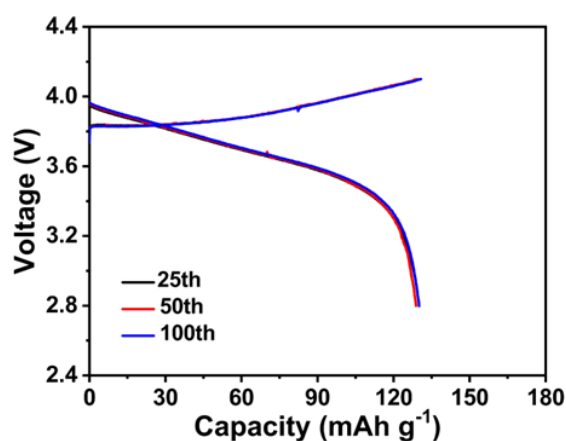


Fig. S9. Typical charge/discharge voltage profiles of the Li||NCA cell with the LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte at -30 °C.

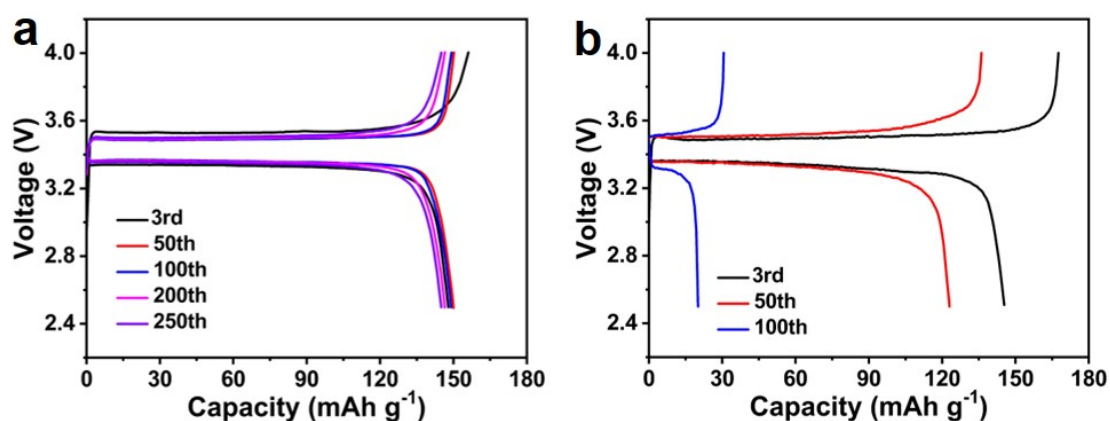


Fig. S10. Typical charge/discharge curves of Li||LFP full-cells with high-loading cathode of 11.5 mg cm<sup>-2</sup> and 50 μm Li at 30 °C: (a) LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte, (b) LiTFSI DOL/DME electrolyte.

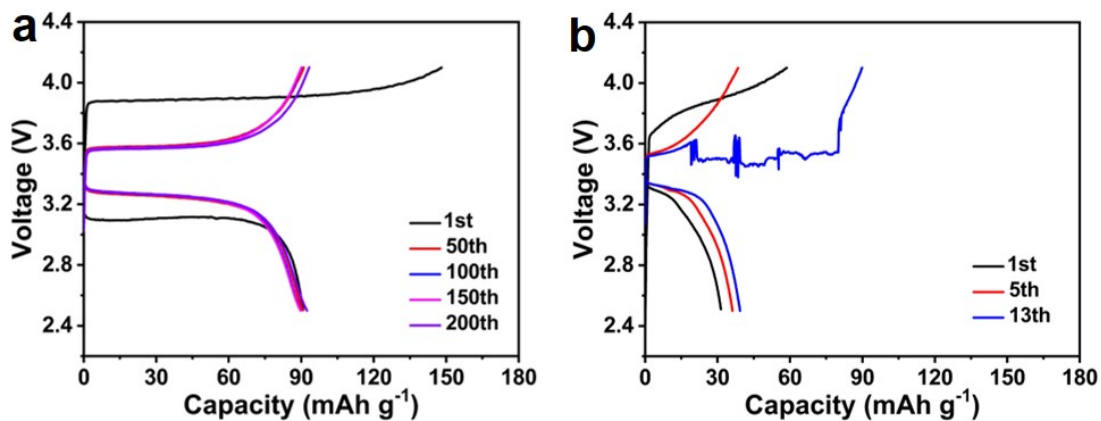


Fig. S11. Typical charge/discharge voltage profiles of Li||LFP cells with (a) LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte, and (b) LiTFSI DOL/DME electrolyte at -30 °C.

