A non-fluorinated, weakly solvating electrolyte for efficient sodium-

sulfurized polyacrylonitrile batteries

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1. Materials and Methods

1.1 Preparation of electrolytes

The solvent including 1,2-dimethoxyethane (DME, \geq 99.9%), ethylene carbonate (EC, \geq 99.95%), propylene carbonate (PC, \geq 99.99%), and the salts including sodium \geq 99.9%), sodium bis(trifluoromethanesulfonyl)imide bis(fluorosulfonyl)imide (NaFSI, (NaTFSI, >99.5%), hexafluorophosphate (NaPF₆, >99.8%), sodium sodium trifluoromethanesulfonate (NaOTF, \geq 99.8%), and sodium-difluoro(oxalato)borate (NaDFOB, ≥99.8%) were supplied from DodoChem. Tetrahydropyran (THP, 99.0%) and dibutyl ether (DBE, 99.3%) were purchased from Sigma Aldrich, and dimethoxy methane (DMM, 98%) was purchased from Aladdin. Before use, all solvents were dehydrated using 4 Å molecular sieves, and all salts were dried overnight at 60°C in an Ar-filled glove box. To prepare the electrolyte, the appropriate sodium salt was dissolved in the corresponding solution. For instance, 2 mmol NaFSI was dissolved in 1 mL of THP solvent to prepare the 2 M NaFSI THP electrolyte. Similarly, 2 M NaFSI DME and 2M NaFSI EC/PC (1:1, v/v) electrolytes were prepared by substituting the THP solvent with the DME or EC/PC mixtures, respectively.

1.2 Preparation of SPAN cathode

The SPAN slurry was prepared by blending SPAN (40% sulfur content) powder, Super P, carboxymethyl cellulose, and styrene butadiene rubber in a mass ratio of 8:1:0.5:0.5 with deionized water. This mixture was then uniformly coated on carbon-coated aluminum (Al/C) foil and dried in a vacuum oven at 80 °C overnight. Circular SPAN electrode discs ($\Phi 6$ mm) were subsequently punched out for further use. The typical mass loading of the SPAN electrode was approximately 3.5-4.0 mg cm⁻².

1.3 Characterizations

Field-emission scanning electron microscopy (FESEM, HITACH 8010) and transmission electron microscopy (TEM, FEI F20 S-TWIN) were used to characterize the morphology and structure of all samples. To analyze the morphology of Na deposits in the specific electrolyte, Na||Al/C coin cells were disassembled inside the glove box after plating 2 mAh cm⁻² of Na at 0.5 mA cm⁻². The samples were gently rinsed with DME and immediately transferred to the SEM for further analysis. XPS (Thermo Escalab 250xi) was employed to examine the

compositions of electrode-electrolyte interphases. Raman spectroscopy (Thermo Scientific DXR3xi) and NMR (JEOL 600 MHz) were conducted to investigate the solvation structures of different electrolytes. For NMR characterization, a coaxial insert containing 0.1 M NaPF₆ salt dissolved in deuterated dimethyl sulfoxide (DMSO-d6) was used as the reference. The mechanical properties and surface roughness of the cycled SPAN electrode and sodium metal deposited on Al/C foil were characterized by atomic force microscopy (AFM, SPM-9700HT, Japan). The water content in different electrolyte systems was measured using Karl-Fisher titration (Metrohm 831KF). The values for the 2 M NaFSI THP, 2 M NaFSI EC/PC, and 2 M NaFSI DME electrolytes are approximately 12.6 ppm, 4.7 ppm, and 15.1 ppm, respectively.

1.4 Cell assembly and electrochemical measurements

The electrochemical performance of the cells was evaluated using CR2025-type coin cells on a battery testing system (LANHE CT3001A, Wuhan, China). All coin cells were assembled in an argon-filled glove box (H₂O and $O_2 < 0.1$ ppm). The reversibility of Na plating/stripping in different electrolytes was analyzed by assembling Na||Al/C cells with Al/C foil as the working electrode and Na as the reference/counter electrode. Before measurements, the cells were cycled between 0 and 1 V vs. Na/Na⁺ at 50 μ A cm⁻² for five cycles to remove surface impurities. Subsequently, 1.0 mAh cm⁻² of Na was deposited onto the current collectors at various areal currents, followed by stripping to 1 V to remove the predeposited sodium. CE was defined as the ratio of the stripped capacity to the plated capacity. To investigate Na plating/stripping behavior under different current densities and capacities, symmetric NallNa cells were assembled. For NallSPAN coin cells, a glass fiber A membrane (Whatman) soaked with 50 µL of electrolyte was placed between the SPAN cathode (6 mm disk) and Na anode. The electrochemical stability of the electrolyte was examined using linear sweep voltammetry (LSV) within a voltage window of 2 to 6 V vs Na/Na⁺ at a scan rate of 1 mV s⁻¹. A stainlesssteel (SS) disc served as the working electrode, while Na was used as the counter/reference electrode. EIS measurements were conducted using a CHI760E electrochemical workstation over a frequency range of 0.1 Hz to 100 kHz. The ionic conductivity of the electrolyte was measured in a symmetric SS||SS cell configuration. The specific value was computed using the following formula:

