

Supplementary Information

Directing Selective Solvent Presentations at Electrochemical Interfaces to Enable Initially Anode-Free Sodium Metal Batteries

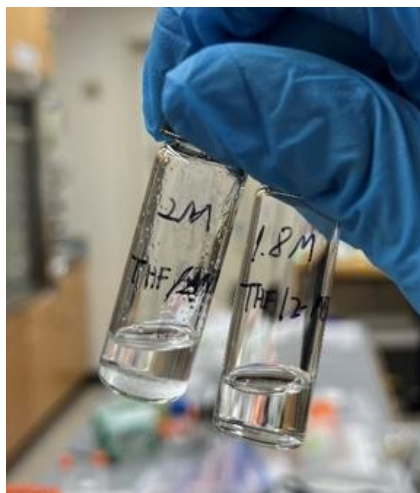
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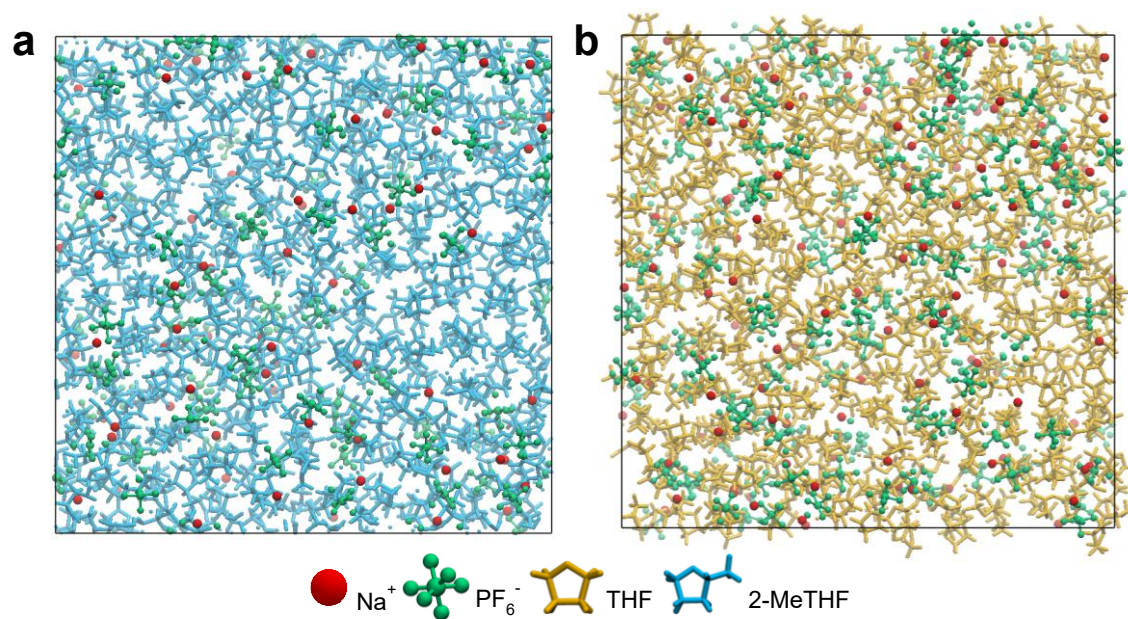
Supplementary Fig. 1 | The optical photo of the 2.0M NaPF₆ in THF/2-MeTHF and 1.8M NaPF₆ in THF/2-MeTHF, respectively.

Supplementary Note 1:

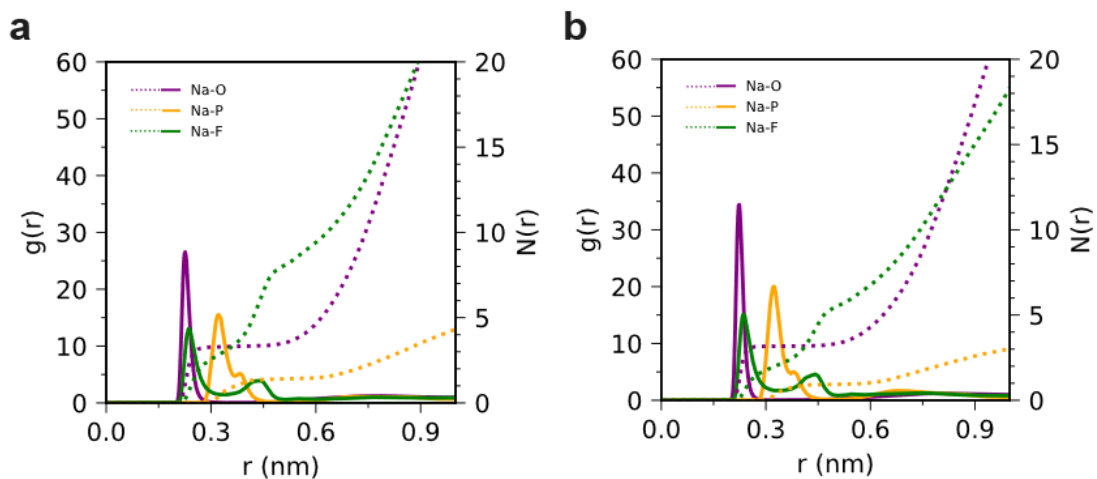
According to our ICP result, the saturation points for THF and 2-MeTHF are 2.2 mol/L and 1.3 mol/L, respectively. The solubility of a blended system can be estimated within the range determined by the individual solvents, as shown in equation (S1),^{S1}

$$\ln X_m = f_1 \ln X_1 + f_2 \ln X_2, \quad (\text{S1})$$

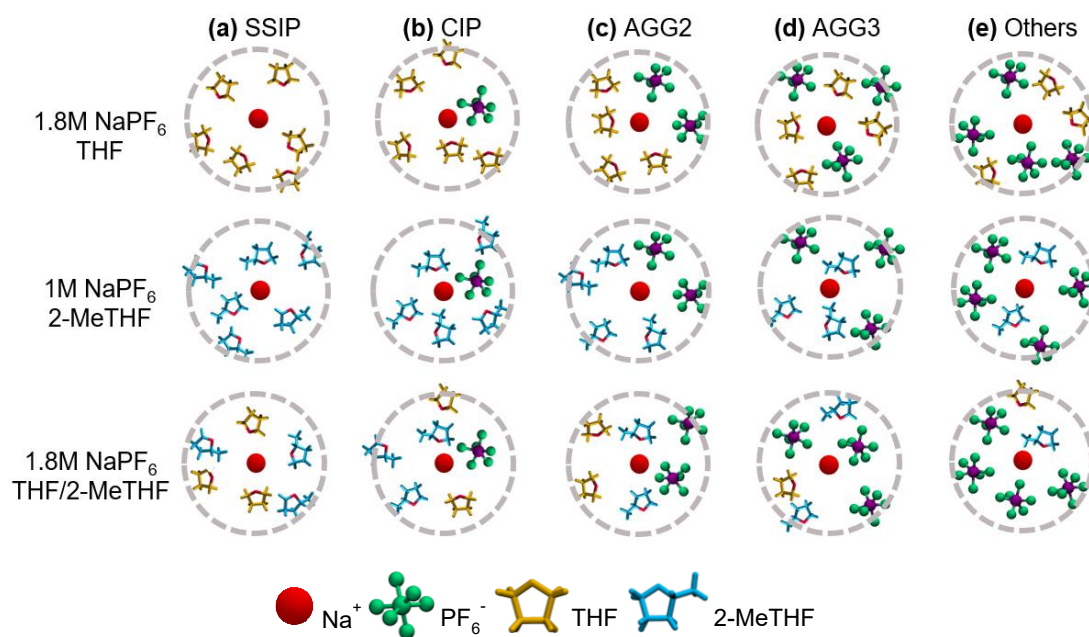
where X_m represents the salt solubility of the binary mixture, f_1 and f_2 are the solvent volume fractions of solvents 1 and 2 in the solvent mixture, X_1 and X_2 represent the solubilities of salt in solvents 1 and 2, respectively. Based on the calculation, the estimated solubility of NaPF₆ in THF/2-MeTHF is around 1.69 M. Our experiment found that 1.8M NaPF₆ can be dissolved in THF/2-MeTHF and is stable at room temperature, while 2M NaPF₆ cannot be fully dissolved (Supplementary Fig. 1). To avoid the influence of salt concentration, we choose the same concentration for the THF-based electrolyte despite its higher solubility. Meanwhile, we found that 1.3 M NaPF₆ in 2-MeTHF is unstable at room temperature, so we chose 1.0 M as its concentration, which is also the common salt concentration in electrolytes.



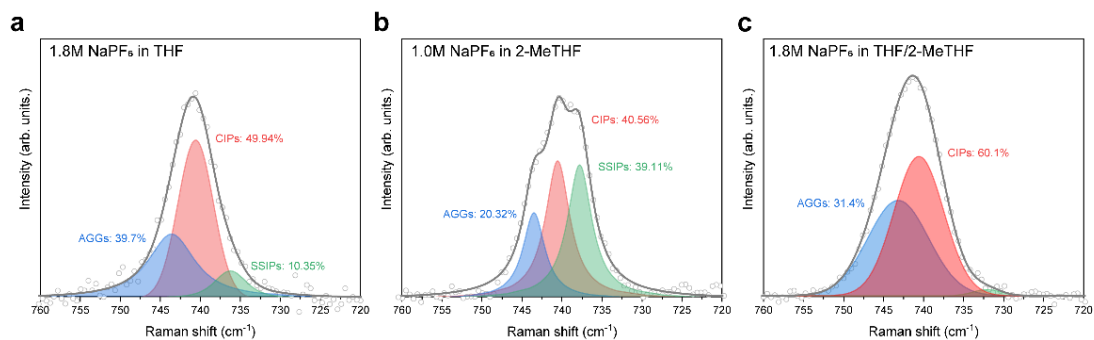
Supplementary Fig. 2 | Snapshots of the MD simulation systems for: a. 1.8M NaPF₆ THF and b. 1.0M NaPF₆ 2-MeTHF.



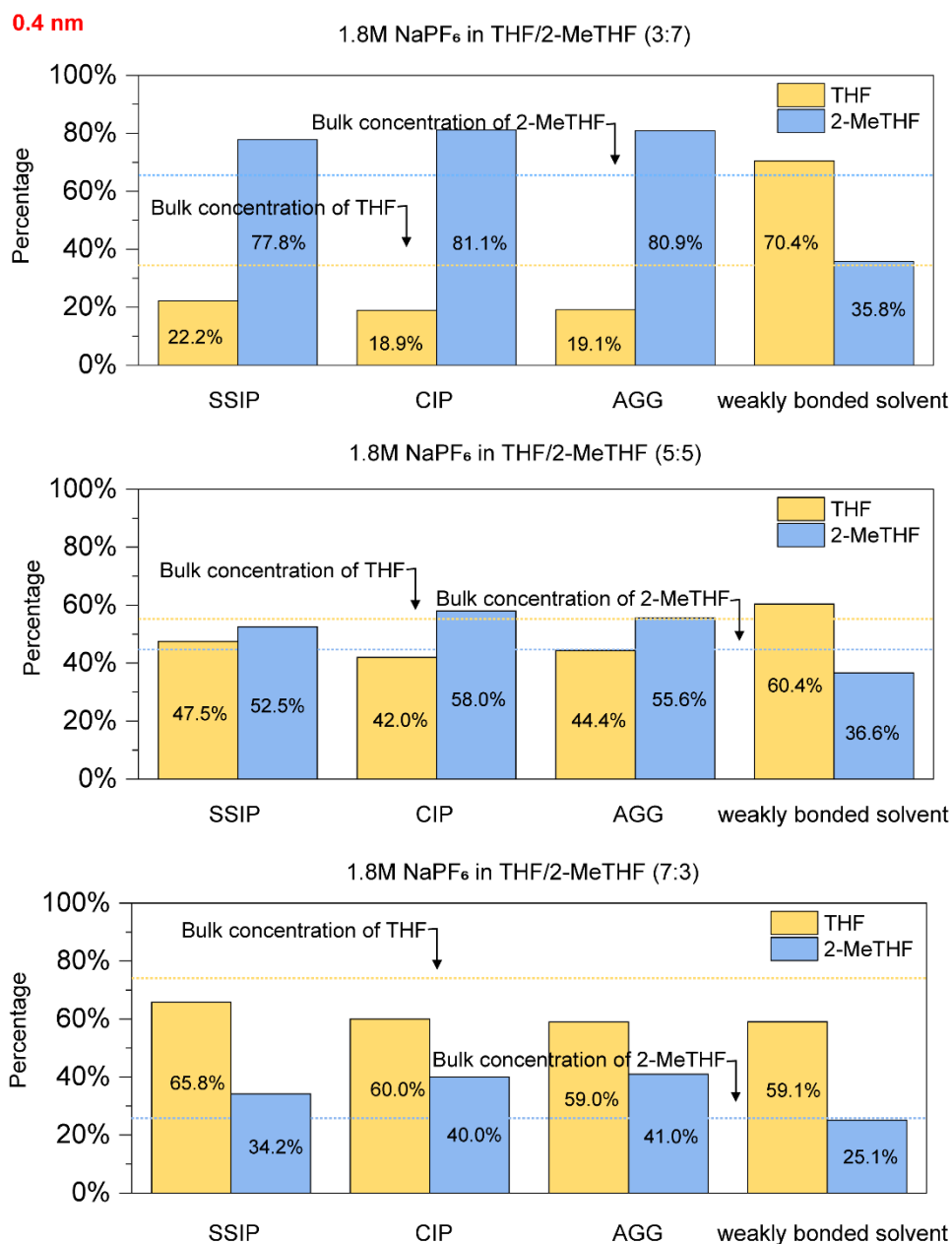
Supplementary Fig. 3 | Radial distribution functions (RDFs) from MD simulations across the following systems: a. 1.8M NaPF₆ THF and b. 1M NaPF₆ 2-MeTHF. Solid lines represent $g(r)$, while dotted lines correspond to $N(r)$.



