

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

Corresponding Author: Professor Fang Liu

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The manuscript tries to address the interfacial challenges of anode-free sodium batteries by directing the two different selective solvents to achieve optimal stability at both electrodes. Its novelty remains to be verified. The proposed electrolyte is limited and only Na-Cu and half coin cells for NFM (Na-NFM and Al/C-NFM) cathodes were tested. Because ether solvents are very compatible with sodium metal, we have reason to believe that only the weakly bonded THF solvent has a protective effect on NFM. It is hard to link this single experimental phenomenon with the universal law that "solvents in the solvation shell protect the anode, and free or weakly bonded solvents protect the cathode." However, the performance of anode-free Al/C-NFM and Na-NFM is impressive, thus, I think this manuscript is suitable for publication after major revision.

1. Could you provide other electrolytes following your proposed principle? The electrolytes proposed in other published papers are also OK, the most important is that there are still other samples meeting the design principle you proposed.
2. The lack of a pouch cell test reduces the experiment's credibility. It is suggested to add the test data of the Na-NFM or anode-free Al/C-NFM.
3. I wonder if there are any differences among the three electrolytes' electrochemical behaviors, so it is recommended to supplement CV of the three electrolytes under 25oC and -30oC.
4. Although there is a comparative analysis of the cycling performances of the Na||Cu cells in this work and other relevant studies on electrolytes, it is strongly recommended to supplement the comparative cycling performances of the anode-free Al/C-NFM in this work and other relevant studies on electrolytes.

Reviewer #2

(Remarks to the Author)

The manuscript entitled "Directing Selective Solvent Presentations at Electrochemical Interfaces to Enable Anode-Free Sodium Metal Batteries" presents an electrolyte regulation strategy aimed at directing selective solvent presentations to enhance the interphases of both the anode and cathode. The authors demonstrate that anode stability is influenced by solvents within the solvation sheath of Na ions, while cathode stability primarily depends on weakly solvated solvents. Consequently, an electrolyte incorporating two distinct solvents is designed to comprehensively improve the performance of both the anode and cathode. The anode-free sodium cells exhibit excellent cycling performance with a high loading of cathode materials. Nevertheless, several issues must be addressed before I can recommend this work for publication in Nature Communications.

1. Three kinds of electrolytes were compared in the manuscript. Why is the concentration of NaPF6 different in the electrolytes? How do the authors determine to explore the certain concentration? For 1.8 M NaPF6-THF, will the anode stability be significantly improved after improving the concentration to the saturated state?
2. The authors have made some MD simulations and revealed that 2-MeTHF can bind with Na⁺ stronger than THF. The solvation free energy is simulated to elucidate it. However, the saturated concentration of NaPF6 in THF is higher than MeTHF. How to explain the discrepancy? In addition, the 2-MeTHF-based electrolyte promotes more CIPs rather than SSIPs compared to that of THF, which also seems to be not consistent with the stronger solvation capability of 2-MeTHF.
3. The normalized impedance in Page 13 is meaningless when the Ω/cm^2 is used. The normalization with Ωcm^2 can avoid

the effect of the electrode geometric area while Ω/cm^2 cannot. Please correct it.

4. For the Na-Cu cells, the 1M NaPF₆ in 2-MeTHF can not facilitate the long-term cycling. The ionic conductivity is ascribed as the reason while it is 2.3 mS cm^{-1} which is not too low. The impedance experiments may be needed to confirm the hypothesis.

5. The LSV in figure 5a shows the low oxidation stability for 1 M NaPF₆-2-MeTHF. However, the Na-NFM cells seem to work with high Coulombic efficiencies in the three kinds of electrolytes. How to confirm the fading capacity is not from the anode stability for 1 M NaPF₆-2-MeTHF and 1.8 M NaPF₆-THF?

6. The high-loading cathode is promising to the practical application in the Na-NFM cell and anode-free cell. However, the materials or the cathode foils are not supplied with the purchase or detailed preparation process. It is not conducive to repeat the experiments.

Reviewer #3

(Remarks to the Author)

Review primarily addresses MD simulations. For note, comment 1-7 from early career researcher.

1. Check cross references between the main text and SI documents. The SI references numbered main-text sections, but no section numbering appears in the main text document.

2. Can you comment more on the rescaling of Na⁺ and PF₆⁻ OPLS-AA/OPLS-2009IL parameters to simulation polarization effects? Is this strictly the $\pm 0.8e$ rescaling of the charge parameter described in the abstracted of the cited article? Or are there other rescalings?

3. The cited article (Doherty et al.) cautions that rescaling charges can degrade local intermolecular interactions at short ranges, which would seem to challenge the solvation shell speciation results characterizing your main hypotheses about what provides anode and cathode stability. Can you comment on why this isn't a problem for your system?

4. Figure 4(c): The Na surface morphology definitely looks a lot better with the mixed THF/2-MeTHF electrolyte than with either single electrolyte alone. Can you talk more about the conditions under which the SEM imaging was done? Is this smooth morphology what the surface looks like after 5000 h or 400 cycles? Or is this what it looks like at the time the first cell with a single THF or 2-MeTHF electrolyte fails?

5. For the MD simulations, can you comment on the average density attained by each system in the final NPT equilibration and production periods? Does this differ significantly from the initial density you specified in Supplementary Table 3, or from the experimentally measured density of the THF, 2-MeTHF, and THF/2-MeTHF electrolyte solutions? This might help reinforce your conclusions about the cutoff radius used to define a solvation shell and thus your speciation analysis.

6. Did you investigate compositions other than a 1:1 v:v composition for the mixed THF/2-MeTHF solvent, either in experiment or in the MD simulations? Can you comment on why you chose a 1:1 v:v ratio?

7. Out of curiosity, in the MD simulations, are the AGG ($P = 2$), AGG ($P = 3$), AGG ($P \geq 4$), CIP, or SSIP shells stereoselective towards either 2-MeTHF enantiomer? I'm guessing they aren't, but there are some reports of enantiodiscriminatory electrochemical devices (e.g., 10.1016/j.chempr.2023.11.001). Stereoselectivity by electrode might also inform design guidelines for functionalizing solvent molecules in ways that further optimize each electrode's stability.

8. The authors report and comment on the significance of single-ion solvation free energies in each electrolyte. Are surface potentials of the respective electrolytes reflected in the single-ion values? Single-ion free energies computed in periodic boundaries require determination of the solvent surface potential from a slab calculation. (These cancel for ion pairs, so the Na + PF₆ result will be unaffected) Also, did you use the soft-core potential? Is 5 ns enough time to sample the local coordination environment sufficiently? If you doubled the simulation time per window, do your results change? Are these NVT ensemble calculations?

9. The authors write, "Finally, a 50 ns production simulation was performed at the same temperature and pressure as the NPT equilibration and using the same thermostat and barostat." Do the authors mean "... was performed in the NVT ensemble with the average box size taken from the NPT equilibration procedure"?

10. The authors write, "Van der Waals interactions were modeled using a shifted Lennard-Jones potential that smoothly transitioned to zero at 1.3 nm." Truncating the Lennard-Jones potential is known to cause issues with transport properties which can effect relaxation times in simulation. This issue is remedied by using the long-range correction (or the PME LJ potential). It would be helpful to show the evolution of the Na-P, Na-O coordination numbers vs time to show that they have stabilized. Analysis of the coordination environment would be more convincing this way.

11. The authors write, "All systems were independently simulated and analyzed twice to quantify uncertainty in simulation measurements." Do the authors mean they generated multiple replicates with each starting from different initial configurations?

12. Related to point 2, have the authors considered computing transport properties (e.g., self-diffusion + viscosity correction, total ionic conductivity - compare with figures in Fig 3b, transference number, ionicity) to compare against experiment to validate their force field? How do densities compare between experiment and theory for each of these electrolytes?

Comparison of predicted speciation against Raman bands is very good for 1.8 M NaPF₆ in THF but much less so for 1.0 NaPF₆ in 2MeTHF. Given the issues with the 2MeTHF electrolyte, the excellent agreement between the speciation in Fig 2d and Supp Fig 4c could also just be fortuitous.

13. Can the authors use density functional theory to identify the oxidation mechanism of 2-MeTHF occurring at ~3.4 V? Or cite a reference if known.

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

It can be accepted now.

Reviewer #2

(Remarks to the Author)

Previous questions have been addressed, it is now recommended for acceptance.

Reviewer #3

(Remarks to the Author)

The simulation team really knocked this out of the park. Quite pleased to see the extensive analysis to confirm the simulations results are reasonably converged, best exemplified in Figs S22 and S25. Happy to support publication.

Reviewer #4

(Remarks to the Author)

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

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A point-to-point response to referee' comments (in black)

Referee #1 (Remarks to the Author):

The manuscript tries to address the interfacial challenges of anode-free sodium batteries by directing the two different selective solvents to achieve optimal stability at both electrodes. Its novelty remains to be verified. The proposed electrolyte is limited and only Na-Cu and half coin cells for NFM (Na-NFM and Al/C-NFM) cathodes were tested. Because ether solvents are very compatible with sodium metal, we have reason to believe that only the weakly bonded THF solvent has a protective effect on NFM. It is hard to link this single experimental phenomenon with the universal law that "solvents in the solvation shell protect the anode, and free or weakly bonded solvents protect the cathode."

However, the performance of anode-free Al/C-NFM and Na-NFM is impressive, thus, I think this manuscript is suitable for publication after major revision.

Response:

We thank the referee for reviewing our manuscript and offering valuable suggestions. We are glad that the referee acknowledges our achievement in advancing the electrochemical performances of anode-free Al/C-NFM and Na-NFM cells. We appreciate the reviewer's concern regarding whether other electrolytes follow the proposed principle, and we have systematically addressed this point in our response to Referee #1's Comment 1.

1. Could you provide other electrolytes following your proposed principle? The electrolytes proposed in other published papers are also OK, the most important is that there are still other samples meeting the design principle you proposed.

Response:

We thank the referee for this great suggestion. This electrolyte design principle of selective solvent presentation is proposed and demonstrated here for the first time, but there are previous electrolyte combinations that inadvertently fall into this category. Here, we present three prior works that follow the same working mechanism and added corresponding discussion in the revised manuscript.

First, we refer to the work by Li et al.¹, where the authors developed 1M LiDFOB in ethyl mesylate (EM) and ethyl acetate (EA) for Li-ion batteries. Molecular dynamics (MD) simulations revealed that EA dominantly coordinates with Li⁺ ions and EM largely remains in the free solvent state (Fig. R1a). EA exhibits better stability between the two solvents under reductive conditions, whereas EM is more stable under oxidative conditions. The introduction of EA played a dominating role in anode and significantly improved the specific capacity of Gr-Li half cells (Fig. R1b). Meanwhile, EM played a dominating role in cathode and improved the oxidation capability of the LiDFOB/EM/EA electrolyte (Fig. R1c). These results show that the coordinated EA improves anode stability, and the free EM enhances oxidative stability.

Second, we refer to the work by Wang et al.², where the authors developed 1M LiFSI/6FDMH-DME electrolyte (1,6-dimethoxyhexane is denoted as 6FDMH). MD simulations revealed that DME dominantly stays in the first solvation shell, and FDMH remained mainly in the free solvent state (Fig. R1d). DME exhibits better stability between the two solvents under reductive conditions (Fig. R1e), whereas FDMH is more stable under oxidative conditions (Fig. R1f). The introduction