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

where σ , *L*, *A*, and *R* represent the ionic conductivity, the separator thickness, the area of stainless steel, and the resistance, respectively. The values of t_{Na} of different electrolytes were measured by DC polarization for 5000 s combined with EIS tests of Na||Na symmetric cells using the following equation:

$$t_{Na^{+}} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}$$
(2)

where ΔV is the bias voltage (10 mV), I_0 and I_{ss} are the initial and steady-state currents, respectively. R_0 and R_{ss} are the interfacial resistance before and after polarization, respectively.

1.5 Theoretical simulations

Density functional theory (DFT) calculation was performed by Gaussian 16 software.^{S1, 2} Molecule structures were optimized using the B3LYP functional with the 6–311G++(d,p) basis set.^{S3} The geometries of the molecules and complexes were first optimized to obtain accurate structures. The binding energy (E_b) was calculated by the following formula:

$$E_{\rm b} = E_{\rm total} - E_{\rm A} - E_{\rm B} \tag{3}$$

where E_{total} , E_A , and E_B represent the energies of the A-B complex, the isolated molecule A, and isolated molecule B, respectively. Notably, we also calculated the E_b of Na⁺ and solvent molecules, taking into account solvation effects using the Polarizable Continuum Model (PCM) as well as the influence of counterion effects. The results are shown in Table S2.

Molecular dynamics (MD) simulations were performed using the GROMACS package.^{S4} The OPLS-AA force field,^{S5} previously designed for small ionic liquids, was employed in conjunction with restricted electrostatic potential (RESP) charges generated by Multiwfn.^{S6} It is worth noting that the use of the OPLS-AA force field represents a balance between computational feasibility and the ability to capture the dynamic behaviors of electrolytes. However, it should be acknowledged that this force field may not fully account for the polarization of atoms resulting from the local electrostatic environment. To simulate the DME system, 80 NaFSI molecules and 385 DME molecules were packed into a 43.5×43.5×43.5 Å³ simulation box using the Packmol software.^{S7} Similarly, the THP system was simulated by packing 80 NaFSI and 409 THP molecules into the same box dimensions. The temperature of

the system was controlled using a Nosé-Hoover thermostat with a time constant of 2 ps.^{S8}

Supporting Figures



Fig. S1. Densities of different electrolytes: THP, DME, and EC/PC refer to 2 M NaFSI in THP, 2 M NaFSI in DME, and 2 M NaFSI in EC/PC, respectively. CE, HCE, and LHCE refer to 1 M NaClO₄ in PC/FEC (95/5,v/v), 5 M NaFSI in DME, and DME:NaFSI:TTE = 1:1.2:1 (molar ratio), respectively.



Fig. S2. Binding energies of different solvents with Na⁺ without the consideration of solvation effect.



Fig. S3. Optical photographs. (a) Dissolution test of 1 M THP electrolytes with different sodium salts. (b) Optical images of 1 M NaFSI THP and 1 M NaTFSI THP at different temperatures.



Fig. S4. Optical photographs of THP electrolytes with NaFSI salt concentrationsrangingfrom1to6M.



Fig. S5. Nyquist plots of THP electrolytes with different concentrations.



Fig. S6. Dissolution of 0.2 mmol NaFSI in 1 mL of (a) cyclopentyl methyl ether (CPME), (b) dimethoxy methane, and (c) dibutyl ether

Fig. S7. The three most dominant solvation structures of DME electrolytes calculated from MD simulations.



Fig. S8. The four most dominant solvation structures of THP electrolytes calculated from MD simulations.



Fig. S9. Raman spectra of different electrolytes.



Fig. S10. Chronoamperometry curves of symmetric Na||Na cells using (a) DME and (b)THP electrolytes. The inset shows impedance spectra before and after polarization. (c)Electrochemicalimpedancespectroscopyplots.



Fig. S11. Sodium plating/stripping CEs in (a) THP, (b) DME, and (c) EC/PC electrolytes at 0.5 mA cm⁻² with a deposition capacity of 0.5 mAh cm⁻².

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Fig. S12. Voltage profiles of Na||Al/C cell using THP electrolyte at 0.5 mA cm $^{-2}$ for aplating/strippingcapacityof1mAhcm $^{-2}$.