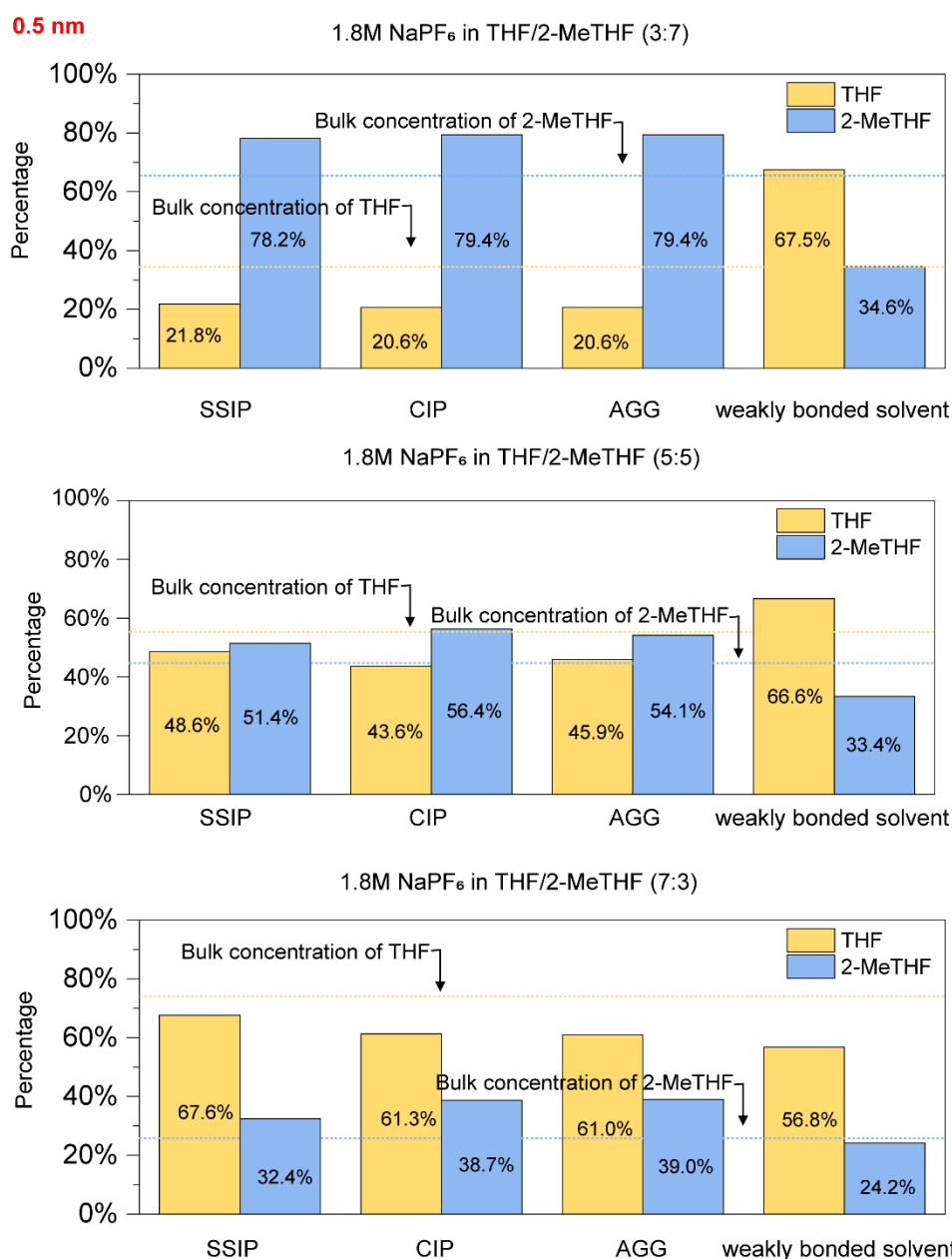
Supplementary Fig. 4 | Schematic representations of solvation shell structures (radius = 0.5 nm) for the following contact types: a. Solvent-Separated Ion Pair (SSIP, $P = 0$), b. Contact Ion Pair (CIP, $P = 1$), c. AGG ($P = 2$), d. AGG ($P = 3$), and e. AGG ($P \geq 4$). These diagrams are conceptual and not derived from MD simulations.



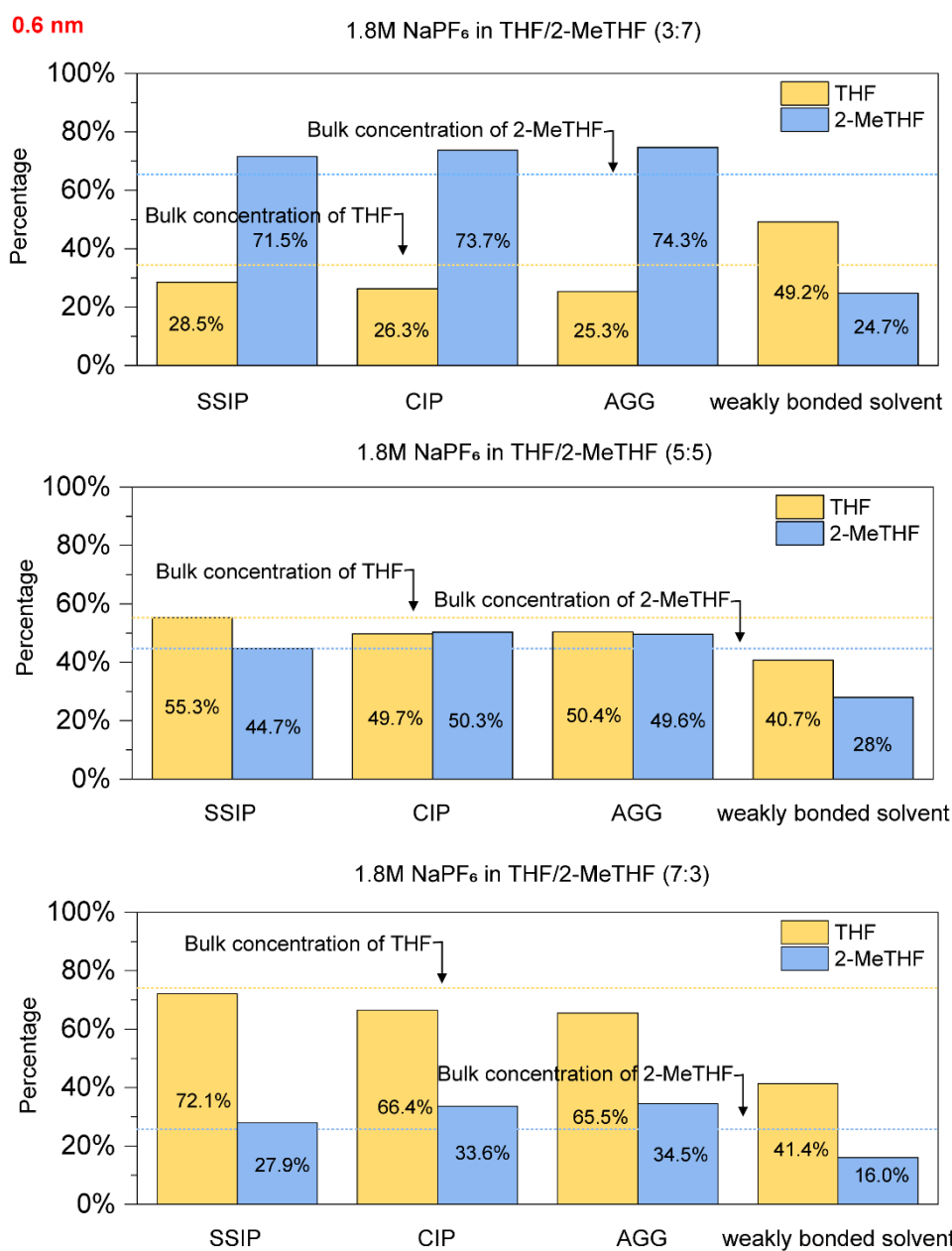
Supplementary Fig. 5 | Raman spectra of various electrolytes showing percentages of AGGs, CIPs, and SSIPs in each electrolyte. a. 1.8M NaPF₆ in THF, b. 1M NaPF₆ in 2-MeTHF and c. 1.8M NaPF₆ in THF/2-MeTHF.



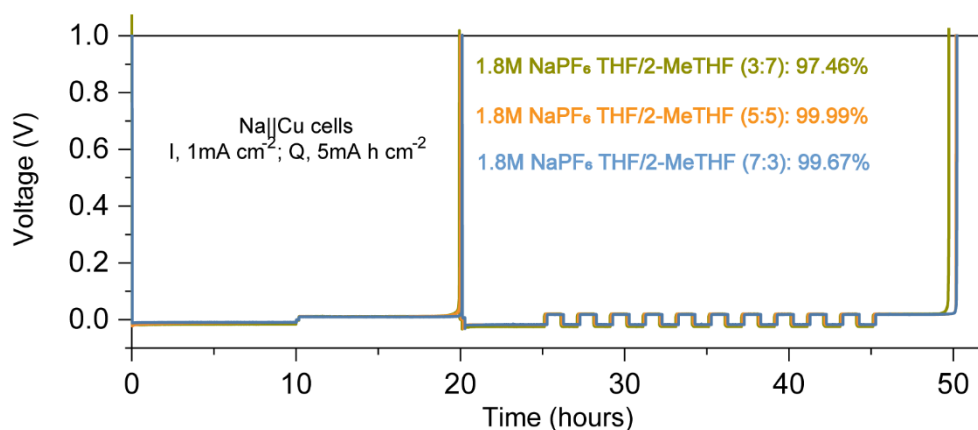
Supplementary Fig. 6 | Ratio of THF and 2-MeTHF in each solvation shell (SSIP, CIP, and AGG) for a cutoff distance of 0.4 nm. Dotted lines indicate the bulk composition of each solvent.



