Electronic Supplementary Information

Polyeutectic-Based Stable and Effective Electrolytes for High-

Performance Energy Storage Systems

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Fig. S1 Photo of the NIPAM-NaTFSI (left) and NIPAM-KTFSI at molar ratio of 4:1.



Fig. S2 Photo of the NIPAM-LiTFSI at different molar ratios.



Fig. S3 Photo of NIPAM-LITFSI at 4:1 after two months standing.



Fig. S4 Molecular structures of different systems. The mole ratio is 1:1 for NIPAM and alkali TFSI salts.



Fig. S5 Molecular electrostatic potential energy surface of NaTFSI-NIPAM and KTFSI-NIPAM.

Length / Å	NIPAM	NIPAM-LiTFSI	NIPAM-NaTFSI	NIPAM-KTFSI
1 (C=C)	1.33486	1.33549	1.33563	1.33556
2	1.49740	1.48888	1.49062	1.49176
3	1.22884	1.25030	1.24764	1.24426
4		1.84710	2.19580	2.25266

Table S1 The bond length at different systems as shown in Fig. S4.



Fig. S6 TG curves of different electrolytes at from 30 to 700 °C at rate of 5 °C/min.



Fig. S7. SEM image of the surface of the Li-based PEE.



Fig. S8. Photo of the LiTFSI-EC EEs at the molar ratios of 1:2 (a) and 1:5 (b).



Fig. S9 Molecular structures of NIPAM-LiTFSI-EC samples at different molar ratios.
For 1:1:2 NIPAM-LiTFSI-EC sample, one EC molecule can interact with Li⁺, and another one EC interacts with NH bond of NIPAM. While for 2:1:2 and 3:1:2 NIPAM-LiTFSI-EC samples, both EC molecules are prone to interact with NH bond of NIPAM.

Samples	EC-Li /	EC-NH /	Mean interaction	Mean interaction
	kcal/mol	kcal/mol	energy with EC	energy without EC
1:1:2	-15.11	-6.07	-48.43	-88.31
2:1:2		-6.68	-39.62	-62.56
3:1:2		-11.92	-34.85	-48.45
3:3:2	-13.85	-6.02	-55.9	-61.27
Poly (3:3:2)	-13.48	-5.61	-69.87	-90.77

Table S2. The calculated interaction energy between EC and NIPAM-LiTFSI samples (1:1:2: the atom ratio of NIPAM, LiTFSI and EC in the calculated system).







Fig. S11 FT-IR spectra of the LiTFSI and Li-based PEE sample.



Fig. S12 Nyquist plot of the electrochemical impedance spectra of Li-based PEE before and after polarization. Inset: Current as response to potentiostatic polarization at 18 mV and 50 °C.



Fig. S13 Nyquist plot of the electrochemical impedance spectra of Na-based PEE before and after polarization. Inset: Current as response to potentiostatic polarization at 18 mV and 50 °C.



Fig. S14 Nyquist plot of the electrochemical impedance spectra of K-based PEE before and after polarization. Inset: Current as response to potentiostatic polarization at 18 mV and 50 °C.



Fig. S15 CV curves of the Li-based PEE and LiTFSI-NIPAM (molar ratio of 1:3) with the scan rate of 0.5 mV s^{-1} .



Fig. S16 LSV curves of the different PEE samples at the scan rate of 0.5 mV s⁻¹.



Fig. S17 The surface of the Na-based PEE after cycling.



Fig. S18 The electrochemical performance of Na-Na₃V₂(PO₄)₃ solid-state battery at 50 °C.

It is known that the high cycling rate will give rise to high overpotential and lower the utilization of cathode materials, which could be attributed to the high thickness of the Na-based PEE (300-350 μ m). The slight increase of capacity (from 67 to 70 mAh g⁻¹) along cycling may result from the increased material utilization along cycling.



Fig. S19 The electrochemical performance of K-SR solid-state battery at 50 °C.



Fig. S20 Permeability of Fc in DME at different times (a) the PEE hybrid separator; (b) Celgard.



Fig. S20 (a) UV-vis absorption spectra of Fc in DME solvent at different concentrations. (b-c) UV-vis absorption spectra of Fc with Celgard and PEE hybrid separator at different times, respectively.