Fig. S13. Voltage profiles of Na||Al/C cell using (a) EC/PC and (b) DME electrolyte at 1.0 mA cm⁻² for a plating/stripping capacity of 1 mAh cm⁻².



Fig. S14. Capacity-voltage curves of Na||Na symmetric cells with different electrolytes at 0.5 mA cm⁻² for a plating/stripping capacity of 0.5 mAh cm⁻² at (a) 10th and (b) 60th cycles.



Fig. S15. Optical photographs of Na deposits on Al/C foils.



Fig. S16. Optical photographs of a homemade device for in-situ UV-Vis measurement.



Fig. S17. Cyclic voltammetry curves of Na||SPAN cells with (a) DME and (b) THP electrolyte at a scan rate of 0.1 mV s⁻¹.



Fig. S18. Cyclic performance of Na||SPAN cells in DME electrolyte with pre-cycled SPAN electrode using the THP electrolyte, as compared to the cell without exchanging electrolyte.



Fig. S19. 3D AFM images of surface roughness of cycled SPAN cathodes in (a) DMEand(b)THPelectrolytes.



Fig. S20. Charge-discharge curves of Na||SPAN cells using (a) DME, (b) EC/PC, and

(c)	THP	electrolytes	at	various	С	rates.



Fig. S21. Cyclic performance of Na||SPAN cells employing DME and THP electrolytes at 2.0 C and room temperature.



Fig. S22. Cyclic performance of Na||SPAN cells employing DME and THP electrolytes at 0.1 C and -10 °C.

Solvent	Tetrahydropyran (THP)	1,2-Dimethoxyethane (DME)
Molecular structure		_0
Boiling point	88°C	84-86°C
Hydrogen bonding receptors	1	2
Molecular weight	86.1	90.1
LD50 (mouse mouth, mg kg ¹)	None	3460
Cancer	None	None

Table S1. Solvent properties

System	Without solvation effect	With solvation effect
Na ⁺ -DME	-2.12 eV	-0.67 eV
Na ⁺ -THP	-1.44 eV	-0.38 eV
Na ⁺ -FSI ⁻ -DME	-1.41 eV	-0.71 eV
Na ⁺ -FSI ⁻ -THP	-1.06 eV	-0.57 eV

Table S2. Comparison of binding energies between Na⁺ and DME/THP solvent with and without the consideration of solvation and counterion effects.

Elements (Atomic ratio) Electrolytes	Na	С	F	N	0	S
THP	39.10%	27.41%	0.66%	0.44%	31.74%	0.67%
DME	34.09%	30.95%	0.54%	0.88%	32.50%	1.04%

Table S3. Elements of different SEIs formed in THP and DME electrolytes based on XPS characterization.

Electrolytes	Current density (A g _s ⁻¹)	Cycle numb ers	Capacity (mAh g _s ⁻¹)	Capacity retention (%)	Cathode materials	Mass loading	Electrolyte amount $(\mu L mg_s^{-1})$	Na plating/stripping CEs	Ref.
2 M NaFSI THP	2.5	500	825	90	SPAN	~3.5-4.0 mg _{SPAN} cm ⁻²	~30-35	99.1% at 1 mA cm ⁻² /1 mAh cm ⁻² over 1000 cycles	This work
(DME:NaFSI: TTE = 1:1.2:1 molar ratio)	0.2	300	675	73	KB/S	$2.0 \text{ mg}_{\text{S}}$ cm ⁻²	~15	/	S9
2 M NaFSI DME/toluene (5:3 v/v)	2	200	750	85	SPAN	\sim 2-2.5 mg _{SPAN} cm ⁻²	~40	1	S10
1 M NaClO4- TEGDME with 10% FEC	0.2	200	587	55	SPAN	~2-2.5 mg _{SPAN} cm ⁻²	/	/	S11
2 M NaOTF/0.4M DTD/0.08 M Bi(OTf) ₃ -DME	0.75	150	1188	79	SPAN	$\begin{array}{c} 4.0\\ mg_{SPAN}\\ cm^{-2} \end{array}$	~30	99.1% at 0.5 mA cm ⁻² /0.5 mAh cm ⁻² over 150 cycles	S12
2 M NaFSI TMP/FEC (7:3 v/v),	2.5	300	788	88	SPAN	$\sim 1.2-1.5$ mg _S cm ⁻²	~100	/	S13
1M NaTFSI TEP/FEC- Sn(OTf) ₂	0.5	100	906	76	S@C	1	/	97.2% using modified Aurbach's protocol	S14
2 M NaFSI in MeTHF/TTE (3:2 v/v)	0.16	200	815	88	KB/S	1.8 mg _s cm ⁻²	18	99.4% at 1 mA cm ⁻² /1 mAh cm ⁻² using modified Aurbach's protocol	S15

Table S4. Comparison of RT-Na/S battery performance with different electrolytes.

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