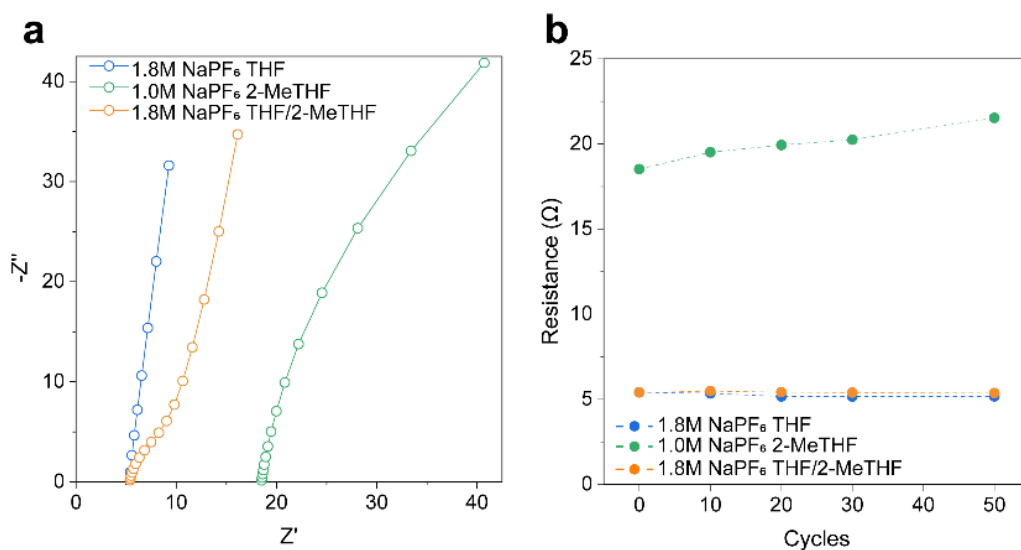
Supplementary Fig. 7 | Ratio of THF and 2-MeTHF in each solvation shell (SSIP, CIP, and AGG) for a cutoff distance of 0.5 nm. Dotted lines indicate the bulk composition of each solvent.



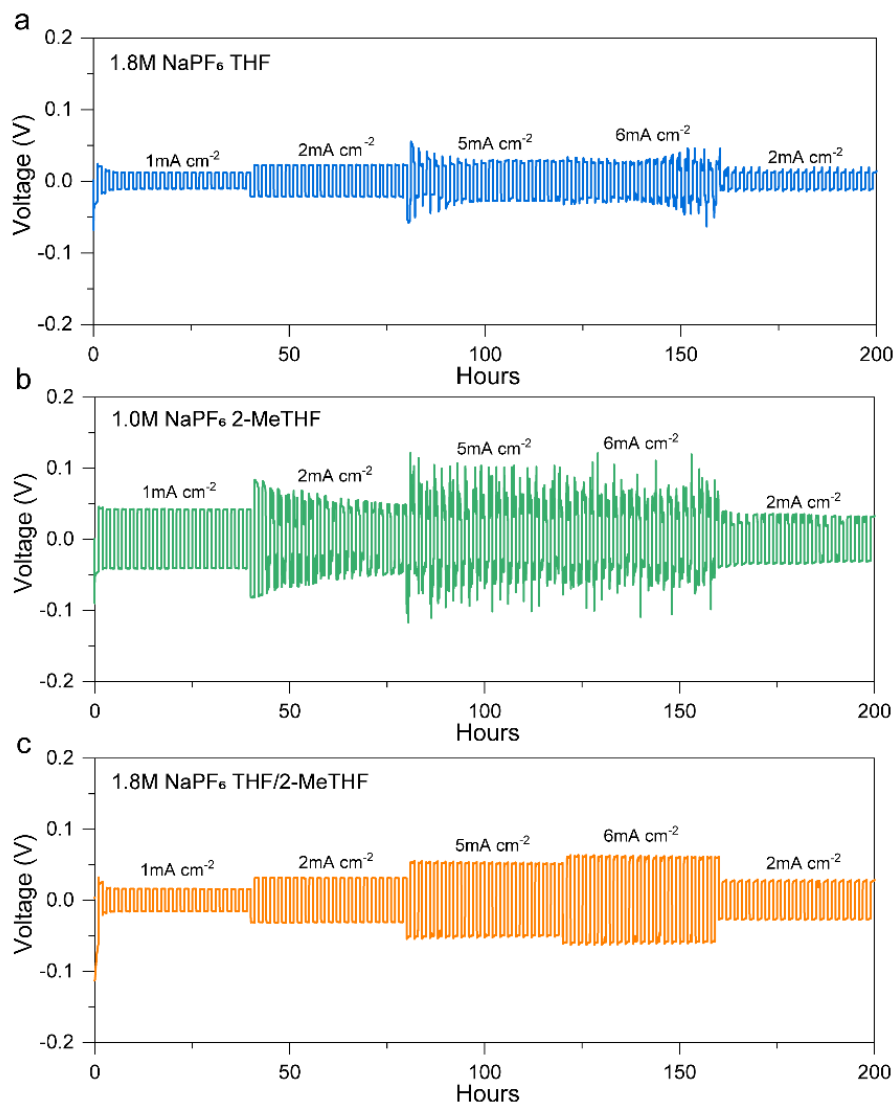
Supplementary Fig. 8 | Ratio of THF and 2-MeTHF in each solvation shell (SSIP, CIP, and AGG) for a cutoff distance of 0.6 nm. Dotted lines indicate the bulk composition of each solvent.



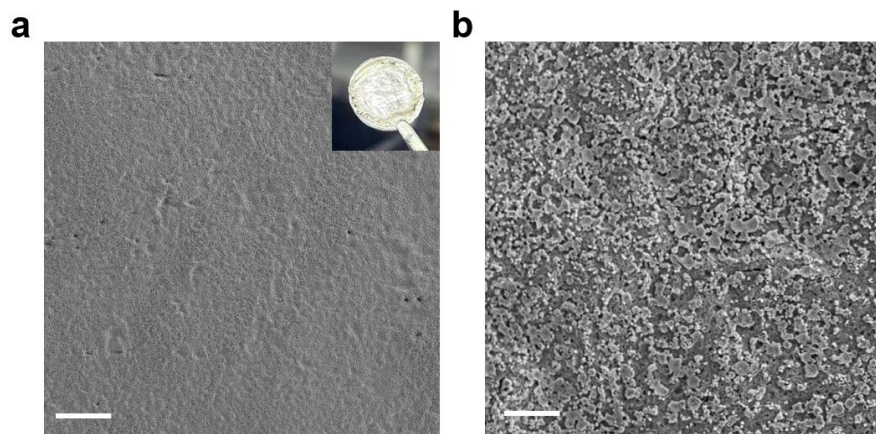
Supplementary Fig. 9 | Measurement of CE of Na plating/stripping in Na||Cu cells using an Aurbach method.



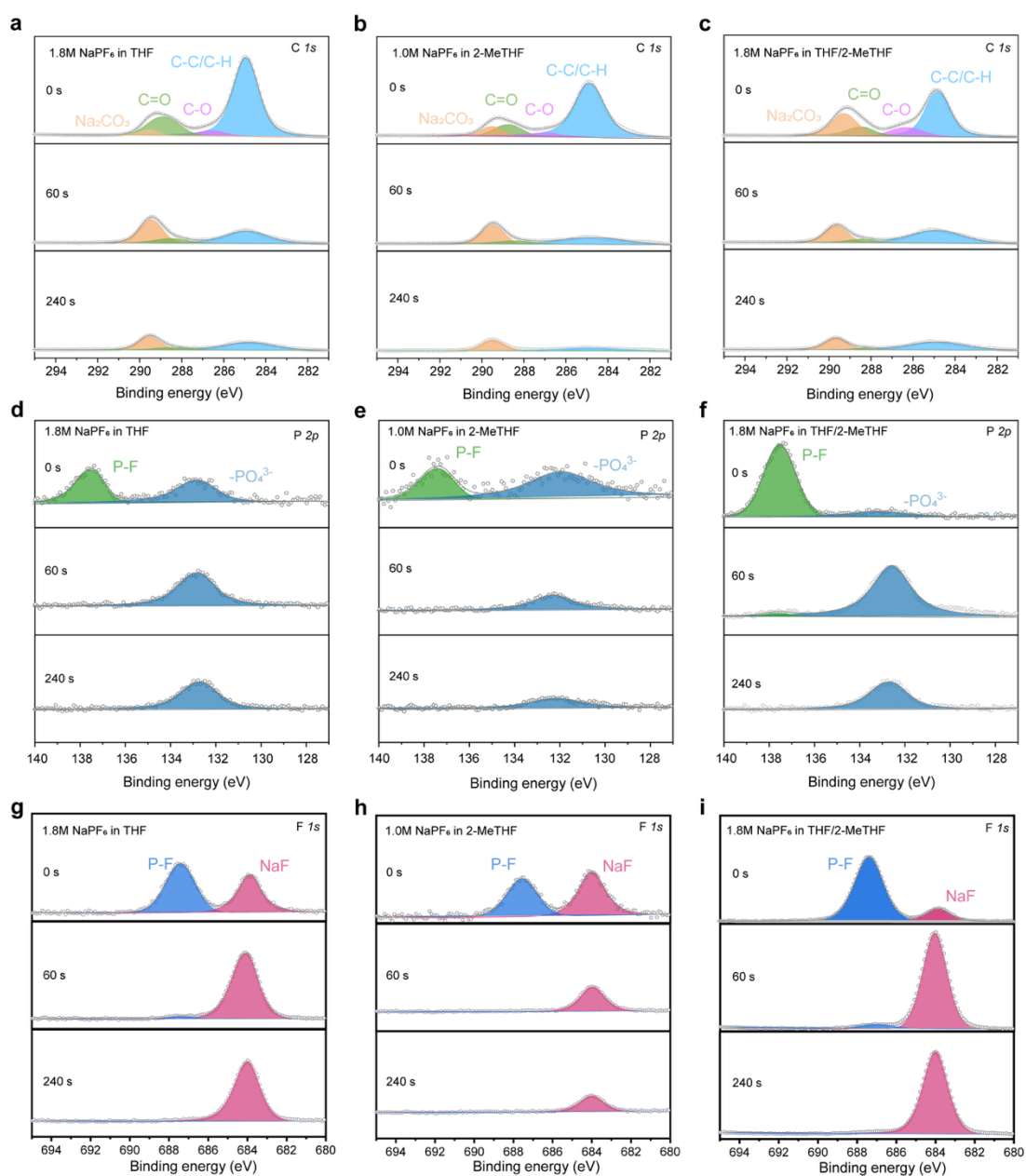
Supplementary Fig. 10 | a. EIS measure of Na||Cu half cells with 1.8M NaPF₆ in THF, 1.0M NaPF₆ in 2-MeTHF and 1.8M NaPF₆ in THF/2-MeTHF before cycling tests. b. Cycles-dependent changes of interfacial resistance in Na||Cu coin cells. All cells were cycled under I, 1mA cm⁻², Q, 1mAh, cm⁻² condition.



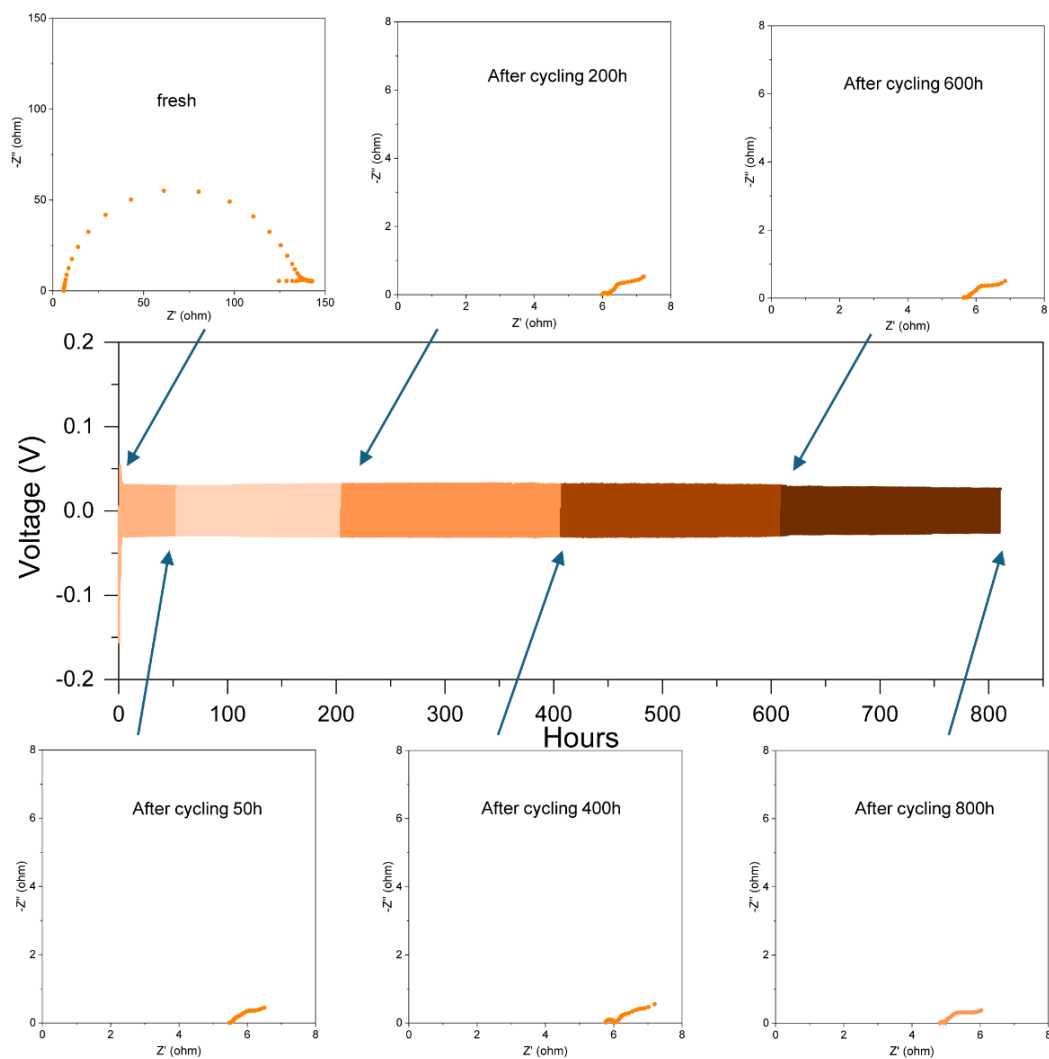
Supplementary Fig. 11 | Rate performance of Na||Na symmetric cell with a. 1.8M NaPF₆ in THF, b. 1.0M NaPF₆ in 2-MeTHF and c. 1.8M NaPF₆ in THF/2-MeTHF.