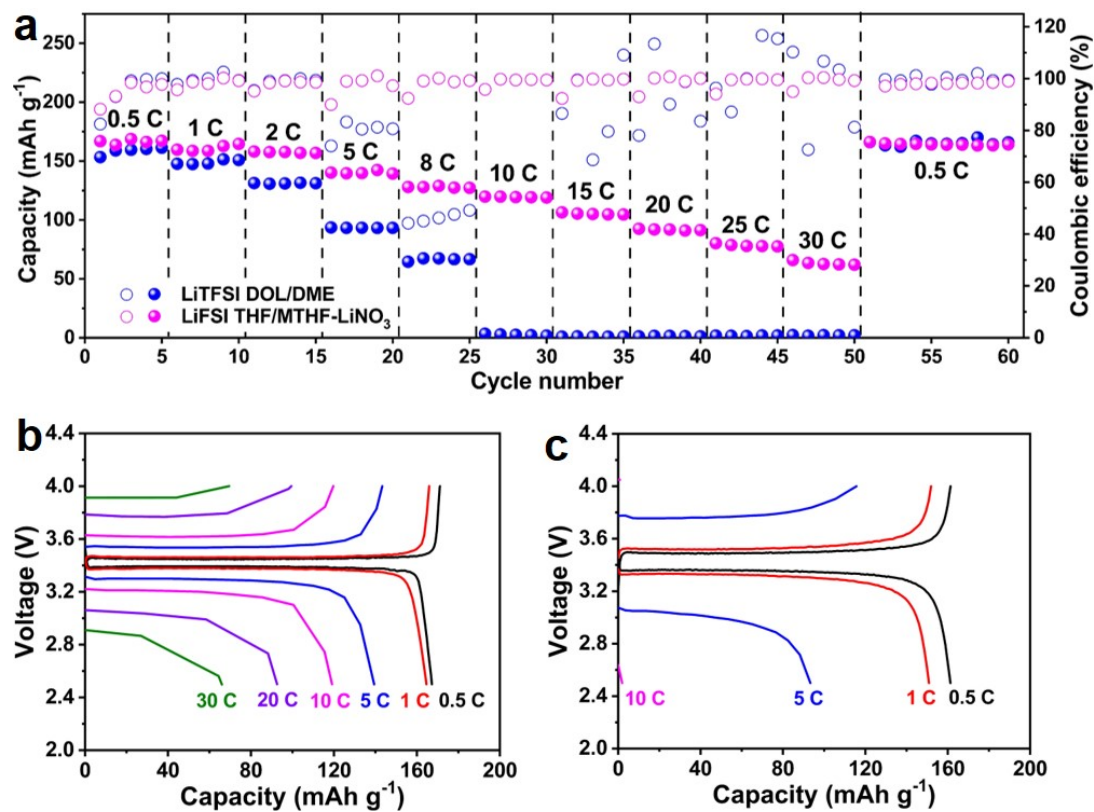


Fig. S12. (a) Rate performances of both electrolytes in Li||LFP cells at 30 °C. Corresponding charge-discharge profiles of the cells with (b) the LiFSI THF/MTHF-LiNO<sub>3</sub> electrolyte and (c) the LiTFSI DOL/DME electrolyte.



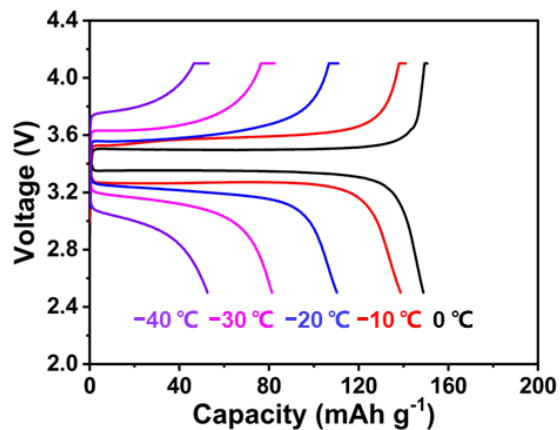


Fig. S13. Typical charge/discharge voltage profiles of the Li||LFP pouch cell with the designed electrolyte at different temperatures.

### References

1. Y. L. Liu and H. Li, *Energy Storage Science and Technology*, 2014, **3**, 262-282.
2. D. Luo, M. Li, Y. Zheng, Q. Ma, R. Gao, Z. Zhang, H. Dou, G. Wen, L. Shui, A. Yu, X. Wang and Z. Chen, *Adv. Sci.*, 2021, **8**, 2101051.
3. N. Zhang, T. Deng, S. Q. Zhang, C. H. Wang, L. X. Chen, C. S. Wang and X. L. Fan, *Adv. Mater.*, 2022, **34**, 2107899.