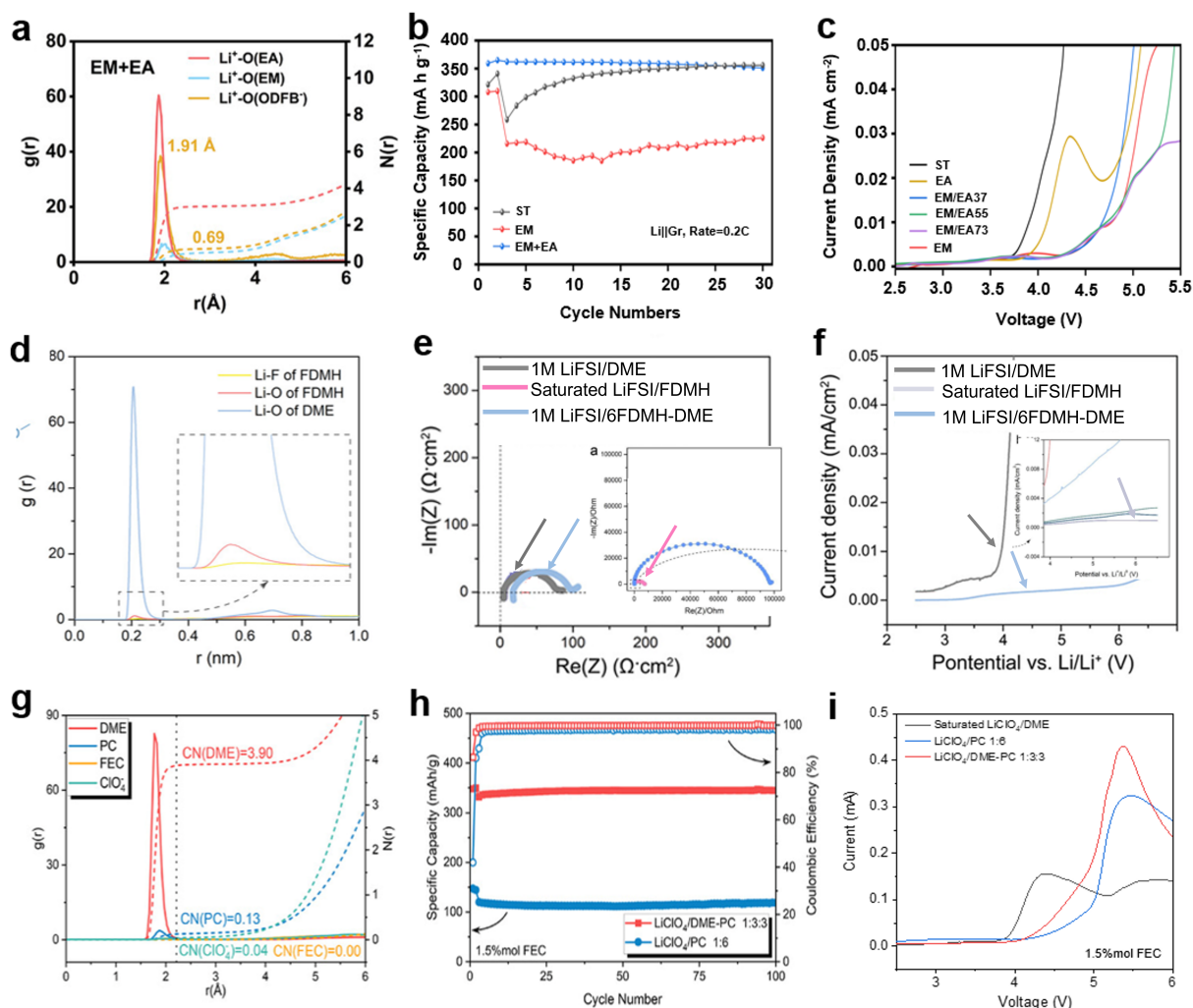


Fig. R1 | a. The radial distribution function of Li^+ in LiDFOB/EM/EA electrolyte. b. Galvanostatic cycling performance of Gr-Li half cells with various electrolytes. c. Oxidative stability characterized by LSV for Steel-Li cells with 0.5 mV/s scan rate. d. The radial distribution function of Li^+ in 1M LiFSI/6FDMH-DME electrolyte. e. Impedance of Li||Li symmetric cells. f. Oxidative stability characterized by LSV for Al-Li cells with 1 mV/s scan rate. g. the radial distribution function of solvents. h. Galvanostatic cycling performance of graphite-Li half-cell with two different electrolytes (1.5%mol FEC), current density is 20 mA g^{-1} for the first two cycles and then 100 mA g^{-1} for the subsequent cycle. i. Oxidative stability characterized by LSV for Al-Li cells with 0.1 mV/s scan rate. Arrows in e and f are pointing to the samples of interest. Results in a-c are extracted from reference 1, d-f from reference 2, and g-h from reference 3.

of DME played a dominating role in anode and significantly reduced the Li symmetric cell impedance, indicating a lower interfacial resistance than the cell with saturated LiFSI/FDMH electrolyte (Fig. R1e). Meanwhile, the addition of FDMH played a dominating role in cathode and enhanced the oxidative stability of the electrolyte mixture (Fig. R1f). These results show that the coordinated DME in improves Li metal stability, and the free FDMH enhances oxidative stability.

Third, we refer to the study by Chen et al.³, in which the authors studied LiClO₄ in DME-PC electrolyte. MD simulations revealed that DME dominantly stays in the first solvation shell, and PC largely remains in the free solvent state (Fig. R1g). DME exhibits better stability between the two solvents under reductive conditions, whereas PC is more stable under oxidative conditions. The introduction of DME played a dominating role in anode and delivered a high reversible capacity of 345 mAh g⁻¹ and an initial CE of 86.47 %, both of which are far higher than those of the half-cell with LiClO₄/PC (1:6) electrolyte with 1.5% mol FEC (Fig. R1h). Due to the lack of electrochemical testing of oxidation stability in this work, we prepared and tested the LSV curves of the electrolytes shown in label to evaluate the oxidation stability. We found the addition of PC played a dominating role in cathode and enhanced the oxidative stability of the electrolyte mixture (Fig. R1i). These results show that the coordinated DME improves anode stability, and the free PC enhances oxidative stability.

References:

1. Li et al. A new strategy for sulfone-containing electrolytes design enabling long cycling high-voltage lithium-ion batteries. *Adv. Funct. Mater.* 241687(2025).
2. Wang et al. Dual-solvent Li-ion solvation enables high-performance Li-metal batteries. *Adv. Mater.* **33**, 2008619(2021).
3. Chen et al. Identifying the role of solvation entropy for the solvation chemistry in non-aqueous electrolytes. *Angew. Chem. Int. Ed.* e202501315(2025).

Main Text Page 17 Line 467 to Line 471: “This electrolyte design principle of selective solvent presentation is proposed and demonstrated here for the first time, but there are previous electrolyte combinations that inadvertently fall into this category, such as LiDFOB/EM/EA electrolyte³⁰ and LiClO₄/DME/PC electrolyte for Li-ion batteries³¹ and LiFSI/6FDMH/DME for Li-metal batteries³². ”

Main Text Reference Page 22 Line 643 to Line 648: “[30] Li et al. A new strategy for sulfone-containing electrolytes design enabling long cycling high-voltage lithium-ion batteries. *Adv. Funct. Mater.* 241687(2025). [31] Wang et al. Dual-solvent Li-ion solvation enables high-performance Li-metal batteries. *Adv. Mater.* **33**, 2008619(2021). [32] Chen et al. Identifying the role of solvation entropy for the solvation chemistry in non-aqueous Electrolytes. *Angew. Chem. Int. Ed.* e202501315(2025). ”

2. The lack of a pouch cell test reduces the experiment's credibility. It is suggested to add the test data of the Na-NFM or anode-free Al/C-NFM.

Response:

We thank the referee for this suggestion. Per the referee's request, we have tested anode-free Cu-NFM pouch cell purchased from Li-Fun Technology and included the results in the revised manuscript. The corresponding figure, discussion, and method section are also included here for the referee's convenience.

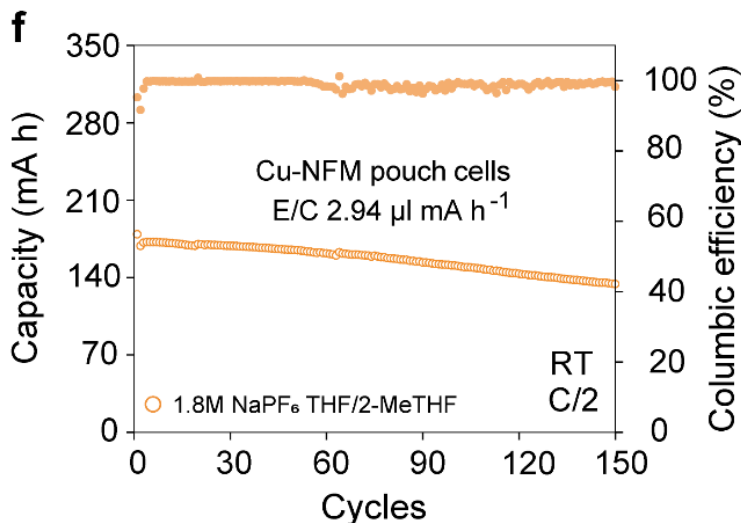


Fig. 6 | f. Cycling performance of the anode-free pouch cell at 0.5C rate.

Main Text Page 17 Line 457 to Line 460: “We further tested the electrolyte in a multilayer anode-free pouch cell with NFM cathodes under lean electrolyte conditions (E/C ratio= $2.94 \mu\text{L}/\text{mAh}$), which delivered an initial capacity of 171.6 mAh at 0.5 C rate ($1C = 170 \text{ mAh}$) and maintained a reversible capacity of 78.17% after 150 cycles at room temperature (Fig. 6f).”

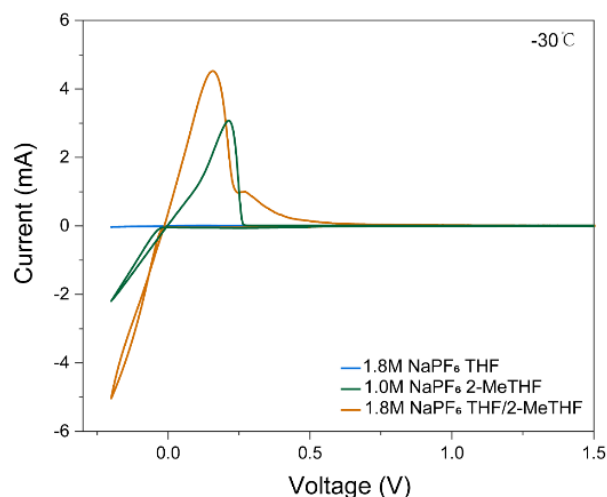
Main Text Methods Page 18 Line 504 to Line 510: “Dry Cu-NFM pouch cells with a capacity around 170 mAh were purchased from Li-Fun Technology and used as received. 0.5 mL of electrolyte was used in each cell ($E/C = 2.94 \mu\text{L}/\text{mAh}$), and the cells were vacuum-sealed at -90 kPa using an MSK-115A (MTI corporation) vacuum sealer. The pouch cells were rested at the open-circuit voltage for 24 hours and went through two formation cycles under a current of 20 mA. Long-term cycling stability test was conducted at 0.5C-rate between 2 - 3.8V.”

3. I wonder if there are any differences among the three electrolytes' electrochemical behaviors, so it is recommended to supplement CV of the three electrolytes under 25 °C and -30 °C.

Response:

We thank the referee for this suggestion. Temperature indeed affects the physical property, kinetics, and stability of the electrolytes. Per the referee's request, we performed cyclic

voltammetry with these three electrolytes under $-30\text{ }^{\circ}\text{C}$ and included the results in the revised manuscript. The corresponding figure, discussion, and method section are also included here for the referee's convenience.



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

Main Text Page 16 Line 446 to Line 450: “At $-30\text{ }^{\circ}\text{C}$, 1.0M NaPF_6 in 2-MeTHF and 1.8M NaPF_6 in THF/2-MeTHF exhibit reversible sodium stripping and plating behaviors (Supplementary Fig. 20), while 1.8M NaPF_6 in THF failed to cycle due to solidification. This observation is consistent with our previous DSC results (Supplementary Fig. 19), which show that 1.8M NaPF_6 in THF has a melting temperature of $-21\text{ }^{\circ}\text{C}$. ”

Main Text Methods Page 18 Line 510 to Line 511: “The cyclic voltammetry tests were carried out over a voltage range of -0.2 to 1.5 V for Cu-Na cells at 5 mV/s under room temperature and -30°C . ”

4. Although there is a comparative analysis of the cycling performances of the Na||Cu cells in this work and other relevant studies on electrolytes, it is strongly recommended to supplement the comparative cycling performances of the anode-free Al/C-NFM in this work and other relevant studies on electrolytes.

Response:

We thank the referee for this suggestion. We have summarized the cycling performances of the anode-free Al/C-NFM with other relevant studies (Supplementary Table 16). Despite the high areal capacity, our anode-free cells show excellent electrochemical stability, presenting the lowest degradation rate of $0.06\%/cycle$ in coin cells and $0.15\%/cycle$ in pouch cell. The table and discussion have been added to the revised manuscript and listed below for the referee's convenience.

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

Electrolytes	Cathode	Areal Capacity (mAh/cm ²)	Current Density (mA/cm ²)	Cycle #	Decay (%/cycle)	Cell type	Ref.
1.8M NaPF₆ in THF/2-MeTHF	NFM	1.71	0.38	150	0.06	Coin	This work
1.8M NaPF₆ in THF/2-MeTHF	NFM	\	\	150	0.15	Pouch	This work
1M NaPF ₆ in G2/G4 (9:1 v:v)	O3-NaLNFMB	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. 23
2M NaPF ₆ in DEE	NFM	\	\	50	0.4	Pouch	Ref. 23
2M NaPF ₆ in DME	NFM	0.50	0.32	100	0.51	Coin	Ref. 23
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

Main Text Page 17 Line 460 to Line 464: “Benefiting from this design principle of selective solvent presentation, this new electrolyte of 1.8M NaPF₆ in THF/2-MeTHF enables the extremely stable cycling of anode-free sodium metal batteries, presenting exceptionally low degradation rate of 0.06%/cycle in coin cells and 0.15%/cycle in pouch cell, which are the lowest among literature (Supplementary Table 16).”

SI Reference Page 41 Line 470 to Line 475: “[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).”

Referee #2 (Remarks to the Author):

The manuscript entitled “Directing Selective Solvent Presentations at Electrochemical Interfaces to Enable Anode-Free Sodium Metal Batteries” presents an electrolyte regulation strategy aimed at directing selective solvent presentations to enhance the interphases of both the anode and cathode. The authors demonstrate that anode stability is influenced by solvents within the solvation sheath of Na ions, while cathode stability primarily depends on weakly solvated solvents. Consequently, an electrolyte incorporating two distinct solvents is designed to comprehensively improve the performance of both the anode and cathode.