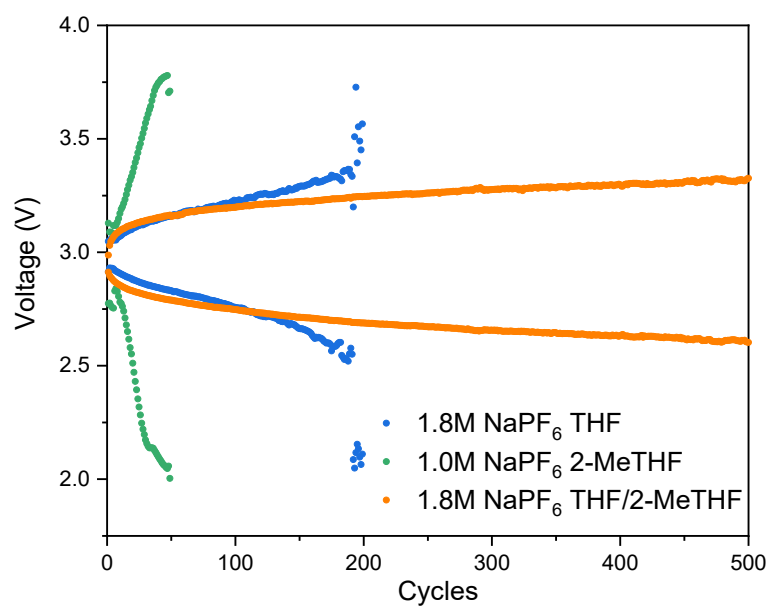
Supplementary Fig. 12 | a-b. SEM images and corresponding optical photo of Na harvested from Na||Na cells. a. scale bar, 100 μ m, b. scale bar, 10 μ m. The Na chip was harvested after 5000 hours cycling with 2mA/cm², 2mAh/cm² at 22°C $\pm$ 1°C.



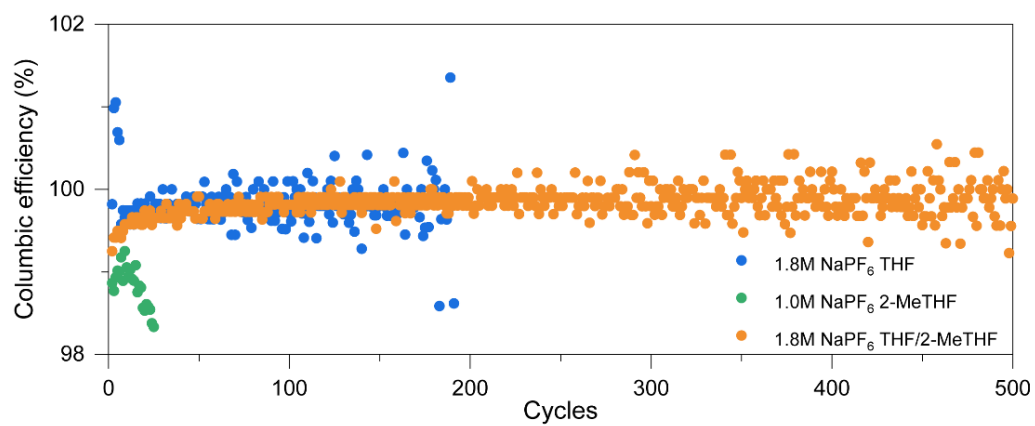
Supplementary Fig. 13 | Depth-profiling XPS spectra of the formed SEIs. a-c. C $1s$, d-f. P $2p$ and g-i. F $1s$. The Cu electrodes were harvested from Na||Cu half cells after 10 cycles under a current density of 1 mA/cm^2 with a capacity of 1 mAh/cm^2 at $22 \pm 1^\circ\text{C}$



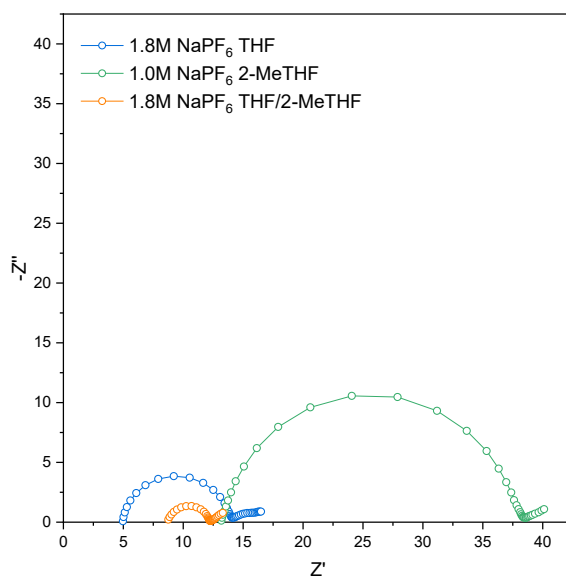
Supplementary Fig. 14 | Galvanostatic cycling performances of Na||Na symmetric coin cells with 1.8M NaPF₆ THF/2-MeTHF and the corresponding impedance spectra at various cycles.



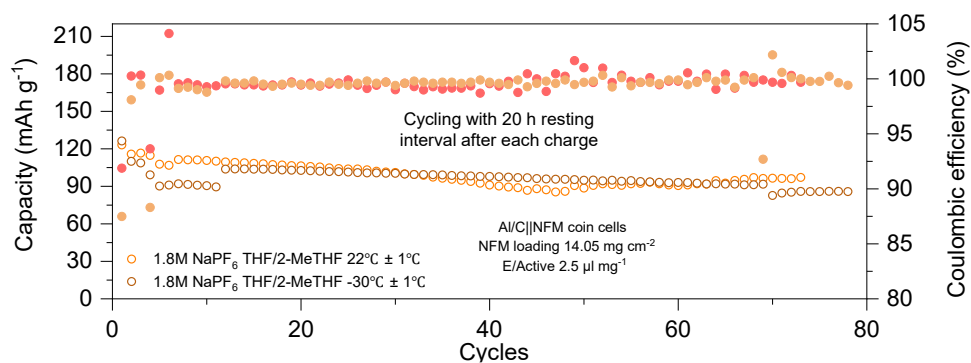
Supplementary Fig. 15 | Average voltage profiles for different electrolytes.



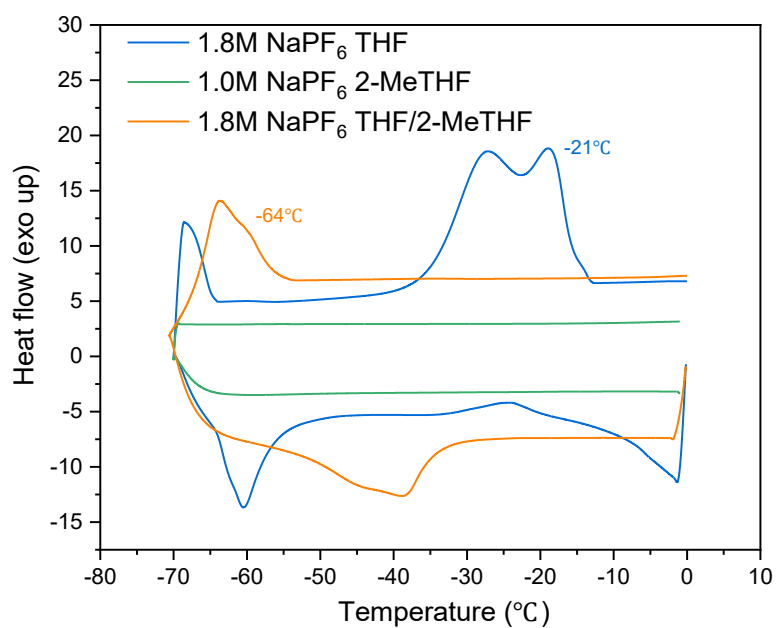
Supplementary Fig. 16 | Coulombic efficiencies of different electrolytes in Na||NFM cells.



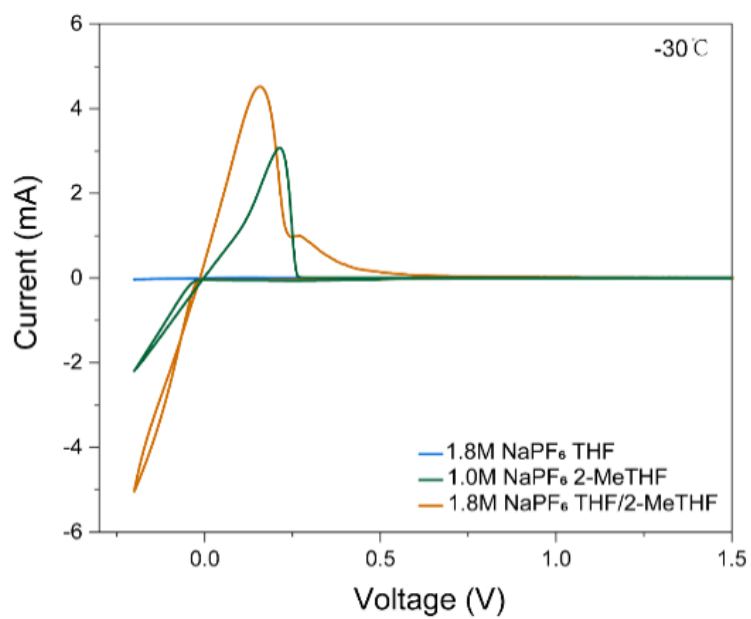
Supplementary Fig. 17 | EIS measure of Na||Na symmetric cell with various electrolytes. All cells were cycled at 1 mA cm^{-2} for one cycle before EIS testing.



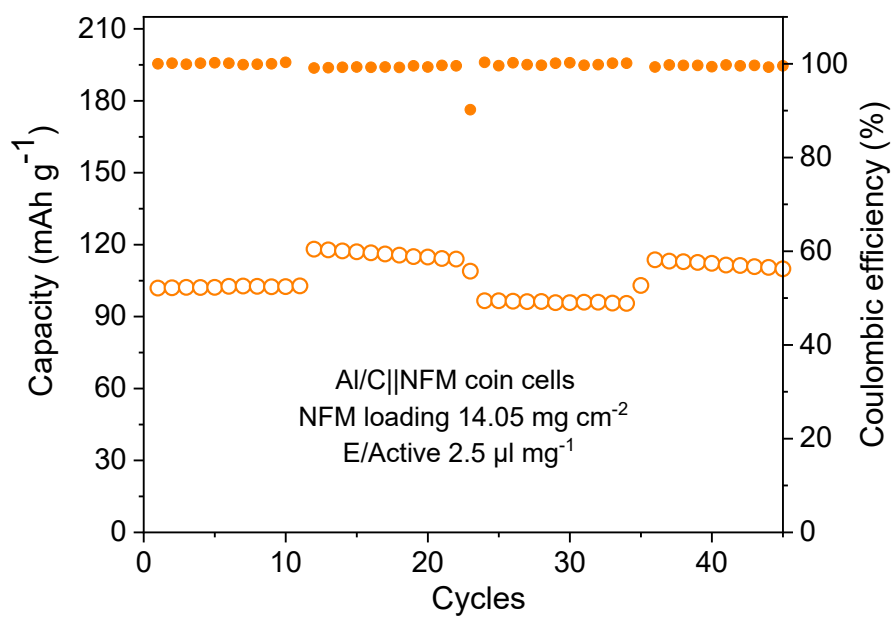
Supplementary Fig. 18 | The cycling performance of the Al/C||NFM full cells for the aging evaluation with the combined testing protocol between 2.0 V and 3.8 V at room temperature and -30°C , charging at 0.2C and resting for 20 h then discharging at 0.2C , $1\text{C} = 120 \text{ mA/g}$.



Supplementary Fig. 19 | The Differential scanning calorimetry (DSC) thermograms from 0 °C to -70 °C.



Supplementary Fig. 20 | CV curves of the Na||Cu cells with various electrolytes under -30°C.



Supplementary Fig. 21 | The cycling performance of the 1.8M NaPF₆ THF/2-MeTHF Al/C||NFM full cells for the temperature-dependent galvanostatic cycling at 0.2C between room temperature and -30 °C with voltage cutoffs of 2.0 V and 3.8 V, 1C = 120 mA/g.

Supplementary Table 1. A comparative analysis of the cycling performances of the symmetric cells in this work and other relevant studies on electrolytes.

Electrolyte	Current density (mA/cm ²)	Capacity (mAh/cm ²)	Over-potential (mV)	Time(h)	Ref.
1.8M NaPF ₆ THF/2-MeTHF	2.0	2.0	21	5000	This work
HCE (5.2M NaFSI in DME)	2	1	> 200	600	Ref. S2
LHCE (2.1M NaFSI in DME-BTFE)	2	1	50	960	Ref. S2
LHCE (NaFSI/DME/TTE 1:1.2:1)	1	1	26	590	Ref. S3
0.8M NaPF ₆ in TMP/FEC/DDT-E	1	5	50	720	Ref. S4
0.8M NaOTf in THF/DME (3:1)	3	1	250	900	Ref. S5
0.3M NaPF ₆ in EC/PC+2%BSFTA	0.5	0.5	40	350	Ref. S6
1M NaTFSI-TEP/FEC (3:1)	-	-	500	300	Ref. S7
1M NaClO ₄ in PC+EC+0.5 M Co(NO ₂) ₆	2	2	50	1100	Ref. S8
LHCE+1 wt% SbF ₃	0.5	0.5	40	1200	Ref. S9
0.067M Na ₂ S ₆ additive	10	1	50	80	Ref. S10
1M NaDFOB in EC/DMC	1.5	0.1	500	515	Ref. S11
1 M NaPF ₆ in DME	0.25	1	~20	1050	Ref. S12
1 M NaPF ₆ in DME/FEC/HFPM	1	1	60	900	Ref. S13
1M NaPF ₆ in FEC/PC/HFE+5%P FMP	0.5	1	150	1100	Ref. S14
0.9M NaPF ₆ -0.1 M NaBF ₄ in diglyme	1	2	15	50	Ref. S15
2M NaTFSI in PC-FEC = 1:1 Vol%-InI ₃	0.1	0.1	900	130	Ref. S16
2M NaPF ₆ in DEE	1	1	11	350	Ref. S28
1M NaPF ₆ in DEGDME/MTHF	0.5	1	10	7000	Ref. S27
1.7M NaTFSI in TMP-FEC/DFBn	1	1	210	2500	Ref. S18
NaFSI-NaNO ₃ -TMP (1.1M NaFSI and 0.3M NaNO ₃ in TMP)	2	2	35	2500	Ref. S17

Supplementary Table 2. A comparative analysis of the cycling performances of the Na||Cu cells in this work and other relevant studies on electrolytes.

Electrolyte	Current density (mA/cm ²)	Capacity (mAh/cm ²)	Stabilized CE	Cycle number	Ref.
1.8M NaPF ₆ THF-2-MeTHF	1	1	99.91%	400	This work
NaFSI-NaNO ₃ -TMP (1.1M NaFSI and 0.3M NaNO ₃ in TMP)	1	1	99.20%	200	Ref. S17
1.7M NaTFSI in TMP-FEC/DFBn	1	1	97.50%	600	Ref. S18
1M NaPF ₆ in DEGDME/MTHF	0.5	1	99.74%	300	Ref. S27
2M NaPF ₆ in DEE	1	1	99.89%	150	Ref. S28

Supplementary Table 3. Physical properties of THF and 2-MeTHF.

	Dielectric constant	Donor number	HOMO (eV)	LUMO (eV)
THF	7.58	20.5	-6.87	2.24
2-MeTHF	6.97	18	-6.61	2.27

Supplementary Table 4. | The saturation points of NaPF₆ salt in various solvents.

Solvent	Saturation Point (M)
THF	2.2
2-MeTHF	1.3
THF/2-MeTHF (v:v =1:1)	1.69

*The saturation point of NaPF₆ in THF/2-MeTHF (v:v =1:1) is estimated by equation S1.

Supplementary Table 5. The detailed compositions of the MD simulation systems. Numbers indicate the number of molecules in each system. 2-MeTHF was modeled as a racemic mixture of R- and S-enantiomers.

	1.8M NaPF ₆ THF	1.0M NaPF ₆ 2- MeTHF	1.8M NaPF ₆ THF/2-MeTHF (3:7)	1.8M NaPF ₆ THF/2-MeTHF (5:5)	1.8M NaPF ₆ THF/2-MeTHF (7:3)
THF	919	n/a	276	459	642
2-MeTHF-R	n/a	373	261	186	112
2-MeTHF-S	n/a	373	261	186	112
Na ⁺	135	75	135	135	135
PF ₆ ⁻	135	75	135	135	135

Supplementary Table 6. Average values of $g(r)$ and $N(r)$ computed from the MD simulations with standard deviations shown in parentheses.

				0.4 nm	0.5 nm	0.6 nm
		r (nm)	$g(r)$	N(r)		
1.8M NaPF ₆ THF/2-MeTHF (3:7)	Na-O(2-MeTHF)	0.22 (0.00)	40.87 (0.06)	2.49 (0.01)	2.54 (0.00)	2.99 (0.00)
	Na-O(THF)	0.23 (0.00)	15.76 (0.18)	0.61 (0.01)	0.67 (0.01)	1.07 (0.01)
	Na-O	0.22 (0.00)	31.99 (0.07)	3.09 (0.01)	3.21 (0.01)	4.06 (0.00)
	Na-P	0.32 (0.00)	13.26 (0.09)	1.02 (0.01)	1.13 (0.01)	1.22 (0.00)
	Na-F	0.24 (0.00)	10.40 (0.10)	3.40 (0.01)	6.54 (0.03)	8.13 (0.03)
1.8M NaPF ₆ THF/2-MeTHF (5:5)	Na-O(2-MeTHF)	0.22 (0.00)	44.43 (0.59)	1.75 (0.25)	1.78 (0.25)	2.06 (0.30)
	Na-O(THF)	0.23 (0.00)	20.01 (1.63)	1.35 (0.22)	1.44 (0.23)	2.10 (0.26)
	Na-O	0.22 (0.00)	29.70 (0.63)	3.10 (0.04)	3.22 (0.04)	4.16 (0.04)
	Na-P	0.32 (0.00)	13.55 (0.57)	1.13 (0.06)	1.25 (0.06)	1.33 (0.07)
	Na-F	0.24 (0.00)	10.86 (0.40)	3.74 (0.20)	7.17 (0.38)	8.74 (0.44)
1.8M NaPF ₆ THF/2-MeTHF (7:3)	Na-O(2-MeTHF)	0.22 (0.00)	48.10 (0.21)	1.24 (0.00)	1.26 (0.00)	1.44 (0.00)
	Na-O(THF)	0.23 (0.00)	22.24 (0.02)	1.95 (0.01)	2.07 (0.01)	2.91 (0.01)
	Na-O	0.23 (0.00)	28.26 (0.01)	3.19 (0.01)	3.33 (0.01)	4.35 (0.01)
	Na-P	0.32 (0.00)	14.46 (0.08)	1.14 (0.00)	1.27 (0.00)	1.34 (0.00)
	Na-F	0.24 (0.00)	11.84 (0.00)	3.80 (0.01)	7.28 (0.02)	8.77 (0.01)
1.8M NaPF ₆ THF	Na-O(THF)	0.23 (0.00)	26.74 (0.25)	3.33 (0.02)	3.49 (0.02)	4.64 (0.01)
	Na-P	0.32 (0.00)	15.55 (0.06)	1.24 (0.01)	1.38 (0.01)	1.46 (0.02)
	Na-F	0.24 (0.00)	12.95 (0.16)	4.12 (0.04)	7.90 (0.09)	9.34 (0.10)
1.0M NaPF ₆ 2-MeTHF	Na-O(2-MeTHF)	0.23 (0.00)	34.51 (0.13)	3.18 (0.00)	3.31 (0.00)	4.29 (0.00)
	Na-P	0.32 (0.00)	20.27 (0.35)	0.85 (0.00)	0.94 (0.01)	1.02 (0.00)
	Na-F	0.24 (0.00)	15.22 (0.17)	2.87 (0.01)	5.47 (0.01)	6.75 (0.00)

Supplementary Table 7. Experimentally measured densities of NaPF₆ electrolyte solutions in THF, 2-MeTHF, and mixed THF/2-MeTHF systems.

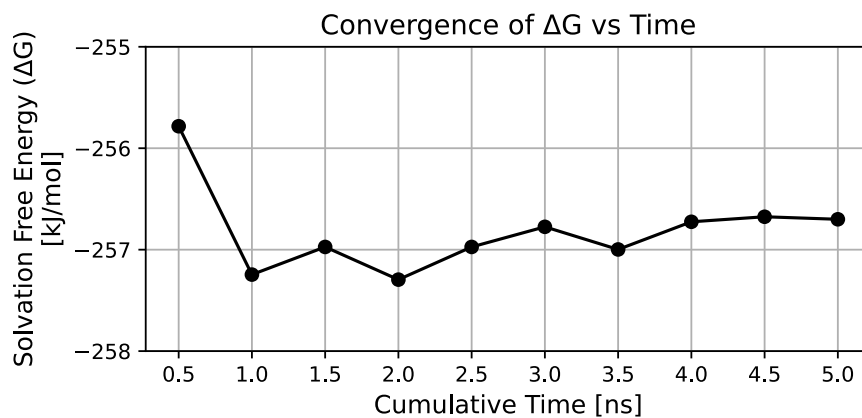
	Volume (mL)	Weight (g)	Density (g/mL)
1.8M NaPF ₆ in THF	0.200	0.198	0.990
1M NaPF ₆ in 2-MeTHF	0.200	0.180	0.900
1.8M NaPF ₆ in THF/2-MeTHF (5:5)	0.200	0.194	0.970

Supplementary Table 8. Time-averaged densities from *NPT* production simulations for electrolyte and pure solvent systems.