The anode-free sodium cells exhibit excellent cycling performance with a high loading of cathode materials. Nevertheless, several issues must be addressed before I can recommend this work for publication in Nature Communications.

Response:

We thank the referee for reviewing our manuscript and offering constructive suggestions. We are glad that the referee acknowledges our work's excellent electrochemical performances. We have addressed the issues raised by the referee and incorporated the referee's suggestions into the revised manuscript.

1a. Three kinds of electrolytes were compared in the manuscript. Why is the concentration of NaPF₆ different in the electrolytes? How do the authors determine to explore the certain concentration?

Response:

The concentrations of NaPF₆ in THF, 2-MeTHF and their mixture were chosen based on their solubility. We have included the experimental details, calculation and discussions in the revised manuscript, SI, which were also attached below for the referee's convenience.

SI Supplementary Note 1 Page 2 Line 28 to Line 43: “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},

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

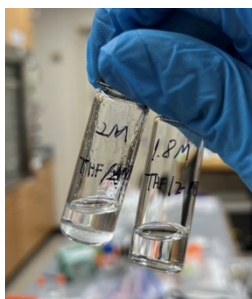
where X_m represents the salt solubility of the binary mixture, f_1 and f_2 are the solvent volume fractions of solvents 1 and 2 in the solvent mixture, X_1 and X_2 represent the solubilities of salt in solvents 1 and 2, respectively. Based on the calculation, the estimated solubility of NaPF₆ in THF/2-MeTHF 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.”

Main Text Page 4 Line 114 to Line 116: “The salt concentration in these electrolytes was chosen based on the solubility of NaPF₆ in THF, 2-MeTHF and their mixture (Supplementary Fig. 1, Supplementary Note 1, Supplementary Table 4).”

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 the equation S1.*



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

1b. For 1.8 M NaPF₆-THF, will the anode stability be significantly improved after improving the concentration to the saturated state?

Response:

We thank the referee for this question. Higher salt concentration will lead to improved anode stability. To eliminate the influence of salt concentration in the comparison with 1.8M NaPF₆ in THF/2-MeTHF, we selected 1.8M NaPF₆ in THF instead of saturated NaPF₆ in THF.

Per the referee’s request, we further tested the anode stability of saturated NaPF₆ in THF electrolyte in Cu-Na half cells (Fig. R2). First, we compared the electrochemical behaviors of these three electrolytes during the 1st cycle, all three electrolytes exhibit low Na stripping/plating overpotential. Although the saturated NaPF₆ in THF cell shows slightly higher ICE compared to 1.8M NaPF₆ in THF (81.72% vs. 74.31%), both cells with pure THF show obviously low ICE in comparison with 1.8M NaPF₆ in THF/2-MeTHF cell (93.52%), which demonstrates poor stability against Na (Fig. R2a). In addition, these three cells behave quite differently during the first 10 cycles. 1.8M NaPF₆ in THF/2-MeTHF cell quickly stabilized at 99.9%, while the other two show large fluctuations and cannot be stabilized in the first 10 cycles (Fig.R2b). We further calculate the average CE of three electrolytes for the first ten cycles. Cu-Na cells with 1.8M NaPF₆ in THF/2-MeTHF (99.22%) shows a much higher average CE compared with 1.8M NaPF₆ in THF (95.8%) and saturated NaPF₆ in THF (93.22%), which indicates that the THF/2-MeTHF mixture electrolyte has less capacity loss at the initial stage of cycling and thus extends the life of the AF-SMBs (Fig.

R2c). In terms of long-term stability, both cells with pure THF-based electrolytes show obvious fluctuations in CEs, indicating unstable interface between electrolytes and Na metal (Fig. R2d). In conclusion, saturated NaPF₆ in THF exhibits a slightly better electrochemical stability compared to 1.8M NaPF₆ in THF, but remains less stable compared to 1.8M NaPF₆ in THF/2-MeTHF due to the lack of 2-MeTHF to stabilize anode.

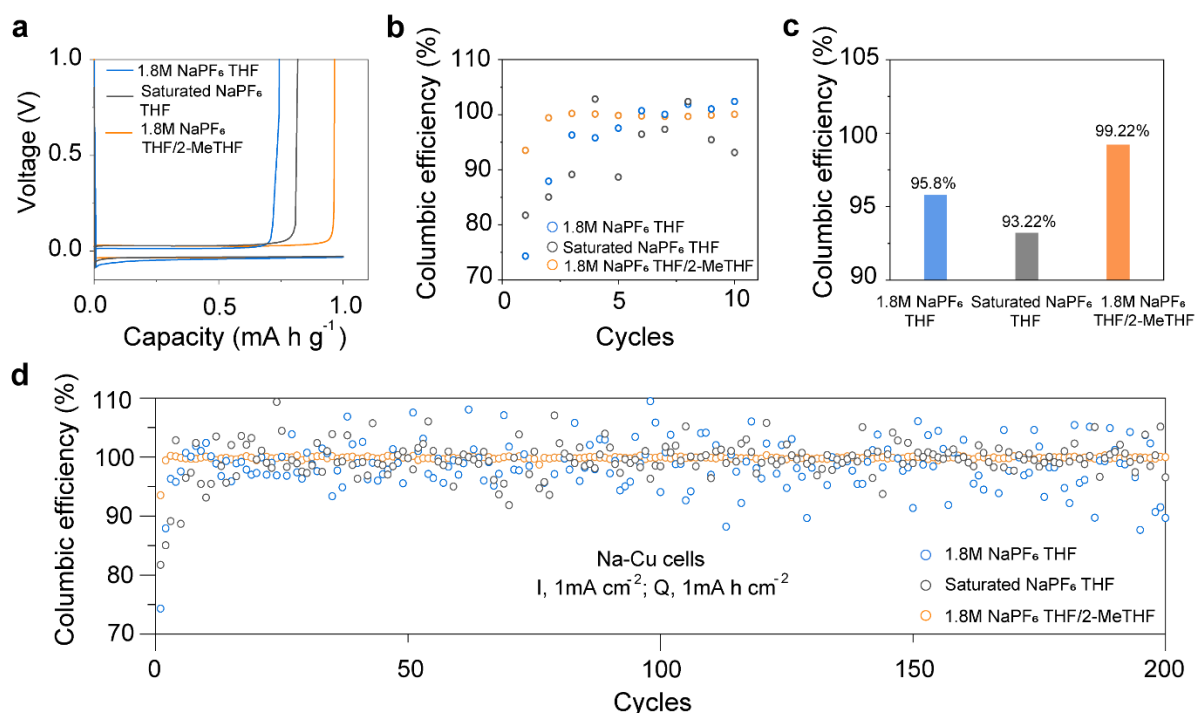


Figure R2 | a. 1st cycle voltage profile with investigated electrolytes. b. First ten cycles of plating-stripping Coulombic efficiency. c. The average CE of three electrolytes for the first ten cycles. d. Coulombic efficiencies of Na-Cu cells with different electrolytes.

2. The authors have made some MD simulations and revealed that 2-MeTHF can bind with Na⁺ stronger than THF. The solvation free energy is simulated to elucidate it. However, the saturated concentration of NaPF₆ in THF is higher than MeTHF. How to explain the discrepancy? In addition, the 2-MeTHF-based electrolyte promotes more CIPs rather than SSIPs compared to that of THF, which also seems to be not consistent with the stronger solvation capability of 2-MeTHF.

Response:

In our initial submission, we indicated that 2-MeTHF leads to a lower solvation free energy for Na⁺ while THF leads to a lower solvation free energy for PF₆⁻. In the revision, we have recalculated the solvation free energies to account for correction terms as suggested by Reviewer 3 (see Comment 8, below), but these trends have not changed – 2-MeTHF consistently shows a stronger affinity for Na⁺ than THF. What we computed but did not discuss in the initial submission was the total solvation free energy associated with introducing an Na⁺ and PF₆⁻ ion pair – as opposed to single ions – into the various electrolyte solutions. This free energy, which would correspond to the overall affinity of the ion pair for the solvent, was lowest for THF compared to 2-MeTHF or any of the THF/2-MeTHF mixtures. We attribute this to the strong solvation of PF₆⁻

by THF. Since we expect the saturated concentration of NaPF₆ to depend on the affinity of the solvent for both Na⁺ and PF₆⁻, the solvation free energy computed for the ion pair is consistent with the experimental finding that THF promotes a higher saturation concentration than 2-MeTHF. Similarly, the enrichment of CIPs in 2-MeTHF compared to THF is likely due to less favorable solvation of PF₆⁻ than in THF, which would promote ion pairing. Thus, while 2-MeTHF preferentially solvates Na⁺, leading to its enrichment in solvation shells as found in all THF/2-MeTHF mixtures, the overall solvation affinity of THF when considering both Na⁺ and PF₆⁻ explains the higher saturated concentration of NaPF₆ and higher fraction of SSIPs, with both trends attributed to the solvation of PF₆⁻.

SI Page 25 Line 280 to Line 285: “Although 2-MeTHF exhibits stronger solvation of Na⁺ than THF, PF₆⁻ is more favorably solvated by THF. As a result, the total solvation free energy for NaPF₆ is lowest in THF among all solvents and mixtures studies (Supplementary Tables 10 and 11). This is consistent with the experimentally observed higher saturation concentration of NaPF₆ in THF compared to 2-MeTHF. The results indicate that the solvation behavior of both ions, not just Na⁺, must be considered when interpreting solubility trends.”

3. The normalized impedance in Page 13 is meaningless when the Ω/cm^2 is used. The normalization with $\Omega \text{ cm}^2$ can avoid the effect of the electrode geometric area while Ω/cm^2 cannot. Please correct it.

Response:

We thank the referee for pointing this out. We have revised the corresponding figures (Fig. 6a) and discussions, which are also listed below for the referee’s convenience.

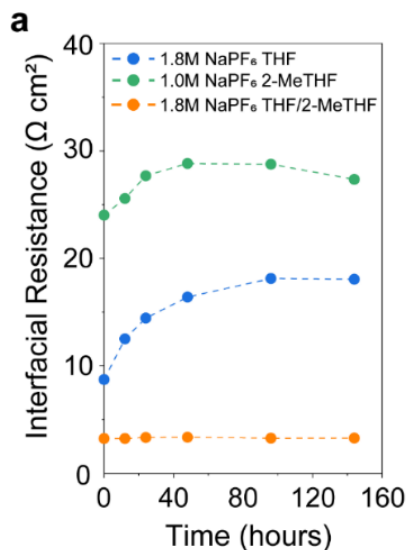


Fig. 6 | a. Time-dependent changes of interfacial resistance in Na-Na coin cells.

Main Text Page 14 Line 388 to Line 394: “Among these three electrolytes, the Na electrode in 1.8M NaPF₆ in THF/2-MeTHF has a significantly lower interfacial resistance (3.25 $\Omega \text{ cm}^2$),

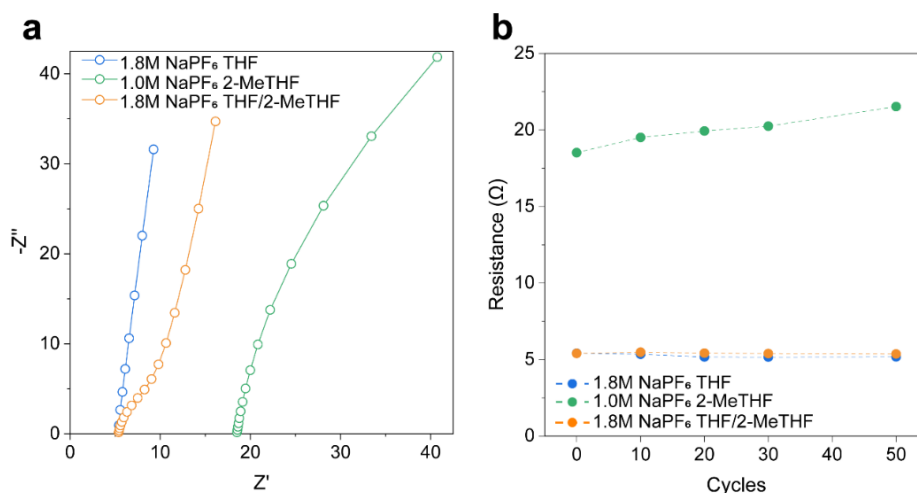
compared to that in 1.8M NaPF₆ in THF (8.73 Ω cm²) and 1M NaPF₆ in 2-MeTHF (24.02 Ω cm²), indicating the formation of a thin and ionically conductive SEI. We further monitored the evolution of interfacial resistance in these electrolytes during resting (Fig. 6a-b). The cell with 1.8M NaPF₆ in THF exhibits a dramatic increase in interfacial resistance, rising from 8.73 to 18.06 Ω cm², representing a 2.1-fold increase over 5 days.”

4. For the Na-Cu cells, the 1M NaPF₆ in 2-MeTHF can not facilitate the long-term cycling. The ionic conductivity is ascribed as the reason while it is 2.3 mS cm⁻¹ which is not too low. The impedance experiments may be needed to confirm the hypothesis.