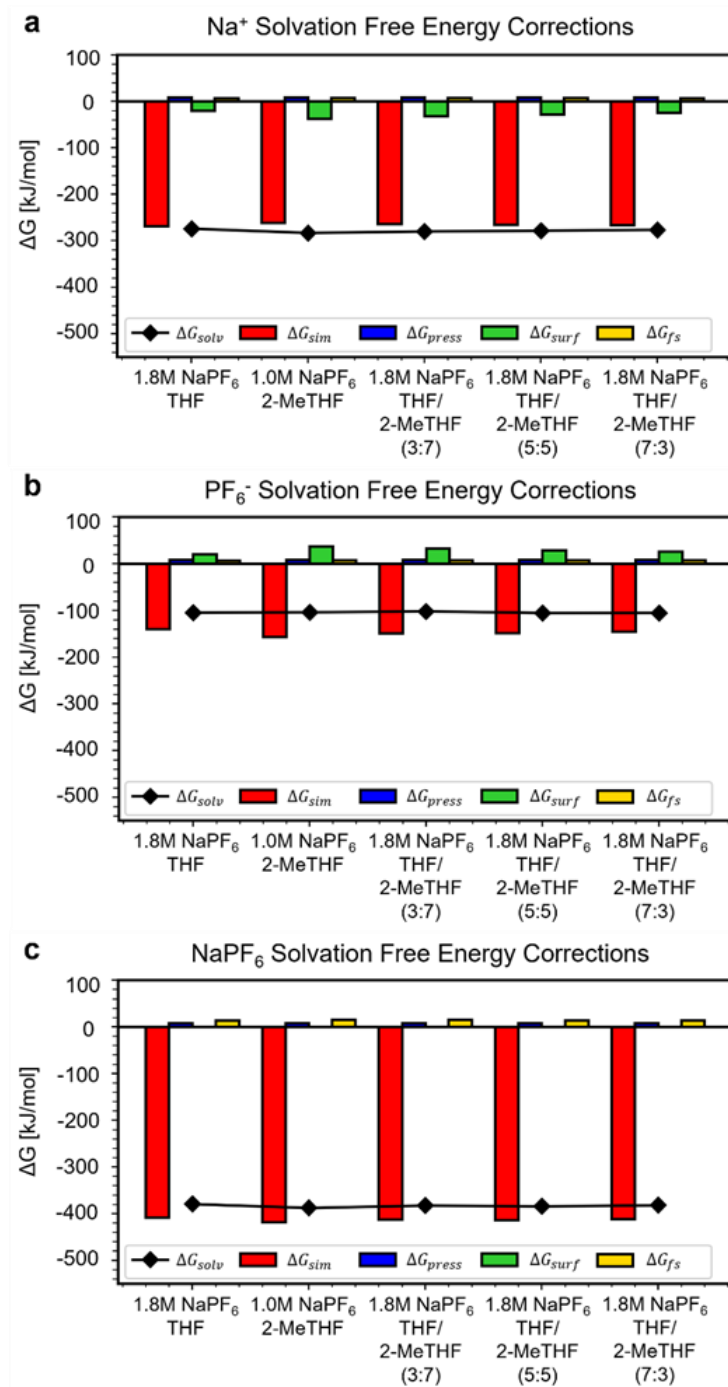
Multi-ion system	Density (g/mL)		Pure solvent system	Density (g/mL)	
	Rep1	Rep2		Rep1	Rep2
1.8M NaPF ₆ in THF	1.08967	1.08919	THF	0.85993	0.86006
1M NaPF ₆ in 2-MeTHF	0.99895	0.99908	2-MeTHF	0.86154	0.86128
1.8M NaPF ₆ in THF/2-MeTHF (3:7)	1.09348	1.09353	THF/2-MeTHF (3:7)	0.86095	0.86083
1.8M NaPF ₆ in THF/2-MeTHF (5:5)	1.09235	1.12187	THF/2-MeTHF (5:5)	0.86077	0.86084
1.8M NaPF ₆ in THF/2-MeTHF (7:3)	1.09131	1.09117	THF/2-MeTHF (7:3)	0.86040	0.86034

Supplementary Table 9. Densities of pure solvents (THF and 2-MeTHF) obtained using OPLS-AA force fields (average values from Supplementary Table 8) and compared to literature experimental values. Simulated values deviate from experimental data by less than 3%, which is consistent with the expected accuracy of the OPLS-AA force field.

Solvent	Simulated Density (g/mL)	Experimental Density (g/mL)	% Error	Reference
THF	0.8600	0.8837	2.68	S22
2-MeTHF	0.8614	0.8529	1.00	S23



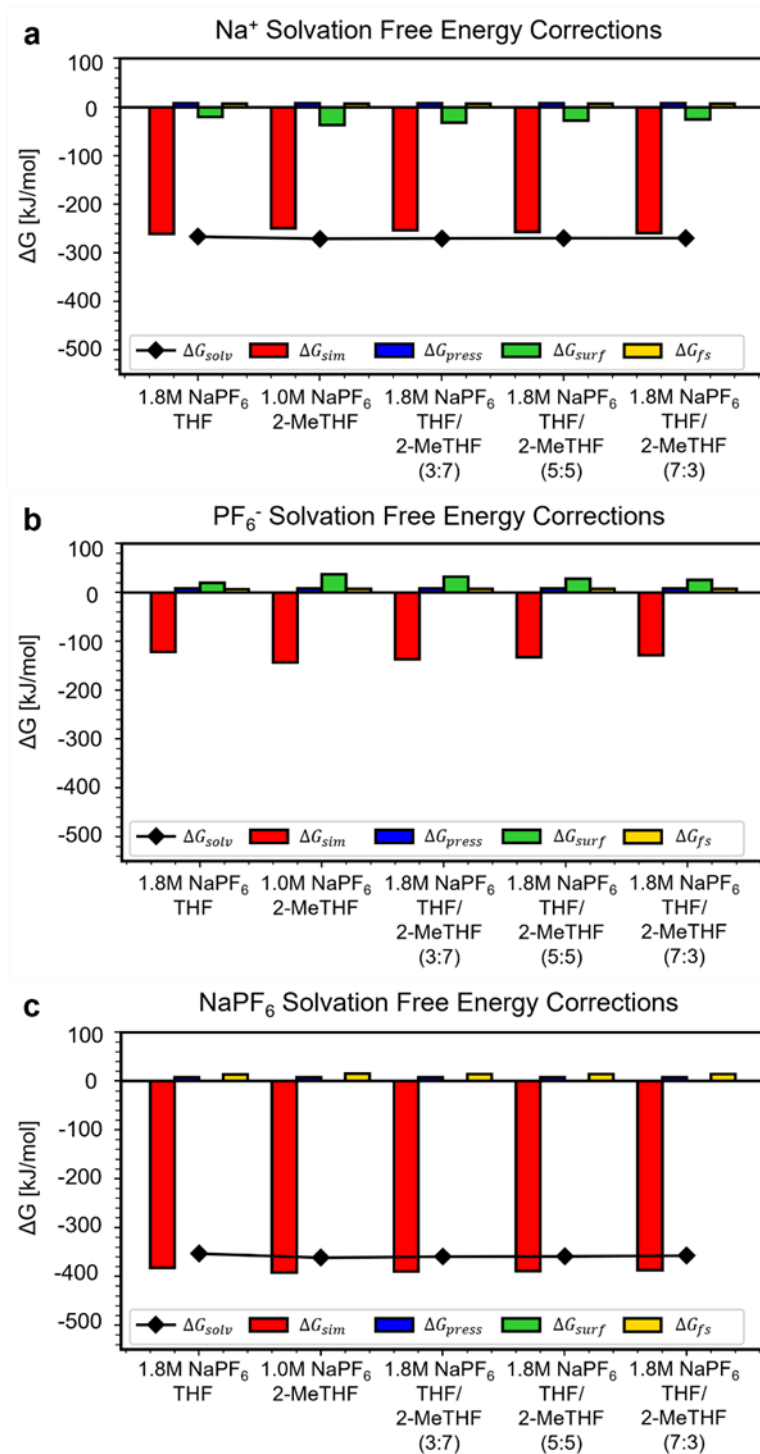
Supplementary Fig. 22 | Convergence of Na^+ solvation free energy as a function of sampling time. The free energy was computed using increasing portions of a 5 ns trajectory (replicate 2, 1.8M NaPF₆ in THF/2-MeTHF 5:5 v:v), showing that ΔG_{sim} plateaus with sufficient sampling.



Supplementary Fig. 23 | Decomposition of solvation free energy terms for the multi-ion systems. a. Na⁺, b. PF₆⁻, and c. NaPF₆ in five electrolyte systems: 1.8M NaPF₆ in THF, 1.0M NaPF₆ in 2-MeTHF, and 1.8M NaPF₆ in THF/2-MeTHF mixtures (3:7, 5:5, 7:3 v:v). Bars show the simulation result (ΔG_{sim} , red), compression correction (ΔG_{press} , blue), interfacial potential correction (ΔG_{surf} , green), and finite-size correction (ΔG_{fs} , yellow). Black diamonds represent the final corrected solvation free energy (ΔG_{solv}).

Supplementary Table 10. Summary of solvation free energy terms for the multi-ion system.

	ΔG_{sim} [kJ/mol]			ΔG_{press} [kJ/mol]	ΔG_{fs} [kJ/mol]			ΔG_{surf} [kJ/mol]			ΔG_{solv} [kJ/mol]		
	Na ⁺	PF ₆ ⁻	NaPF ₆	-	Na ⁺	PF ₆ ⁻		Na ⁺	PF ₆ ⁻		Na ⁺	PF ₆ ⁻	NaPF ₆
	Replicate 1												
1.8M NaPF ₆ in THF	-268.6	-138.3	-406.9	7.9	6.7	6.8		-20.2	20.2		-274.2	-103.4	-377.6
1.0M NaPF ₆ in 2-MeTHF	-261.6	-156.4	-418	7.9	7.4	7.5		-37.4	37.4		-283.7	-103.6	-387.3
1.8M NaPF ₆ in THF/2-MeTHF (3:7)	-261.9	-152.2	-414.1	7.9	7.3	7.4		-32.2	32.2		-278.9	-104.7	-383.6
1.8M NaPF ₆ in THF/2-MeTHF (5:5)	-264.9	-148.6	-413.5	7.9	7.1	7.2		-28	28		-277.9	-105.5	-383.4
1.8M NaPF ₆ in THF/2-MeTHF (7:3)	-266.3	-146	-412.3	7.9	7	7.1		-25.3	25.3		-276.7	-105.7	-382.4
	Replicate 2												
1.8M NaPF ₆ in THF	-268.4	-141.6	-410	7.9	6.8	6.9		-20.2	20.2		-273.9	-106.6	-380.5
1.0M NaPF ₆ in 2-MeTHF	-261.5	-157.1	-418.6	7.9	7.5	7.6		-37	37		-283.1	-104.6	-387.7
1.8M NaPF ₆ in THF/2-MeTHF (3:7)	-265	-146.7	-411.7	7.9	7.3	7.4		-31.8	31.8		-281.6	-99.6	-381.2
1.8M NaPF ₆ in THF/2-MeTHF (5:5)	-266.2	-148.6	-414.8	7.9	7.1	7.2		-28	28		-279.2	-105.5	-384.7
1.8M NaPF ₆ in THF/2-MeTHF (7:3)	-266	-145.1	-411.1	7.9	7	7.1		-25.3	25.3		-276.4	-104.8	-381.2



Supplementary Fig. 24 | Decomposition of solvation free energy terms for the single-ion systems. a. Na⁺, b. PF₆⁻, and c. NaPF₆ in five solvent environments: pure THF, pure 2-MeTHF, and THF/2-MeTHF mixtures (3:7, 5:5, 7:3 v:v). Bars show the simulation result (ΔG_{sim} , red), compression correction (ΔG_{press} , blue), interfacial potential correction (ΔG_{surf} , green), and finite-size correction (ΔG_{fs} , yellow). Black diamonds represent the final corrected solvation free energy (ΔG_{solv}).

Supplementary Table 11. Summary of solvation free energy terms for the single-ion system.