Response:

We thank the referee for this comment. We would like to clarify that the differences in electrochemical kinetics and stability are not solely attributed to differences in ionic conductivity (Fig. 3b), but are more significantly influenced by AGGs content in the electrolytes (Fig. 2d). This is because negatively charged AGG species are preferentially transported to the anode surface due to the presence of the electrical double layer during charging. Since the AGG contents in 1M NaPF₆ in 2-MeTHF (10.3%) is much lower compared to the other two electrolytes (43.6% in 1.8M NaPF₆ in THF, 31.7% in 1.8M NaPF₆ in THF/2-MeTHF), it couldn't offer fast electrochemical kinetics or facilitate long-term cycling.

Per the referee's request, we also conducted EIS measurement and monitored the evolution of solution resistance using Cu-Na half cells with different electrolytes. First, we measured the solution resistance of three electrolytes before cycling. As shown in Supplementary Fig. 10a, the cell with 1.0M NaPF₆ in 2-MeTHF presented the highest impedance (18.52 Ω) compared to that in 1.8M NaPF₆ in THF (5.41 Ω) and 1.8M NaPF₆ in THF/2-MeTHF (5.40 Ω), indicating a much lower ionic conductivity. Moreover, as Na plating/stripping proceeds to 50 cycles, the solution resistance of the cell with 1.0M NaPF₆ in 2-MeTHF increases significantly from 18.52 Ω to 23.53 Ω (Supplementary Fig. 10b), whereas the other two cells have minimum changes in solution resistance. This result indicates that the difference in ionic conductivity between the electrolytes becomes more pronounced with continued cycling.



Supplementary Fig. 10 | a. EIS measure of Cu-Na 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

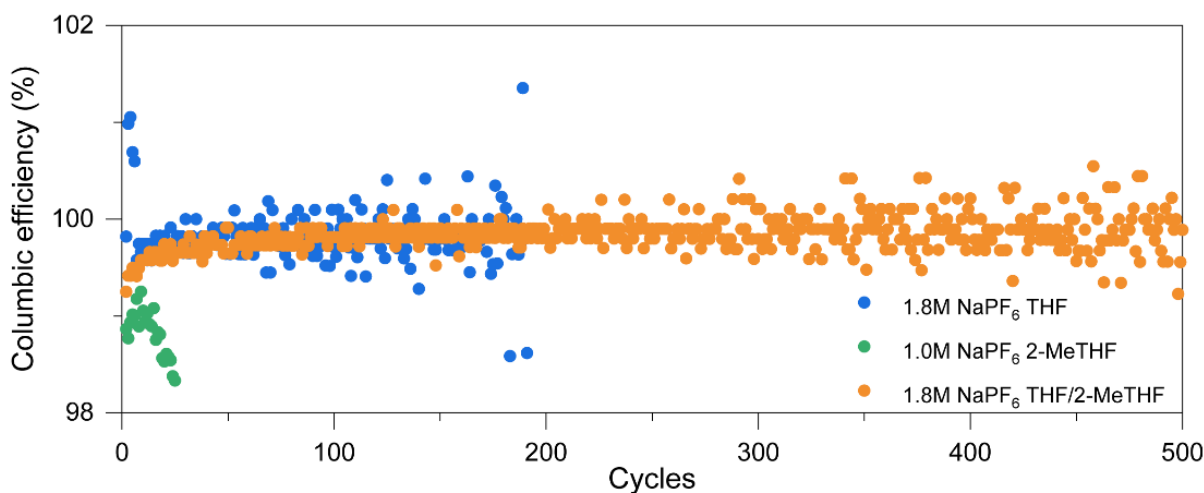
of interfacial resistance in Cu-Na coin cells. All cells were cycled under I , 1 mA cm^{-2} , Q , 1 mAh, cm^{-2} condition.

Main Text Page 8 Line 256 to Line 263: “We conducted EIS measurement to monitor solution resistance in Cu–Na half-cells containing different electrolytes. Initially, the cell with 1.0 M NaPF₆ in 2-MeTHF exhibited significantly higher impedance (18.52 Ω) than cells with 1.8 M NaPF₆ in THF (5.41 Ω) and 1.8 M NaPF₆ in THF/2-MeTHF (5.40 Ω), indicating lower ionic conductivity (Supplementary Fig. 10a). After 50 cycles, this resistance increased notably to 23.53 Ω for the 1.0 M NaPF₆ in 2-MeTHF electrolyte while remaining stable for the other two electrolytes, indicating that the difference in ionic conductivity between the electrolytes becomes more pronounced with continued cycling (Supplementary Fig. 10b).”

5a. The LSV in figure 5a shows the low oxidation stability for 1 M NaPF₆-2-MeTHF. However, the Na-NFM cells seem to work with high Coulombic efficiencies in the three kinds of electrolytes.

Response:

Thanks for the comment. We would like to clarify that Na-NFM half-cells with 1.0M NaPF₆ in 2-MeTHF exhibit significantly lower CE than cells with 1.8M NaPF₆ in THF and 1.8M NaPF₆ in THF/2-MeTHF, which is more obvious in the enlarged figure of Fig. 5d, shown in Supplementary Fig. 16. The corresponding figure have been added to the revised manuscript and also included here for the referee’s convenience.



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

Main Text Page 12 Line 345 to Line 347: “After 25 cycles, the cell exhibits rapid capacity decay, only maintaining 74.5% of its initial capacity with dramatically increased overpotentials (Fig. 5f, Supplementary Fig. 15) and decreased CEs (Supplementary Fig. 16).”

5b. How to confirm the fading capacity is not from the anode stability for 1 M NaPF₆-2-MeTHF and 1.8 M NaPF₆-THF?

Response:

We would like to clarify that Na-NFM cells in Figure 5d are half cells with a significant excess of Na (corresponding to 97.23 mAh, which is 50.91 times of cathode capacity). Even with some side reactions occurring at the Na anode, due to the significant excess of Na, the capacity and CE of half cells mainly reflect the electrochemical behavior of electrolytes at the NFM cathode.

Main Text Methods Page 18 Line 489 to Line 491: “High-purity sodium chips (MTI corporation, 15.6 mm in diameter, 0.45 mm in thickness, total capacity of 97.23 mAh) were used in NFM-Na half cells, Cu–Na half cells, and Na-Na symmetric cells.”

6. The high-loading cathode is promising to the practical application in the Na-NFM cell and anode-free cell. However, the materials or the cathode foils are not supplied with the purchase or detailed preparation process. It is not conducive to repeat the experiments.

Response:

We thank the referee for this comment and apologize for the incomplete information on the electrode. We incorporated detailed information on the electrode in the Supplementary Information, and also include here for the referee’s convenience.

Main Text Methods Page 18 Line 487 to Line 489: “The single-side coated layered oxide NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ cathode purchased from MTI Corporation and used as received. The detailed information on the electrode is shown in Supplementary Table 17.”

Supplementary Table 17. Information about NFM electrode.

Vendor	MTI Corporation
Composition	NaNi _{1/3} Fe _{1/3} Mn _{1/3} O ₂
Electrode thickness	80 μm
Al foil thickness	16 μm
Mass loading of NFM	15.88 mg/cm ²
NFM: Carbon: PVDF	95.5: 2.5: 2 (wt%)
Theoretical capacity (0.1C)	120 mAh/g

Referee #3 (Remarks to the Author):

Review primarily addresses MD simulations. For note, comment 1-7 from early career researcher.

Response:

We thank the referee for reviewing our manuscript and offering constructive feedback. We have revised the manuscript based on the referee's comments.

1. Check cross references between the main text and SI documents. The SI references numbered main-text sections, but no section numbering appears in the main text document.

Response:

We thank the referee for pointing this out. We have removed all the cross references in the SI and updated the reference numbers in the revised manuscript.

Deleted Text from Page 21 Line 269 to Page 22 Line 272: “[S16] Zou Y., Zhang. B. et al. Electrolyte Solvation Engineering Stabilizing Anode-Free Sodium Metal Battery With 4.0 V-Class Layered Oxide Cathode. Adv. Mater., 36, 2410261 (2024). and [S17] Vaidyula, R. R. Nguyen, M. H. et al. Binary Solvent Induced Stable Interphase Layer for Ultra-Long Life Sodium Metal Batteries. Adv. Mater., 36, 202312508 (2024).”

2. Can you comment more on the rescaling of Na^+ and PF_6^- OPLS-AA/OPLS-2009IL parameters to simulation polarization effects? Is this strictly the $\pm 0.8e$ rescaling of the charge parameter described in the abstracted of the cited article? Or are there other rescalings?

Response:

We thank the reviewer for this important point. In the revised manuscript, we have clarified that the charge rescaling was strictly limited to $\pm 0.8e$ for Na^+ and PF_6^- , following the approach described in the cited article. Specifically, PF_6^- parameters were taken directly from the reference, with all (partial) atomic charges uniformly scaled by a factor of 0.8 such that the net charge was $-0.8e$. To maintain overall charge neutrality and consistency, the charge of Na^+ was likewise adjusted to $+0.8e$. No rescaling was applied to partial charges on the solvent molecules (THF and 2-MeTHF) or to any Lennard-Jones or other parameters.

Main Text Methods Page 19 Line 534 to Line 539: “Solvent molecules were parameterized using the OPLS-AA force field, while parameters for Na^+ and PF_6^- were taken from the OPLS-2009IL force field with their total charges scaled to $\pm 0.8e$ to simulate polarization effects.¹ Specifically, all partial charges on PF_6^- were uniformly scaled to yield a net charge of $-0.8e$, and the Na^+ charge was adjusted to $+0.8e$ to maintain overall charge neutrality. No charge rescaling was applied to the solvent molecules (THF and 2-MeTHF), and all Lennard-Jones parameters remained unchanged.”

3. The cited article (Doherty et al.) cautions that rescaling charges can degrade local intermolecular interactions at short ranges, which would seem to challenge the solvation shell speciation results characterizing your main hypotheses about what provides anode and cathode stability. Can you comment on why this isn't a problem for your system?

Response:

Doherty et al.³³ (using reference numbers from the revised main text; see below for reproduced references) reported that applying charge scaling may degrade short-range local interactions, as reflected in reduced radial distribution function (RDF) peak intensities (particularly for cation-anion pairs) in highly structured, densely charged ionic liquids such as [EMIM][TfO] and [BMIM][PF₆]. This behavior is consistent with the reduced electrostatic interactions associated with the decreased magnitude of the charges. While the use of a 0.8-scaled force field may introduce some minor attenuation in short-range interactions, the Doherty paper found that this approach yields significant improvements in key bulk properties, including the enthalpy of vaporization, self-diffusivity, and surface tension. Changes in density, viscosity, and heat capacity were comparatively minor, motivating the application of charge-scaling to improve property prediction overall. Recent publications have likewise reported that scaling partial charges improves agreement between simulation and experiment in the determination of both solvation structure and transport properties^{18, 34, 35, 36, 37} for electrolyte solutions, not just ionic liquids.

While these considerations motivate the use of the chosen force field, to directly address the reviewer's comment we note that our system differs substantially from the neat ionic liquids examined in the Doherty study. Rather than simulating an ionic liquid, we investigated a concentrated molecular electrolyte (e.g., 1.8M NaPF₆ in THF/2-MeTHF mixtures) which would have a significantly reduced charge density compared to the ionic liquids. Therefore, the degradation in RDF peak intensity observed by Doherty et al. is not expected to translate directly to our system. Finally, we note that the specific combination of OPLS-AA parameters and the charge-scaled OPLS-AA ionic liquid parameters used in this study have also been utilized in several recent computational and experimental studies of electrolyte solvation structures^{38, 39, 40}.

Importantly, the RDFs in our study were used only to define the cutoff distance for solvation shell classification, not to interpret peak heights (as in the Doherty paper). Our structural speciation was based on atom counts within the first RDF peak (0.5 nm), rather than the magnitude of the peak itself. To ensure the robustness of this approach, we also performed a sensitivity analysis with cutoff distances of 0.4 nm and 0.6 nm. As shown in Supplementary Table R1 (reproduced below), this variation had negligible impact on the cumulative coordination number (N(r)) and did not alter the observed speciation trends. Thus, we believe our conclusions regarding solvation structure are robust with respect to charge scaling and the choice of RDF-based cutoff distance.

Supplementary Table 6. Average values of $g(r)$ and $N(r)$ 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)

Main Text Methods Page 20 Line 567 to Line 571: “This distance cutoff was selected based on the location of the first peak in the RDF between Na⁺ and any other atom. To test the robustness of this approach, we conducted a sensitivity analysis using alternative cutoff values of 0.4 nm and 0.6 nm. As shown in Supplementary Table 6, these variations had a negligible effect on the $N(r)$ and did not affect the overall speciation trends.”

Main Text Methods Page 10 Line 539 to Line 544: “While charge scaling may attenuate short-range RDF peak intensities³³, previous studies have shown that this approach improves the accuracy of solvation structure and transport properties in similar electrolyte systems^{18,34,35,36,37}. Additionally, the specific combination of OPLS-AA parameters and charge-scaled ionic liquid parameters in this work has been validated and used in recent studies of electrolyte solvation structure^{38,39,40}.”