	ΔG_{sim} [kJ/mol]			ΔG_{press} [kJ/mol]	ΔG_{fs} [kJ/mol]			ΔG_{surf} [kJ/mol]			ΔG_{solv} [kJ/mol]			
	Na ⁺	PF ₆ ⁻	NaPF ₆		-	Na ⁺	PF ₆ ⁻	NaPF ₆	Na ⁺	PF ₆ ⁻	NaPF ₆	Na ⁺	PF ₆ ⁻	NaPF ₆
	Replicate 1													
1.8M NaPF ₆ in THF	-260.6	-121.9	-382.5	7.9	6.7	6.8		-20.2	20.2		-266.2	-87		-353.2
1.0M NaPF ₆ in 2-MeTHF	-249.1	-142.7	-391.8	7.9	7.4	7.5		-37.4	37.4		-271.2	-89.9		-361.1
1.8M NaPF ₆ in THF/2-MeTHF (3:7)	-253.3	-136.5	-389.8	7.9	7.3	7.4		-32.2	32.2		-270.3	-89		-359.3
1.8M NaPF ₆ in THF/2-MeTHF (5:5)	-256.4	-132.4	-388.8	7.9	7.1	7.2		-28	28		-269.4	-89.3		-358.7
1.8M NaPF ₆ in THF/2-MeTHF (7:3)	-259.5	-128.4	-387.9	7.9	7	7.1		-25.3	25.3		-269.9	-88.1		-358
	Replicate 2													
1.8M NaPF ₆ in THF	-260.9	-122	-382.9	7.9	6.8	6.9		-20.2	20.2		-266.4	-87		-353.4
1.0M NaPF ₆ in 2-MeTHF	-249	-143.4	-392.4	7.9	7.5	7.6		-37	37		-270.6	-90.9		-361.5
1.8M NaPF ₆ in THF/2-MeTHF (3:7)	-253.4	-136.3	-389.7	7.9	7.3	7.4		-31.8	31.8		-270	-89.2		-359.2
1.8M NaPF ₆ in THF/2-MeTHF (5:5)	-256.7	-132.3	-389	7.9	7.1	7.2		-28	28		-269.7	-89.2		-358.9
1.8M NaPF ₆ in THF/2-MeTHF (7:3)	-258.6	-128.1	-386.7	7.9	7	7.1		-25.3	25.3		-269	-87.8		-356.8

Supplementary Note 2:

Solvation free energies (ΔG_{solv}) for Na^+ and PF_6^- ions in various electrolytes were computed using GROMACS 2021. The free energy was obtained by gradually decoupling the ion from the surrounding solvent using a coupling parameter (λ), which progressively reduced the interactions between the ion and the solvent. The decoupling process was performed in two stages. In the first stage, electrostatic interactions (ΔG^{elec}) were decoupled by varying λ from 0 to 1 over 20 independent simulation windows, while retaining the van der Waals interactions (ΔG^{vdW}). In the second stage, van der Waals interactions were decoupled by varying λ from 0 to 1 over 5 simulation windows with electrostatic interactions completely decoupled.

For each window (*i.e.*, unique λ value), the simulations used the steepest descent for energy minimization and the stochastic dynamics (Langevin) integrator with a 2 fs timestep for both equilibration and production runs. Pressure coupling was applied using stochastic cell rescaling barostat with a time constant of 1 ps. Equilibration was performed in the NVT ensemble for 100 ps, followed by 2 ns in the NPT ensemble. Production simulations were then carried out in the NPT ensemble for 5 ns.

Alchemical free energy simulations employed soft-core potentials with a soft-core α (sc- α) of 0.5 to avoid endpoint singularities. To assess convergence of the calculated solvation free energies from the simulations (ΔG_{sim}), we analyzed ΔG_{sim} for Na^+ in the THF/2-MeTHF (5:5) mixture using progressively longer segments of the 5 ns production trajectory (*e.g.*, from 0–0.5 ns, 0–1.0 ns, *etc.*). As shown in Supplementary Fig. 22, the solvation free energy stabilizes within 1 kJ/mol after 3 ns, indicating that 5 ns of production per window is sufficient.

Solvation free energies were computed in each solvent system for both a single ion in pure solvent with no counterions (referred to as a single-ion system below) and for a single ion in a background electrolyte (referred to as a multi-ion system below). Trends for both types of systems were similar, indicating no substantial impact of the background electrolyte on solvation affinity.

To correct solvation free energies in systems with a net charge (*i.e.*, due to the decoupling of a single ion), we applied the following correction terms^{S24}:

- Compression correction (ΔG_{press}): This term adjusts for the transfer from an ideal gas to the solution phase. It is computed using the equation:

$$\Delta G_{press} = k_B T \ln \left(\frac{p_1}{p_0} \right)$$

where p_1 is the simulated concentration and $p_0 = 1\text{ M}$.

- Finite-size correction (ΔG_{fs}): This correction accounts for long-range electrostatic artifacts in periodic boundary conditions. It is calculated using:

$$\Delta G_{fs} = \frac{e^2(\epsilon - 1)}{6\epsilon\epsilon_0 L} \left[\left(\frac{r_a}{L} \right)^2 - \frac{4\pi}{15} \left(\frac{r_a}{L} \right)^5 \right] - \frac{e^2 \xi}{8\pi\epsilon\epsilon_0 L}$$

where ϵ is the dielectric constant, L is the ensemble-average box length, r_a is the ion radius (0.102 nm for Na^+ ^{S25} and 0.254 nm for PF_6^- ^{S26}, $\epsilon_0 = 5.727 \times 10^{-4} \frac{\text{e}^2 \text{mol}}{\text{kJ}\cdot\text{nm}}$ is the permittivity of free space, $\xi = -2.837$ is the prefactor Wigner energy per particle on a cubic lattice, and $e = 1.602 \times 10^{-19} \text{C}$ is the elementary charge. The dielectric constants used for this term were computed from the final *NPT* production simulations of pure solvents (THF, 2-MeTHF, and THF/2-MeTHF without ions) using *gmx dipoles*.

- Interface correction (ΔG_{surf}): This term corrects for the electrostatic potential at the vacuum-solvent interface and is computed as:

$$\Delta G_{surf} = ze\psi_S$$

where z is the charge and ψ_S is the interfacial potential between vacuum and bulk solvent. To calculate ψ_S , vacuum regions were added along the z-axis of equilibrated bulk systems, and 100 ns of *NVT* production was performed following 10 ns equilibration. Electrostatic potential profiles were then obtained using *gmx potential*, and the vacuum and bulk regions were defined using *gmx density*.

These corrections were applied separately to Na^+ and PF_6^- in each system. The interfacial potential contributions cancel out for neutral ion pairs, and thus do not affect the NaPF_6 results. The final corrected solvation free energy is given by:

$$\Delta G_{solv} = \Delta G_{sim} + \Delta G_{press} + \Delta G_{fs} + \Delta G_{surf}$$

Values for ΔG_{sim} and the individual corrections are provided in Supplementary Tables 10 (multi-ion systems) and 11 (single-ion systems), with associated plots in Supplementary Fig. 23-24. All reported values in the figures are averages of two independent replicates.

Supplementary Table 12. Ratio of THF and 2-MeTHF in each solvation shell type for 1.8M NaPF₆ in THF/2-MeTHF (5:5) from the MD simulations. The values represent the averaged total contents and percentages from two replicas, with standard deviations provided in parentheses. 0.5 nm was used as the cutoff for all results in the main text.

	Contact type	Total contents of the solvation shells		Percentage of each solvation shell (%) [*]		Percentage in total in system (%) ^{**}	
		THF (a)	2-MeTHF (b)	THF (c)	2-MeTHF (d)	THF	2-MeTHF
Cutoff distance [nm]	0.4nm						
	SSIP	39.8 (4.1)	44.0 (8.9)	47.5	52.5	8.7	11.8
	CIP	108.7 (14.7)	150.1 (27.2)	42.0	58.0	23.7	40.3
	AGGs	33.3 (10.6)	41.6 (2.0)	44.4	55.6	7.3	11.02
	Sum	181.8 (n/a)	235.7 (n/a)	n/a	n/a	39.6	63.4
	0.5nm						
	SSIP	24.4 (1.8)	25.9 (5.9)	48.5	51.5	5.3	7.0
	CIP	124.1 (13.9)	160.2 (30.8)	43.7	56.3	27.0	43.1
	AGGs	45.1 (14.0)	53.0 (1.9)	45.9	54.1	9.8	14.3
	Sum	193.6 (n/a)	239.1 (n/a)	n/a	n/a	42.2	64.3
	0.6nm						
	SSIP	25.6 (0.8)	20.7 (4.9)	55.3	44.7	5.6	5.6
	CIP	167.1 (9.6)	169.0 (35.6)	49.7	50.3	36.4	45.4
	AGGs	79.4 (21.3)	78.2 (0.0)	50.4	49.6	17.3	21.0
	Sum	272.1 (n/a)	267.8 (n/a)	n/a	n/a	59.3	72.0
Total in system		459	372	55.2	44.8	n/a	n/a

^{*}The sum of a and b is used as the denominator, and a/(a+b) and b/(a+b) are expressed as percentages. ^{**}Percentages are calculated using the total number of each solvent in the system (i.e., 459 for THF and 372 for 2-MeTHF) as the denominator

Supplementary Table 13. Ratio of THF and 2-MeTHF in each solvation shell type for 1.8M NaPF₆ in THF/2-MeTHF (3:7) from the MD simulations. The values represent the averaged total contents and percentages from two replicas, with standard deviations provided in parentheses. 0.5 nm was used as the cutoff for all results in the main text.

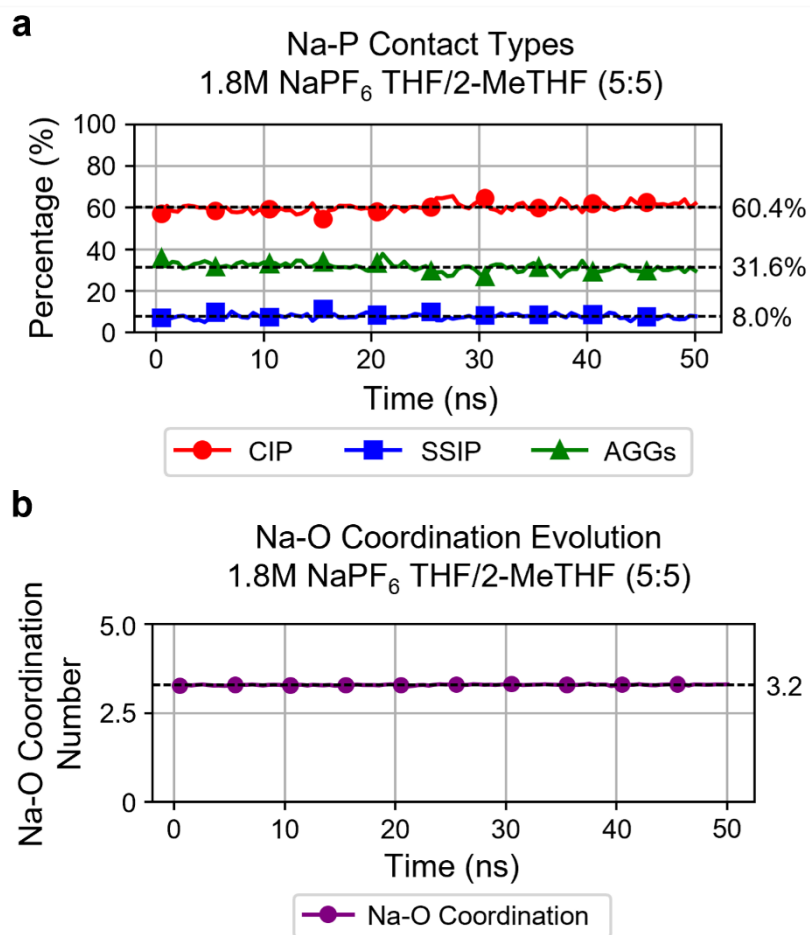
	Contact type	Total contents of the solvation shells		Percentage of each solvation shell (%) [*]		Percentage in total in system (%) ^{**}	
		THF (a)	2-MeTHF (b)	THF (c)	2-MeTHF (d)	THF	2-MeTHF
Cutoff distance [nm]	0.4nm						
	SSIP	20.6 (0.0)	72.3 (0.2)	22.2	77.8	7.5	13.8
	CIP	51.4 (1.2)	221.0 (1.0)	18.9	81.1	18.6	42.3
	AGGs	9.8 (0.0)	41.7 (0.1)	19.1	80.9	3.6	8.0
	Sum	81.8 (n/a)	335.0 (n/a)	n/a	n/a	29.6	64.2
	0.5nm						
	SSIP	13.5 (0.1)	48.3 (0.1)	21.8	78.2	4.9	9.2
	CIP	62.1 (1.2)	239.0 (1.0)	20.6	79.4	22.5	45.8
	AGGs	14.1 (0.1)	54.4 (0.0)	20.6	79.4	5.1	10.4
	Sum	89.7 (n/a)	341.6 (n/a)	n/a	n/a	32.5	65.4
	0.6nm						
	SSIP	15.6 (0.2)	39.1 (0.1)	28.5	71.5	5.6	7.5
	CIP	94.9 (1.0)	266.2 (0.9)	26.3	73.7	34.4	51.0
	AGGs	29.7 (0.2)	87.7 (0.0)	25.3	74.7	10.8	16.8
	Sum	140.2 (n/a)	393.0 (n/a)	n/a	n/a	50.8	75.3
Total in system		276	522	34.6	65.4	n/a	n/a

^{*}The sum of a and b is used as the denominator, and a/(a+b) and b/(a+b) are expressed as percentages. ^{**}Percentages are calculated using the total number of each solvent in the system (i.e., 276 for THF and 522 for 2-MeTHF) as the denominator.