*Main Text References Page 22 Line 649 to Page 23 Line 666: “[33] Doherty, B., Zhong, X., Gathiaka, S., Li, B., Acevedo, O. Revisiting OPLS force field parameters for ionic liquid simulations. J. Chem. Theory Comput. **13**, 6131–6145 (2017). [34] Cui, X. et al. High-voltage Li*

metal batteries enabled by a nonflammable amphiphilic electrolyte. *Energy Storage Mater* **66**, (2024). [35] Hakim, L. et al. Transport properties of ionic liquid and sodium salt mixtures for sodium-ion battery electrolytes from molecular dynamics simulation with a self-consistent atomic charge determination. *Journal of Physical Chemistry B* **124**, 7291–7305 (2020). [36] Mistry, A. et al. Toward bottom-up understanding of transport in concentrated battery electrolytes. *ACS Central Science* **8**, 880–890 (2022). [37] Gerlitz, A. I. et al. Polypropylene carbonate-based electrolytes as model for a different approach towards improved ion transport properties for novel electrolytes. *Physical Chemistry Chemical Physics* **25**, 4810–4823 (2023). [38] Zheng, X. et al. Knocking down the kinetic barriers towards fast-charging and low-temperature sodium metal batteries. *Energy Environ Sci* **14**, 4936–4947 (2021). [39] Ma, B. et al. Molecular-docking electrolytes enable high-voltage lithium battery chemistries. *Nat Chem* **16**, 1427–1435 (2024). [40] Zhang, W. et al. Engineering a passivating electric double layer for high performance lithium metal batteries. *Nat Commun* **13**, (2022).”

4a. Figure 4(c): The Na surface morphology definitely looks a lot better with the mixed THF/2-MeTHF electrolyte than with either single electrolyte alone. Can you talk more about the conditions under which the SEM imaging was done?

Response:

We thank the referee for pointing this out. We have included the detailed procedure for SEM sample preparation and transfer in the Methods section of the revised manuscript and have also attached it here for the referee’s convenience.

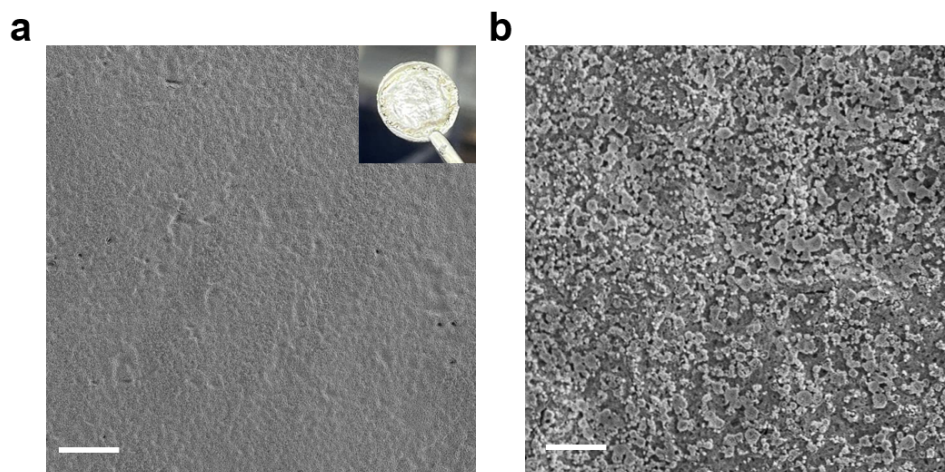
Main Text Methods Page 18 Line 514 to Page 19 Line 520: “The SEM samples were harvested from Cu-Na half cells after one formation cycle at a current density of 0.5 mA cm^{-2} for 2 hours and following by a metal deposition step at 1 mA cm^{-2} for 4 hours to ensure a complete coverage of Cu substrate. The samples were washed with corresponding electrolyte solvents and dried in the Ar-filled glovebox at room temperature before being transferred to the SEM chamber for imaging. During sample transfer process, there was air exposure for less than 1 s, which we believe did not significantly change the morphology of Na deposits.”

Main Text Fig. 4 Caption: “a-c. SEM images and corresponding optical photos of Na harvested from Cu-Na cells. scale bar, $10 \mu\text{m}$.”

4b. Is this smooth morphology what the surface looks like after 5000 h or 400 cycles? Or is this what it looks like at the time the first cell with a single THF or 2-MeTHF electrolyte fails?

Response:

Thanks for this comment. Per the referee’s request, we characterized the morphology of the Na metal electrode in symmetric cells after 5000 hours of cycling in 1.8 M NaPF₆ THF/2-MeTHF and included the results in the revised manuscript. The corresponding figure, discussion, and method section are also included here for the referee’s convenience.



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.

Main Text Page 10 Line 292 to Line 296: “We further characterized the morphology of the Na metal electrode in symmetric cells after 5000 hours of cycling in 1.8 M NaPF₆ THF/2-MeTHF. The harvested Na electrode displayed a shiny appearance, indicating minimal side reactions with the electrolyte. Consistently, SEM images revealed highly uniform sodium deposition across both low (Supplementary Fig. 12a) and high magnifications (Supplementary Fig. 12b).”

5. For the MD simulations, can you comment on the average density attained by each system in the final NPT equilibration and production periods? Does this differ significantly from the initial density you specified in Supplementary Table 3, or from the experimentally measured density of the THF, 2-MeTHF, and THF/2-MeTHF electrolyte solutions? This might help reinforce your conclusions about the cutoff radius used to define a solvation shell and thus your speciation analysis.

Response:

We thank the reviewer for this comment. We would like to clarify that the values in Supplementary Table 5 of the initial submission were not initial densities, but rather the box sizes obtained after NPT production simulations for one replica of each system. However, we recognize that this may have been unclear in the original text and have revised the table to better reflect this. To more accurately report the bulk properties of each system, we now provide average densities calculated from both replicates in Supplementary Table 8. These values were obtained directly from the NPT production trajectories and are reported for both the multi-ion electrolyte systems and the corresponding pure solvents. The updated Supplementary Table 8 offers a clearer view of how well the simulated systems capture realistic bulk behavior.

To validate the reliability of our simulated systems, we compared the simulated densities of the pure solvents (THF and 2-MeTHF) to experimentally measured values reported in the literature, which are compiled in Supplementary Table 9. For THF, our simulated density (0.8600 g/mL) deviates from the room-temperature experimental value (0.8837 g/mL)^{S22} by only 2.7%, and for

2-MeTHF, the simulated density (0.8614 g/mL) deviates from the literature value (0.8529 g/mL)^{S23} by less than 1%. These values are listed in the revised Supplementary Table 9. The deviations from experimental densities are within the expected range of accuracy for OPLS-AA force fields. For context, Ref. S23 benchmarked the performance of OPLS-AA across 235 organic liquids and found average deviations of 2% in liquid density. The agreement between our simulated values and the literature confirms that our simulation setup, including force field parameters and NPT equilibration, yields realistic bulk densities.

We also performed experimental measurements of the density of the electrolyte solutions (Supplementary Table 7), though these data are limited in precision. The data show increased densities upon addition of NaPF₆, with a larger increase in density observed for 1.8M NaPF₆ compared to 1.0M NaPF₆ (as expected). Simulated densities likewise increase for both systems, with the density in the 1.8M NaPF₆ electrolytes exceeding the density in 1.0M NaPF₆ in THF by about 8% in both simulations and experiments. While the experimental measurements deviate somewhat more from the simulated densities than in the case of the pure solvents, this qualitative comparison still provides supports the fidelity of our bulk system representations and justifies the radial distribution functions used for solvation shell and speciation analysis.

Densities of simulated and experimental systems

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 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

SI Reference Page 42 Line 476 to Line 480: “[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]l:Sandia Laboratories.”

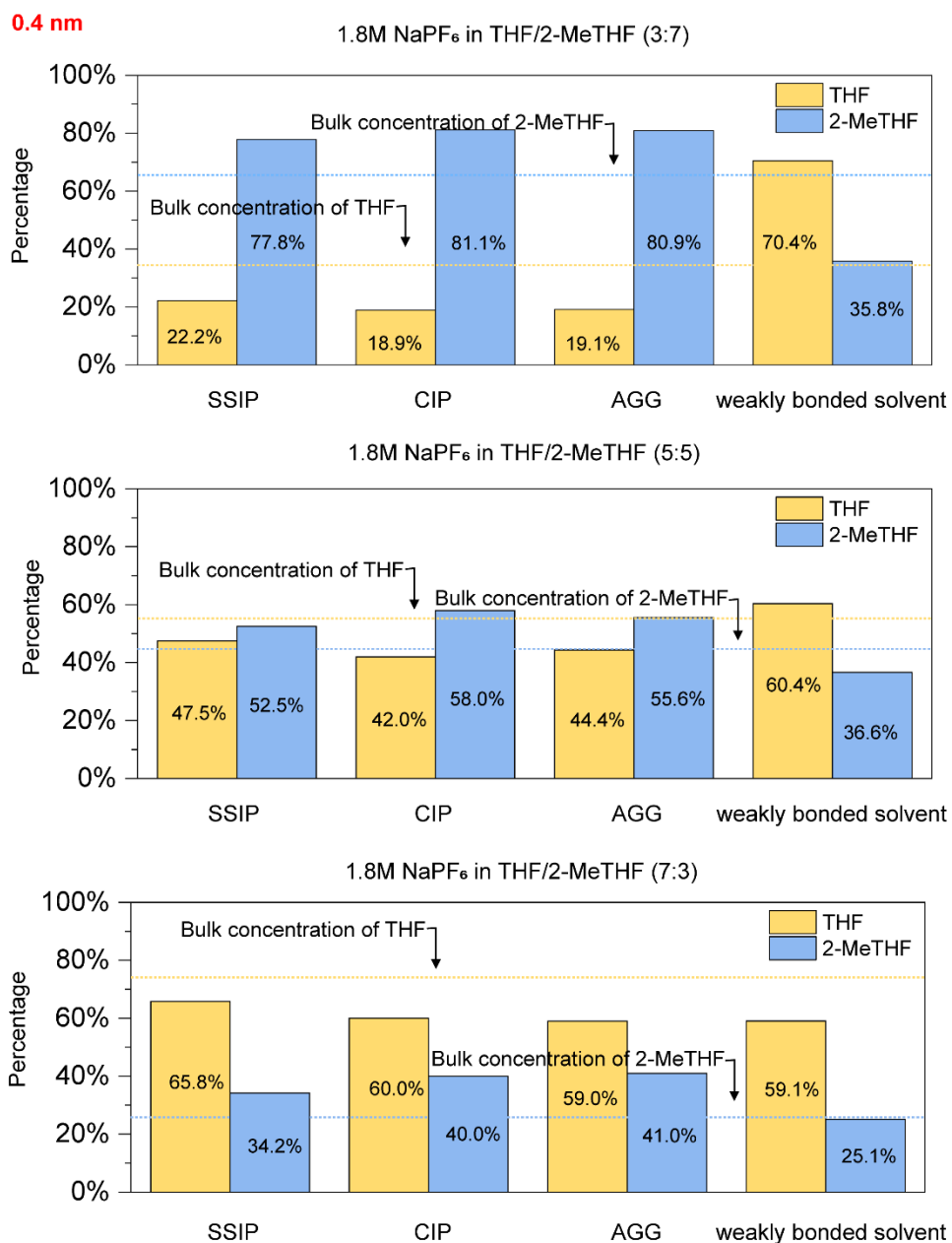
6. Did you investigate compositions other than a 1:1 v:v composition for the mixed THF/2-MeTHF solvent, either in experiment or in the MD simulations? Can you comment on why you chose a 1:1 v:v ratio?

Response:

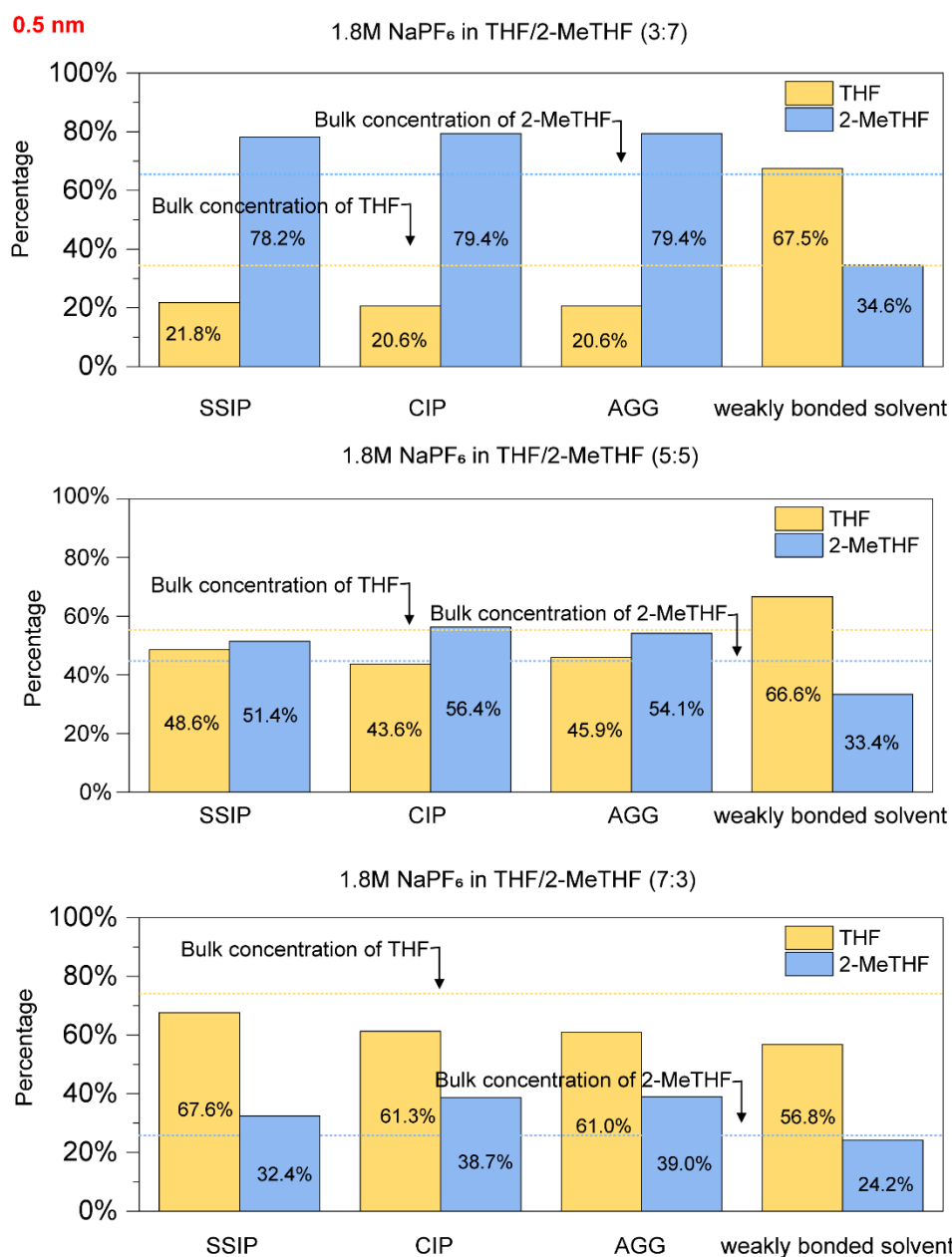
We thank the referee for this comment. The ratio between THF and 2-MeTHF is critical as it affects the amount of AGG and the molecule distributions in each ion clusters. Building upon our prior result, we further evaluated the Coulombic efficiency of Na deposition and stripping in two other mixture electrolytes with different volume ratios (i.e., 3:7 and 7:3) between THF and 2-MeTHF. We observed that the cells with 1.8 M NaPF₆ in THF/2-MeTHF (v:v=1:1) electrolyte exhibited the highest CE over 99.99%. In sharp contrast, the cells with the other two electrolytes demonstrated significantly lower CEs of < 99.7% (Supplementary Fig. 9).

In addition, we performed MD simulations for the 3:7 and 7:3 mixtures and observed consistent solvation trends across all compositions. Supplementary Fig. 6 quantifies solvation structures for all 3 compositions and for both the 0.5 nm cutoff used in the main text and for the 0.4/0.6 nm cutoffs used for sensitivity analysis. In all cases (except for the 5:5 mixture at 0.6 nm, where the

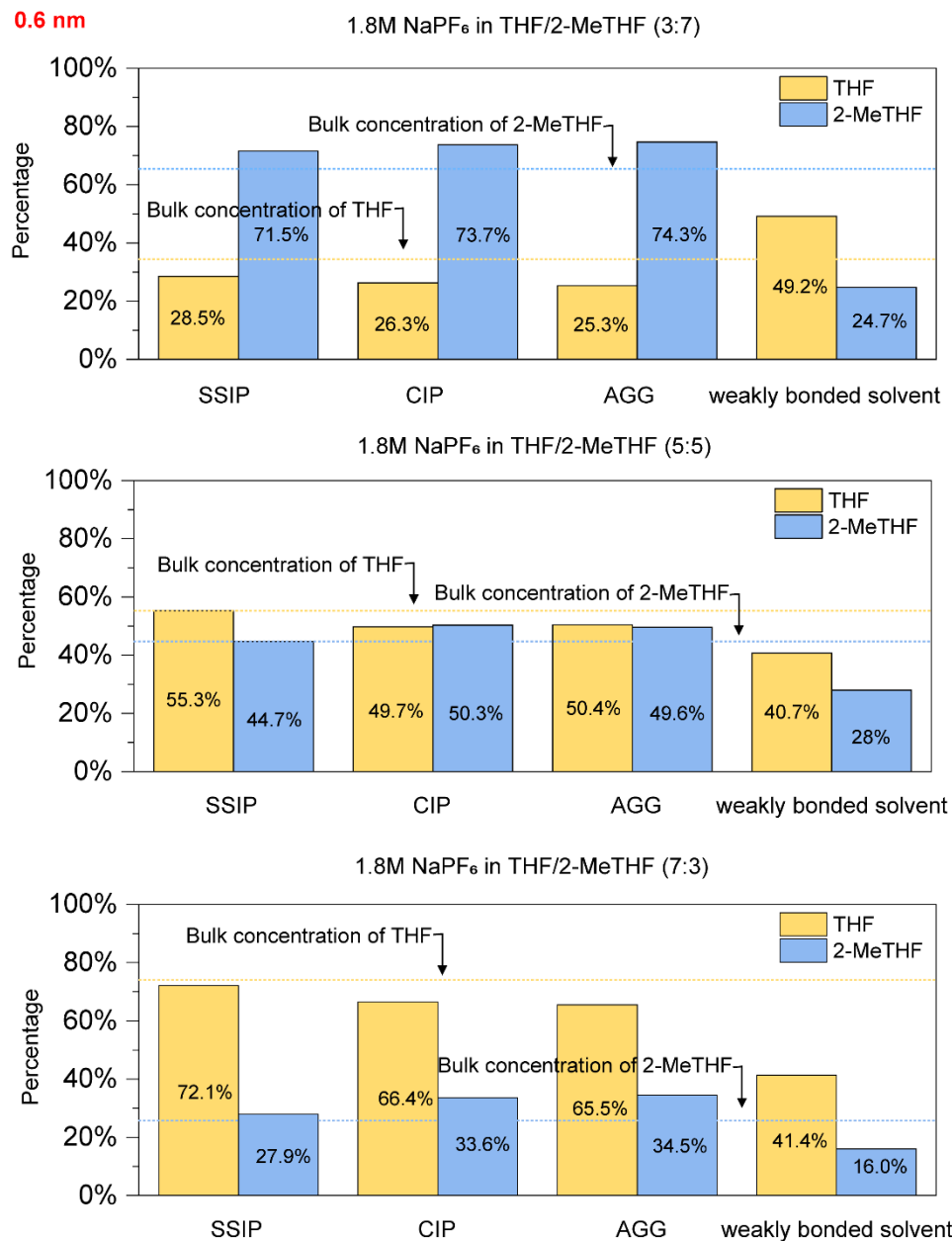
composition equals that of the bulk), 2-MeTHF molecules are enriched in these solvation structures relative to their bulk concentrations, suggesting preferential solvation near Na⁺ while THF remains free in bulk. Interestingly, while the 3:7 THF:2-MeTHF system has the highest 2-MeTHF content in the solvation shells, it also exhibits a low abundance of aggregates (AGGs). Conversely, the 7:3 system has more AGGs but limited availability of 2-MeTHF, possibly constraining its solvation performance. These results help contextualize why the 5:5 mixture, which balances 2-MeTHF enrichment with aggregation, is a meaningful choice for representative analysis.



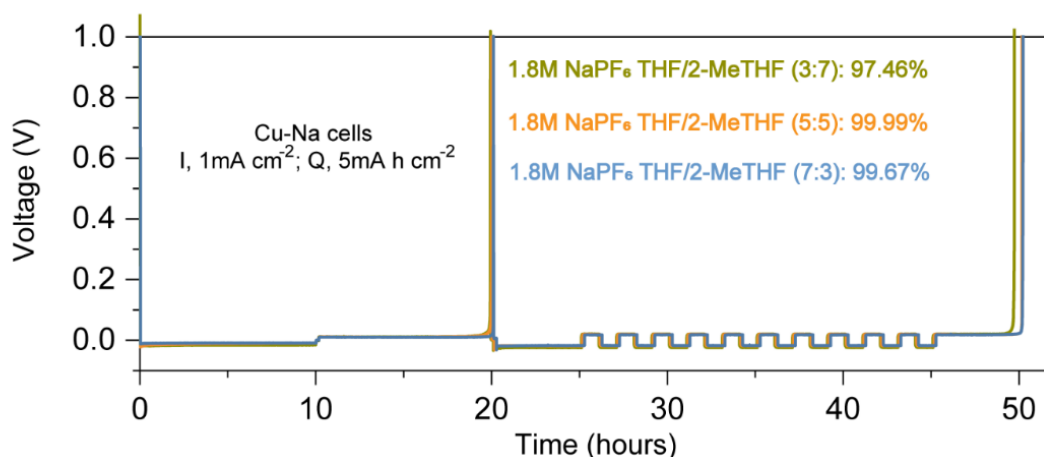
Supplementary Fig. 6 | Ratio of THF and 2-MeTHF in each solvation shell (SSIP, CIP, and AGG) for a cutoff distance of 0.4 nm. Dotted lines indicate the bulk composition of each solvent.



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 | a-c. Measurement of CE of Na plating/stripping in Cu-Na cells using an Aurbach method. a. 1.8 M NaPF₆ in THF/2-MeTHF (3:7), b. 1.8 M NaPF₆ in THF/2-MeTHF (5:5). c. 1.8 M NaPF₆ in THF/2-MeTHF (7:3).

SI Page 32 Line 346 to Line 352: “

Solvent composition in solvation shell

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.”

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]	0.4 nm						
	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
	0.5 nm						
	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
	0.6 nm						
	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 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]	0.4 nm						
	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
	0.5 nm						
	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
	0.6 nm						
	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 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]	0.4 nm						
	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
	0.5 nm						
	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
	0.6 nm						
	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.*

Main Text Page 5 Line 179 to Page 6 Line 191: “To further validate the generality of these findings, we also performed additional MD simulations for 1.8M NaPF₆ in THF/2-MeTHF (3:7 and 7:3 v:v) mixtures. These systems exhibited similar trends in solvation structure, with 2-MeTHF preferentially coordinated near Na⁺ and THF predominantly residing in the bulk (Supplementary Table 13 and 14, Supplementary Fig. 6-8). Notably, the 3:7 mixture exhibited the strongest enrichment of 2-MeTHF within the solvation shell but a relatively low level of ion aggregation, whereas the 7:3 system had more aggregates but lower 2-MeTHF availability. Furthermore, we evaluated the Coulombic efficiency of Na deposition and stripping in two other mixture electrolytes with different volume ratios (i.e., 3:7 and 7:3) between THF and 2-MeTHF. We observed that the cells with 1.8 M NaPF₆ in THF/2-MeTHF (v:v=1:1) electrolyte exhibited the highest CE over 99.99%. In sharp contrast, the cells with the other two electrolytes demonstrated significantly lower CEs of < 99.7% (Supplementary Fig. 9). These results support the idea that the 5:5 (i.e., 1:1) mixture represents a balanced solvation environment.”

7. Out of curiosity, in the MD simulations, are the AGG (P = 2), AGG (P = 3), AGG (P ≥ 4), CIP, or SSIP shells stereoselective towards either 2-MeTHF enantiomer? I'm guessing they aren't, but there are some reports of enantiodiscriminatory electrochemical devices (e.g., 10.1016/j.chempr.2023.11.001). Stereoselectivity by electrode might also inform design guidelines for functionalizing solvent molecules in ways that further optimize each electrode's stability.

Response:

We thank the reviewer for the thoughtful question. In our original analysis of the THF/2-MeTHF systems, we did not differentiate between the R- and S-enantiomers of 2-MeTHF. To address this comment, we have analyzed the solvation shell compositions by distinguishing between the two enantiomers. The results show that the ratio between R- and S- 2-MeTHF remains consistently near 1:1 across all solvation shell types (SSIPs, CIPs, and AGGs), indicating no stereoselectivity under our simulation conditions. As discussed in our response to Comment 6, we also analyzed all three THF/2-MeTHF mixtures (3:7, 5:5, and 7:3 v:v) with two replicates each (six systems total). In all but one case (where the solvation shell composition matched the bulk concentration), we observed enrichment of 2-MeTHF relative to its bulk composition but no stereoselectivity. Further exploring stereoselectivity could be an interesting avenue for further research, particularly if considering the explicit structure of electrolyte near an electrode surface.

8. The authors report and comment on the significance of single-ion solvation free energies in each electrolyte. Are surface potentials of the respective electrolytes reflected in the single-ion values? Single-ion free energies computed in periodic boundaries require determination of the solvent surface potential from a slab calculation. (These cancel for ion pairs, so the Na⁺ PF₆ result will be unaffected) Also, did you use the soft-core potential? Is 5 ns enough time to sample the local coordination environment sufficiently? If you doubled the simulation time per window, do your results change? Are these NVT ensemble calculations?

Response:

We thank the reviewer for the detailed questions, which permit us the opportunity to elaborate upon our simulation approach and reliability. We address each point below.