Supplementary Table 14. Ratio of THF and 2-MeTHF in each solvation shell type for 1.8M NaPF₆ in THF/2-MeTHF (7:3) from the MD simulations. The values represent the averaged total contents and percentages from two replicas, with standard deviations provided in parentheses. 0.5 nm was used as the cutoff for all results in the main text.

	Contact type	Total contents of the solvation shells		Percentage of each solvation shell (%) [*]		Percentage in total in system (%) ^{**}	
		THF (a)	2-MeTHF (b)	THF (c)	2-MeTHF (d)	THF	2-MeTHF
Cutoff distance [nm]	0.4nm						
	SSIP	58.4 (1.2)	30.4 (0.1)	65.8	34.2	9.1	13.6
	CIP	156.0 (0.8)	104.0 (0.5)	60.0	40.0	24.3	46.4
	AGGs	48.0 (1.0)	33.3 (1.0)	59.0	41.0	7.5	14.9
	Sum	262.5 (n/a)	167.8 (n/a)	n/a	n/a	40.9	74.9
	0.5nm						
	SSIP	37.1 (1.2)	17.7 (0.0)	67.6	32.4	5.8	7.9
	CIP	174.2 (0.6)	110.1 (0.6)	61.3	38.7	27.1	49.2
	AGGs	65.8 (1.3)	42.0 (1.1)	61.0	39.0	10.2	18.8
	Sum	277.0 (n/a)	169.9 (n/a)	n/a	n/a	43.2	75.8
	0.6nm						
	SSIP	38.6 (1.2)	15.0 (0.0)	72.1	27.9	6.0	6.7
	CIP	225.8 (0.3)	114.3 (0.7)	66.4	33.6	35.2	51.0
	AGGs	111.9 (1.2)	58.9 (1.2)	65.5	34.5	17.4	26.3
	Sum	376.2 (n/a)	188.1 (n/a)	n/a	n/a	58.6	84.0
	Total in system	642	224	74.1	25.9	n/a	n/a

^{*}The sum of a and b is used as the denominator, and a/(a+b) and b/(a+b) are expressed as percentages. ^{**}Percentages are calculated using the total number of each solvent in the system (i.e., 642 for THF and 224 for 2-MeTHF) as the denominator.



Supplementary Fig. 25 | Time evolution of Na⁺ solvation structure in THF/2-MeTHF (5:5 v:v). a. Na⁺-P contact types (SSIP, CIP, AGG) and b. Na⁺-O coordination number as a function of simulation time. Both are averaged over two replicates and confirm structural stability over time.

Supplementary Note 3:

Supplementary Tables 12–14 summarize the ratio of THF and 2-MeTHF in each solvation shell type for 1.8M NaPF₆ in THF/2-MeTHF mixtures with varying volume ratios (3:7, 5:5, and 7:3). Across all systems, 2-MeTHF is consistently enriched in Na⁺ solvation shells relative to its bulk proportion. Additionally, analysis of R- and S-enantiomers of 2-MeTHF was also conducted and revealed no stereoselectivity in any solvation shell type under our simulation conditions.

To ensure the reliability of our structural analyses, we also evaluated the convergence of solvation structure over time. Specifically, we analyzed the evolution of Na⁺ coordination numbers with P and O atoms throughout the 50 ns production simulations (following 50 ns of equilibration). As shown in Supplementary Fig. 25, both Na–P and Na–O coordination numbers fluctuate around stable average values, confirming that the solvation shell structure is equilibrated and maintained throughout the simulation trajectory.

Supplementary Table 15. CE of Na plating and stripping in different electrolytes with various aging time.

CE (%)	0.2 hours	36 hours	168 hours	504 hours
1.8M NaPF ₆ THF/2-MeTHF	99.99	98.23	89.57	81.83
1.8M NaPF ₆ THF	99.7	98.77	76.389	-
1.0M NaPF ₆ 2-MeTHF	98.66	99.88	93.15	83.45

Supplementary Table 16. A comparative cycling performance of the anode-free Al/C-NFM with other relevant electrolyte studies

Electrolytes	Cathode	Areal Capacity (mAh/cm ²)	Current Density (mA/cm ²)	Cycle #	Decay (%/cycle)	Cell type	Ref.
1.8M NaPF ₆ in THF/2-MeTHF	NFM	1.71	0.34	150	0.06	Coin	This work
1.8M NaPF ₆ in THF/2-MeTHF	NFM	\	\	150	0.15	Pouch	This work
1M NaPF ₆ in G2/G4 (9:1 v:v)	O3-NaLNFB	0.6	0.06	50	0.28	Coin	Ref. S19
3A Zeolite modified electrolyte	O3-NaCu _{1/9} Ni _{2/9} Fe _{1/3} Mn _{1/3} O ₂	0.81	0.24	250	0.13	Coin	Ref. S20
0.1M NaBF ₄ + 0.9M NaPF ₆ in G2	Na[Cu _{1/9} Ni _{2/9} Fe _{1/3} Mn _{1/3}]O ₂	2.08	1.04	200	0.09	Coin	Ref. S15
1M NaPF ₆ in G2	Na[Cu _{1/9} Ni _{2/9} Fe _{1/3} Mn _{1/3}]O ₂	2	1	100	0.39	Coin	Ref. S15
2M NaPF ₆ in DEE	NFM	0.53	0.32	100	0.18	Coin	Ref. S28
2M NaPF ₆ in DEE	NFM	\	\	50	0.4	Pouch	Ref. S28
2M NaPF ₆ in DME	NFM	0.50	0.32	100	0.51	Coin	Ref. S28
1.2 M NaPF ₆ and 0.6 mM NaBF ₄ in DEGDEE	NFM	\	\	150	0.19	Coin	Ref. S21
1.2 M NaPF ₆ and 0.6 mM NaBF ₄ in DEGDEE	NFM	\	\	100	0.17	Pouch	Ref. S21

Supplementary Table 17. Information about NFM electrode.

Vendor	MTI Corporation
Composition	$\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$
Electrode thickness	80 μm
Al foil thickness	16 μm
Mass loading of NFM	14.05 mg/cm^2
NFM: Carbon: PVDF	95.5: 2.5: 2 (wt%)
Theoretical capacity (0.1C)	120 mAh/g

Supplementary References

- [S1] Yalkowsky S. H. et al. Solubilization of drugs by cosolvents. *Techniques of Solubilization of Drugs*, 12, 91-134 (1981).
- [S2] Zheng, J. et al. Extremely stable sodium metal batteries enabled by localized high concentration electrolytes. *ACS Energy Lett.* 3: 315-321 (2018).
- [S3] He, J. et al. Stable dendrite-free sodium–sulfur batteries enabled by a localized high-concentration electrolyte. *J. Am. Chem. Soc.* 143:20241-20248 (2021).
- [S4] Zhu, M. et al. An in-situ formed stable interface layer for high-performance sodium metal anode in a non-flammable electrolyte. *Energy Storage Mater.* 42: 145-153 (2021).
- [S5] Zhou, J. et al. Low-temperature and high-rate sodium metal batteries enabled by electrolyte chemistry. *Energy Storage Mater.* 50: 47-54 (2022).
- [S6] Jiang, R. et al. An acetamide additive stabilizing ultra-low concentration electrolyte for long-cycling and high-rate sodium metal battery. *Energy Storage Mater.* 42: 370-379 (2021).
- [S7] Ma, Y. et al. Delicately tailored ternary phosphate electrolyte promotes ultra stable cycling of $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ -based sodium metal batteries. *ACS Appl. Mater. Interfaces* 14: 17444-17453 (2022).
- [S8] Li, P. et al. Nitro fullerene as an electrolyte-compatible additive for high-performance sodium metal batteries. *Nano Energy* 89: 106396 (2021).
- [S9] Fang, W. et al. Stable sodium metal anode enhanced by advanced electrolytes with SbF_3 additive. *Rare Metals* (2020).
- [S10] Sun, Y. et al. High-safety nonaqueous electrolytes and interphases for sodium-ion batteries. *Small* 15: 1805479 (2019).
- [S11] Gao, L. et al. Revealing the chemistry of an anode-passivating electrolyte salt for high rate and stable sodium metal batteries. *J. Mater. Chem. A.* 6: 12012-12017 (2018).
- [S12] Zhou, L. et al. Engineering sodium-ion solvation structure to stabilize sodium anodes: universal strategy for fast-charging and safer sodium-ion batteries. *Nano Lett.* 20: 3247-3254 (2020).
- [S13] Yi, Q. et al. Fluorinated ether based electrolyte enabling sodium-metal batteries with exceptional cycling stability. *ACS Appl. Mater. Interfaces* 11: 46965-46972 (2019).
- [S14] Zheng, X. et al. Bridging the immiscibility of an all-fluoride fire extinguishant with highly-fluorinated electrolytes toward safe sodium metal batteries. *Energy Environ. Sci.* 13: 1788-1798 (2020).
- [S15] Li, Y. et al. Interfacial engineering to achieve an energy density of over 200 Wh kg^{-1} in sodium batteries. *Nat. Energy* 7: 511-519 (2022).

- [S16] Xu, X. et al. A room-temperature sodium–sulfur battery with high capacity and stable cycling performance. *Nat. Commun.* 9 (2018).
- [S17] He, J. et al. Tuning the solvation structure with salts for stable sodium-metal batteries. *Nat. Energy* 9, 446–456 (2024).
- [S18] Wang, C. et al. A weakly coordinating-intervention strategy for modulating Na⁺ solvation sheathes and constructing robust interphase in sodium-metal batteries. *Nat. Commun.* 15, 6292 (2024).
- [S19] Zhang, Y. Y. et al. Refined electrolyte and interfacial chemistry toward realization of high-energy anode-free rechargeable sodium batteries. *J. Am. Chem. Soc.* 145, 25643–25652 (2023).
- [S20] Lu, Z. et al. Building a beyond concentrated electrolyte for high-voltage anode-free rechargeable sodium batteries. *Angew. Chem. Int. Ed.* 61, e202200410 (2022).
- [S21] Y. Li et al. Sole-solvent high-entropy electrolyte realizes wide-temperature and high-voltage practical anode-free sodium pouch cells. *Adv. Mater.* 37, 2419764 (2025).
- [S22] Caleman, C. et al. Force field benchmark of organic liquids: Density, enthalpy of vaporization, heat capacities, surface tension, isothermal compressibility, volumetric expansion coefficient, and dielectric constant. *J Chem Theory Comput* 8, 61–74 (2012).
- [S23] Engler, B. P. et al. Viscosity and density of 2-methyltetrahydrofuran as a function of temperature [J|I]:Sandia Laboratories.
- [S24] Chew, A. K. et al. Quantifying the stability of the hydronium ion in organic solvents with molecular dynamics simulations. *Front Chem* 7, 439 (2019).
- [S25] Li, X. et al. Synthesis and luminescent properties of CaMoO₄:Tb³⁺, R⁺ (Li⁺, Na⁺, K⁺). *J Alloys Compd* 478, 684–686 (2009).
- [S26] Jow, T. R. et al. *Nonaqueous Electrolyte Development for Electrochemical Capacitors*. (1999).
- [S27] Vaidyula, R. et al. Binary solvent induced stable interphase layer for ultra-long life sodium metal batteries. *Adv. Mater.*, 36, 202312508 (2024).
- [S28] Zou Y. et al. Electrolyte solvation engineering stabilizing anode-free sodium metal battery with 4.0 V-class layered oxide cathode. *Adv. Mater.*, 36, 2410261 (2024).