To correct solvation free energies in systems with a net charge (i.e., due to the decoupling of a single ion), we applied three standard correction terms (including the surface potential suggested by the reviewer):

- Compression correction (ΔG_{press}): This term adjusts for the transfer from an ideal gas to the solution phase.
- Finite-size correction (ΔG_{fs}): This correction accounts for long-range electrostatic artifacts in periodic boundary conditions.
- Interface correction (ΔG_{surf}): This term corrects for the electrostatic potential at the vacuum-solvent interface.

Explicit expressions and additional methodological details for these corrections are included in the revised Supporting Information and copied below, so we ask that the reviewer please review the revised text in italics on the next two pages. Each of these corrections was calculated and applied separately to Na^+ and PF_6^- (see Supplementary Fig. 23-24) for each of the solvent systems. As the reviewer notes, the interfacial potential contributions cancel out for neutral ion pairs, and thus these corrections do not affect the NaPF_6 results.

In this revision, we report corrected solvation free energies for both multi-ion systems (Supplementary Fig. 23 and Supplementary Table 10) and single-ion systems (Supplementary Fig. 24 and Supplementary Table 11). While the multi-ion simulations involve decoupling a single ion (either Na^+ or PF_6^-) in the presence of a background electrolyte, the single-ion systems include no counterions. In all cases, the simulated solvation free energy (ΔG_{sim}), which is the free energy obtained directly from simulations without any correction, was first computed. We then applied the three standard corrections terms listed above (ΔG_{press} , ΔG_{fs} , and ΔG_{surf}) to obtain the final corrected solvation free energy (ΔG_{solv}), where $\Delta G_{solv} = \Delta G_{sim} + \Delta G_{press} + \Delta G_{fs} + \Delta G_{surf}$. The same set of corrections was applied in both cases to ensure consistency. The final values reported in Supplementary Fig. 23-24 represent the average of two independent replicates (Supplementary Tables 10-11, respectively). Of the corrections, only the interfacial potential term varies across solvent systems. We find that, overall, the corrections do not substantially vary any of the reported trends, which is consistent with the similar dielectric behavior of the THF and 2-MeTHF solvents used in this system. However, we do believe that including said corrections is important to more rigorously report simulation findings.

After applying the correction terms, we examined the 3:7 and 7:3 THF/2-MeTHF mixtures and found that their solvation free energies lie between those of the pure solvent systems. The differences between the three mixture ratios were minor.

Regarding the simulation parameters and convergence:

- Yes, soft-core potentials were used in all alchemical free energy simulations, with the Gromacs setting $sc\text{-}\alpha = 0.5$ (as suggested by Gromacs developers) to avoid endpoint singularities.
- To assess whether 5 ns of production per window is sufficient to sample the local coordination environment, we computed the single-ion solvation free energies using progressively longer segments of the production trajectory (e.g., 1 ns, 1.5 ns, 2 ns, ..., up to 5 ns) to compute the free energy. This analysis was performed for an Na^+ ion in the same 5:5 (i.e., 1:1 v:v) mixture as a representative example. As shown in Supplementary Figure

22 (reproduced below), the solvation free energy values plateau within 1 kJ/mol of the converged value as the sampling time increases beyond 3 ns, demonstrating that 5 ns of production per window is sufficient for obtaining converged results and doubling the simulation time would not be expected to affect the reported values. We also note that each window (*i.e.*, unique value of λ) underwent energy minimization, followed by 100 ps NVT and 2 ns NPT equilibration steps prior to the 5 ns NPT production run, as noted in the revised text

- In response to Comment 10, below, we also examined the evolution of Na-P and Na-O coordination numbers over time. This analysis was performed for the most structurally complex system (1.8M NaPF₆ in THF/2-MeTHF (5:5 v:v) mixture) using the average of two independent replicates. These data also show rapid convergence (within 5 ns), which is consistent with the convergence of the solvation free energies shown below.
- Regarding the ensemble used, the solvation free energy calculations for each λ window were conducted in the NPT ensemble. However, the slab simulations used to compute the interfacial potential correction (ΔG_{surf}) were performed in the NVT ensemble. It was necessary to maintain a stable vacuum region along the z-direction during the calculation of the electrostatic potential profile. Therefore, while the main decoupling simulations used the NPT ensemble, the NVT ensemble was used specifically for the newly added slab-based surface potential calculations.

SI Page 25 Line 255 to Line 285: “

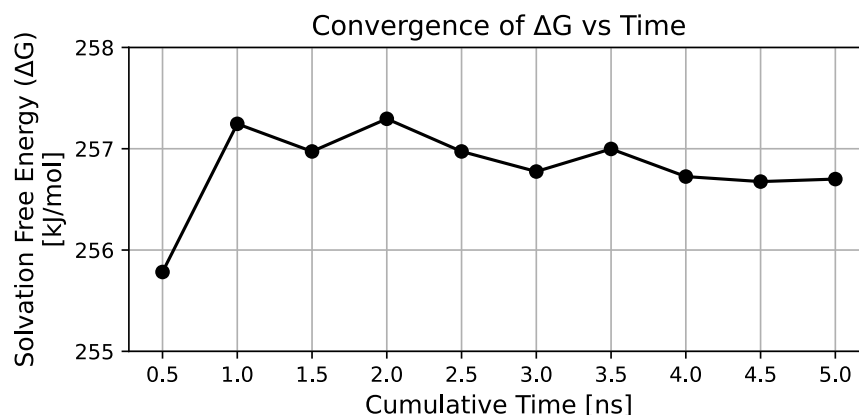
Solvation free energy calculations

Solvation free energies (ΔG_{solv}) for Na⁺ and PF₆⁻ 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-alpha) 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. Although 2-MeTHF exhibits stronger solvation of Na^+ than THF, PF_6^- is more favorably solvated by THF. As a result, the total solvation free energy for NaPF_6 is lowest in THF among all solvents and mixtures studies (Supplementary Tables 10 and 11). This is consistent with the experimentally observed higher saturation concentration of NaPF_6 in THF compared to 2-MeTHF. The results indicate that the solvation behavior of both ions, not just Na^+ , must be considered when interpreting solubility trends.”



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 NaPF_6 in THF/2-MeTHF 5:5 v:v), showing that ΔG_{sim} plateaus with sufficient sampling.

SI Page 27 Line 292 to Line 322: “

Solvation free energy corrections

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:

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

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:

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

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:

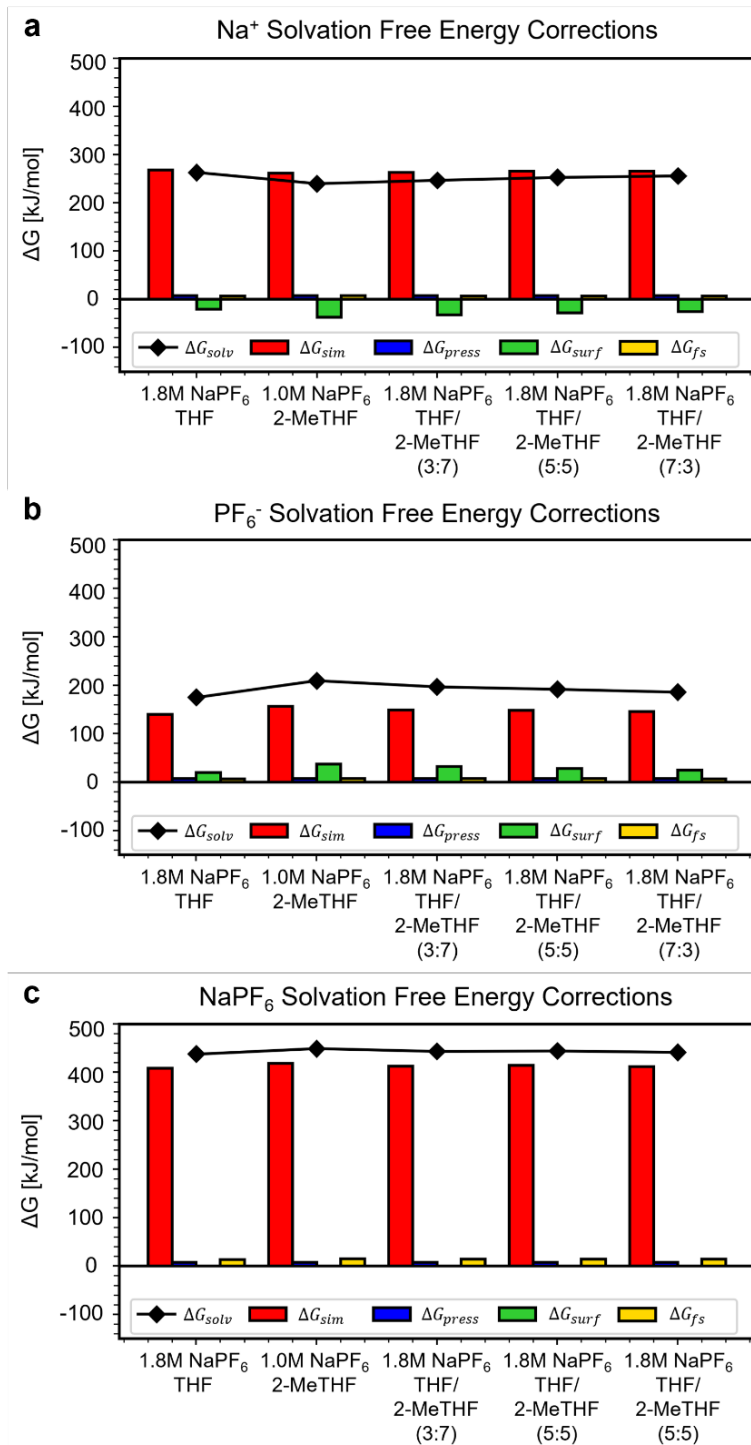
$$\Delta G_{surf} = ze\psi_s$$

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:

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

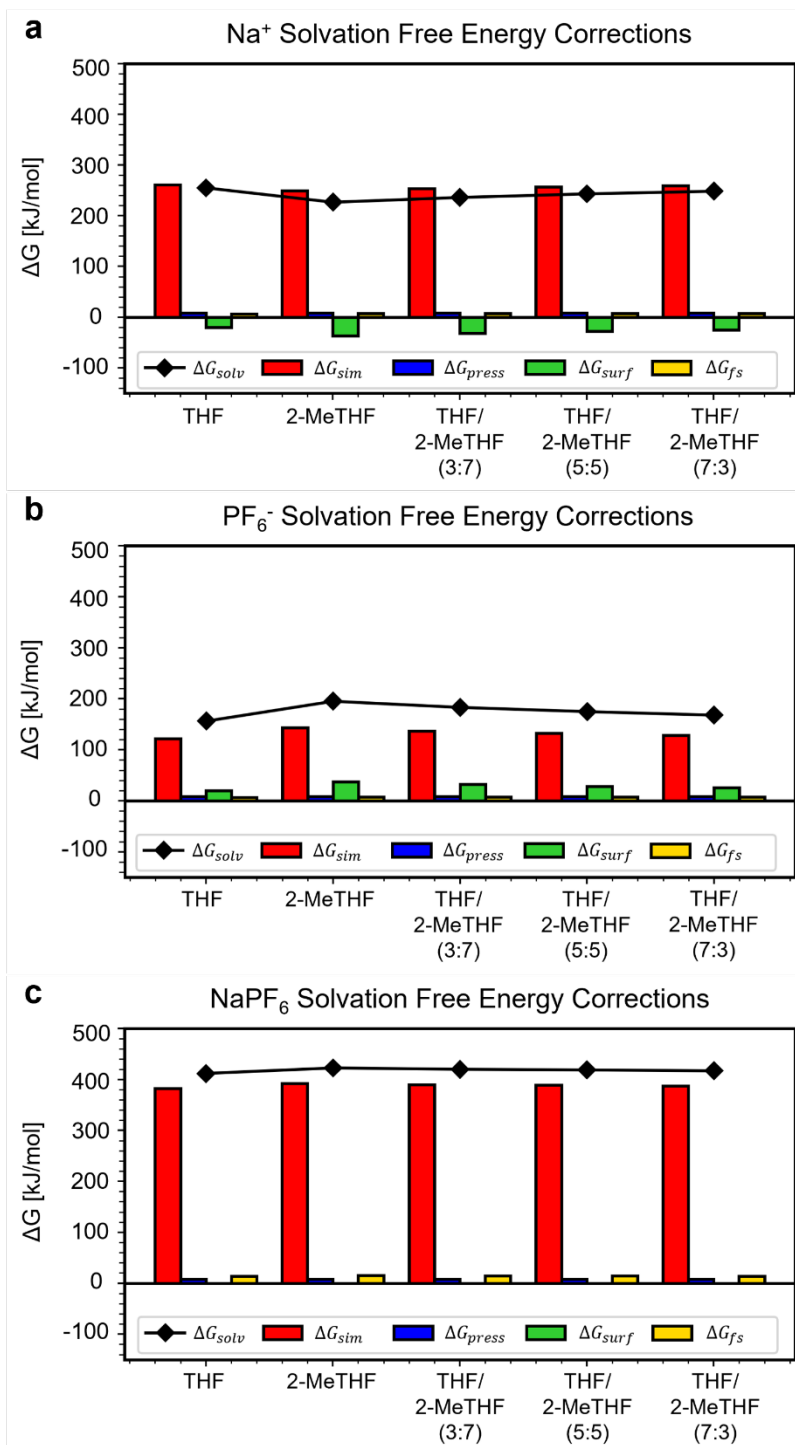
Values for ΔG_{sim} and the individual corrections are provided in Supplementary Tables 10 (multi-ion systems) and 11 (single-ion systems), with associated plots in Supplementary Fig. 23-24. All reported values in the figures are averages of two independent replicates.”



Supplementary 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	263.1	173.2	436.2
1.0M NaPF ₆ in 2-MeTHF	261.6	156.4	418.0	7.9	7.4	7.5	-37.4	37.4	239.4	209.3	448.7
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	244.9	199.7	444.5
1.8M NaPF ₆ in THF/2-MeTHF (5:5)	264.9	148.6	413.5	7.9	7.1	7.2	-28.0	28.0	251.1	192.6	443.7
1.8M NaPF ₆ in THF/2-MeTHF (7:3)	266.3	146.0	412.3	7.9	7.0	7.1	-25.3	25.3	256.0	186.3	442.3
	Replicate 2										
1.8M NaPF ₆ in THF	268.4	141.6	409.9	7.9	6.8	6.9	-20.2	20.2	262.9	176.6	439.5
1.0M NaPF ₆ in 2-MeTHF	261.5	157.1	418.6	7.9	7.5	7.6	-37.0	37.0	239.9	209.5	449.4
1.8M NaPF ₆ in THF/2-MeTHF (3:7)	265.0	146.7	411.7	7.9	7.3	7.4	-31.8	31.8	248.3	193.8	442.1
1.8M NaPF ₆ in THF/2-MeTHF (5:5)	266.2	148.6	414.8	7.9	7.1	7.2	-28.0	28.0	252.5	192.5	445.0
1.8M NaPF ₆ in THF/2-MeTHF (7:3)	266.0	145.1	411.2	7.9	7.0	7.1	-25.3	25.3	255.6	185.4	441.0



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 corrections 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 ⁻	Na ⁺	PF 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	255.0	156.8	411.8
1.0M NaPF ₆ in 2-MeTHF	249.1	142.7	391.8	7.9	7.4	7.5	-37.4	37.4	227.0	195.5	422.5
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	236.3	184.0	420.3
1.8M NaPF ₆ in THF/2- MeTHF (5:5)	256.4	132.4	388.7	7.9	7.1	7.2	-28.0	28.0	242.5	176.3	418.9
1.8M NaPF ₆ in THF/2- MeTHF (7:3)	259.5	128.4	387.9	7.9	7.0	7.1	-25.3	25.3	249.1	168.8	417.9
	Replicate 2										
1.8M NaPF ₆ in THF	260.9	122.0	382.9	7.9	6.8	6.9	-20.2	20.2	255.5	157.0	412.5
1.0M NaPF ₆ in 2-MeTHF	249.0	143.4	392.4	7.9	7.5	7.6	-37.0	37.0	227.4	195.8	423.3
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	236.7	183.4	420.1
1.8M NaPF ₆ in THF/2- MeTHF (5:5)	256.7	132.3	389.0	7.9	7.1	7.2	-28.0	28.0	243.0	176.1	419.1
1.8M NaPF ₆ in THF/2- MeTHF (7:3)	258.6	128.1	368.7	7.9	7.0	7.1	-25.3	25.3	248.2	168.3	416.5

SI Reference Page 41 Line 481 to Line 485: “[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).”

9. The authors write, "Finally, a 50 ns production simulation was performed at the same temperature and pressure as the NPT equilibration and using the same thermostat and barostat." Do the authors mean "... was performed in the NVT ensemble with the average box size taken from the NPT equilibration procedure"?

Response:

To clarify, our simulation procedure involved initial NVT equilibration to stabilize the system temperature, followed by NPT equilibration to adjust the box volume to the target pressure. Subsequently, the 50 ns production simulation was also performed under the NPT ensemble, maintaining constant temperature and pressure throughout. We did not transition to the NVT ensemble for production. Utilizing the NPT ensemble for production ensures the reliability of bulk properties, including density, radial distribution functions, and ion aggregation behaviors.

Main Text Methods Page 19 Line 550 to Line 552: “Finally, a 50 ns production simulation was conducted in the NPT ensemble, maintaining the same temperature, pressure, thermostat, and barostat settings as used during the preceding NPT equilibration.”

10. The authors write, “Van der Waals interactions were modeled using a shifted Lennard-Jones potential that smoothly transitioned to zero at 1.3 nm.” Truncating the Lennard-Jones potential is known to cause issues with transport properties which can effect relaxation times in simulation. This issue is remedied by using the long-range correction (or the PME LJ potential). It would be helpful to show the evolution of the Na-P, Na-O coordination numbers vs time to show that they have stabilized. Analysis of the coordination environment would be more convincing this way.

Response:

As the referee notes, truncating the Lennard-Jones potential can introduce artifacts in transport properties by disrupting the continuity of the potential energy function. In the initial submission and revision, we addressed this concern by both employing a shifted Lennard-Jones potential that smoothly transitions to zero at the cutoff distance of 1.3 nm and by including long-range dispersion corrections to account for the truncated tail of the potential (as also suggested by the reviewer). We mistakenly omitted discussion of the latter correction in the initial submission and have revised the Methods section accordingly.

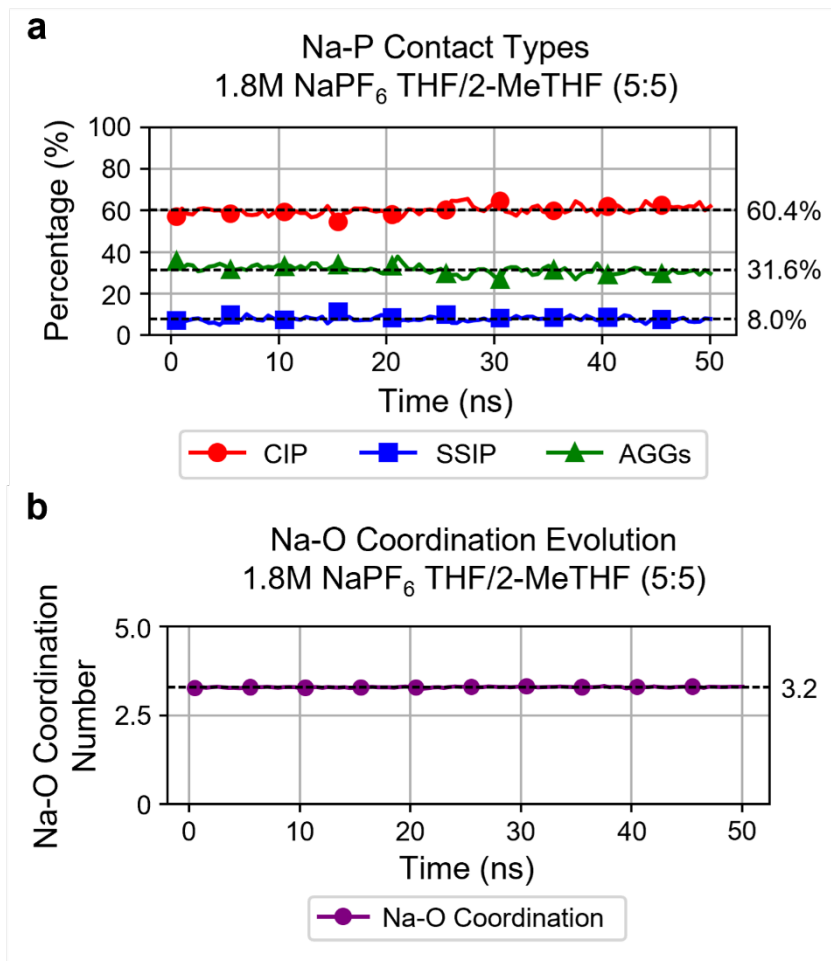
Per the referee’s suggestion, we also analyzed the evolution of Na⁺ coordination with P and O atoms as a function of simulation time (50 ns) during the production trajectories, which followed an initial 50-ns equilibration. As shown in Supplementary Fig. 25, the Na-O coordination number fluctuates around the average over the duration of the simulation, indicating convergence of the solvation shell structure. The Na-P contact types (reflecting their coordination environment) similarly fluctuate around a stable average. Both plots indicate that equilibrium solvation structure are obtained during the equilibrium trajectory and that the coordination environment sampled during the production trajectory is structurally stable for the entire simulation time. Given that our study does not focus on transport properties, the effects of truncation on coordination number and radial distribution function calculations are expected to be minor. We have added these convergence metrics to the Supporting Information and believe they support the reliability of the simulation protocol.

Main Text Methods Page 20 Line 556 to Line 559: “Van der Waals interactions were modeled using a shifted Lennard-Jones potential that smoothly transitioned to zero at 1.3 nm. Standard long-range dispersion corrections to energy and pressure were applied.”

Main Text Methods Page 19 Line 552 to Line 555: The stability of the solvation structure for this simulation time was confirmed by tracking Na–P and Na–O coordination numbers over the production trajectory, which remained stable over time (Supplementary Fig. 25). ”

SI Page 32 Line 353 to Line 358: “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 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.”

11. The authors write, "All systems were independently simulated and analyzed twice to quantify uncertainty in simulation measurements." Do the authors mean they generated multiple replicates with each starting from different initial configurations?

Response:

Both simulations for each system were initiated from the same initial configuration. However, each replicate was run independently from the energy minimization step onward, followed by separate NVT equilibration, NPT equilibration, and NPT production simulations using different initial random seeds. This approach allowed us to capture statistical variability arising from thermal fluctuations and stochastic differences in the simulation trajectories, despite starting from

the same initial atomic arrangement. As noted in the preceding responses, the long-timescale initial equilibration was sufficient to ensure reliable sampling during the production trajectory such that we do not expect any impact of the initial simulation configuration on the reported results.

Main Text Methods Page 20 Line 561 to Line 563: “Two simulation replicas were performed for each system to quantify simulation error. Both replicas were initialized from the same atomic configuration, then separate NVT and NPT equilibration and production simulations were performed using different random seeds”

12. Related to point 2, have the authors considered computing transport properties (e.g., self-diffusion + viscosity correction, total ionic conductivity - compare with figures in Fig 3b, transference number, ionicity) to compare against experiment to validate their force field? How do densities compare between experiment and theory for each of these electrolytes? Comparison of predicted speciation against Raman bands is very good for 1.8 M NaPF₆ in THF but much less so for 1.0 NaPF₆ in 2MeTHF. Given the issues with the 2MeTHF electrolyte, the excellent agreement between the speciation in Fig 2d and Supp Fig 4c could also just be fortuitous.

Response:

We thank the reviewer for this comment. Our study focuses primarily on the structural features of ion solvation and speciation rather than transport properties. While we acknowledge the importance of such properties in evaluating electrolyte performance, we believe they fall outside the scope of the present simulations. That said, several recent publications using the same force field combination (OPLS-AA with scaled partial charges on ions) have found transport properties such as diffusion coefficients to be in very good agreement with experimental measurements (Refs. 18, 36, and 37 of the revised manuscript). With respect to densities, we sought to address the reviewer’s comment in our response to Comment 5, where we highlighted the similarity between the calculated densities and experimental measurements with deviations on the order of 1-3%. Similar literature evaluations of transport properties for bulk solvents. Therefore, this agreement between our simulations and literature values supports the fidelity of our bulk system representations.

With respect to the reviewer’s comparison between Fig. 2d and Supplemental Figure 5 (using the numbering in the revised manuscript), we have slightly revised the text on pg. 5 (Lines 153-163). We note that both simulations and experiments predict the same trend in the preference of different systems for AGGs (1.8M NaPF₆ in THF > 1.8M NaPF₆ in THF/2-MeTHF > 1.0M NaPF₆ in 2-MeTHF), with good agreement between simulations and experiments in predicted percentage of AGGs (with an average difference of 4.7%).

13. Can the authors use density functional theory to identify the oxidation mechanism of 2-MeTHF occurring at ~3.4 V? Or cite a reference if known.

Response:

We thank the referee for this comment. Although we do not have the ability to perform these DFT calculations, we cited a reference that explains the possible oxidation mechanism of 2-MeTHF occurring at ~3.4V. 2-MeTHF may form the radical intermediate derived through hydrogen abstraction from solvent molecules, either by sodium superoxide, if generated, or by

radical anions produced during reactions between sodium and the solvent. This radical intermediate readily reacts with oxygen to yield the corresponding 2-MeTHF peroxide. Under hydroxides conditions, this peroxide intermediate decomposes easily to yield hydroxide and lactone derivatives^{1,2}.

References:

1. Malik, Y. et al, The electrochemical behaviour of 2-methyltetrahydrofuran solutions. *J. Electroanal. Chem.* 282, 73–105 (1990).
2. Li, AM., Borodin, O., Pollard, T.P. et al. Methylation enables the use of fluorine-free ether electrolytes in high-voltage lithium metal batteries. *Nat. Chem.* 16, 922–929 (2024).

Referee #4 (Remarks to the Author):

I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Response:

Thank you for reviewing our manuscript and offering constructive feedback.