nature portfolio

Peer Review File

Dipolar interaction-mediated molecular anchoring electrolyte enables wide-temperature sodium-ion batteries with enhanced safety and durability

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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)
This work reports a molecular anchoring electrolyte to construct a dynamic hierarchical solvation network for safe sodium-ion batteries. The designed NDPP electrolyte showed compatibility with HC negative electrode and NVPOF positive electrode. Multiscale characterizations and theoretical insights reveal the unique interface stabilization mechanism towards robust interphases. While the proposed mechanism involving dipole-mediated SEI/CEI formation is conceptually valuable, substantive concerns regarding methodological rigor and scientific advancement preclude its current suitability for publication in Nature Communications. The key limitations are outlined as follows:
1. The LSV profiles in Fig. 2d-e inadequately characterize the redox thresholds of NDPP electrolyte. The absence of distinctive PFPN decomposition peaks in both anodic and cathodic scans raises questions about the actual decomposition pathways and potential parasitic reactions.
2. Although molecular dynamics (MD) simulations propose specific solvation configurations, the experimental validation remains fragmentary. NMR and vibrational spectroscopy data currently focus solely on identifying selected molecular interactions, rather than systematically correlating with MD-predicted coordination structures.
3. The manuscript lacks in situ/operando analyses (e.g., in situ Raman, in situ FTIR) to probe the potential-dependent evolution of solvation structure and desolvation kinetics during battery operation.
4. Prior works (Angew. Chem. Int. Ed. 2023, 62, e202313447; Nat Commun 16, 3344 (2025); Angew. Chem. 2023, 135, e202216189) have extensively explored weak-solvation electrolytes employing analogous solvent systems (DEE/PFPN), thereby diminishing the novelty of the current approach.
5. The purported "molecular anchoring-solvation-interfacial dynamics" relationship remains conjectural, as no quantitative descriptors or mechanistic models explicitly link these hierarchical processes to the observed electrochemical behaviors.
6. The authors highlighted the thin, uniform and robust organic-inorganic coupling interface on NVPOF. While the continued use of NVP cathodes for extreme-temperature evaluations (despite emphasizing NVPOF's CEI advantages) creates a methodological paradox that undermines the mechanistic conclusions regarding interfacial stability.
7. The absence of large-format pouch cell data substantially weakens the translation potential assessment of this electrolyte technology.

Reviewer #2

(Remarks to the Author)
This work developed a new electrolyte, NDPP, by mixing PC, DEE and PFPN with the NaPF6 salt, to enhance safety and durability of sodium ion battery (SIB). SIB is a promising solution for energy storage and as such the scope of this work addresses a contemporary and highly demanded topic.

I like the concept of "dipolar interaction-mediated solvation-interface synergistic stabilization mechanism". However, this mechanism is short of evidence in the current version of the manuscript. The Raman spectrum of NDPP is almost simply a linear combination of individual solvent molecules, with only difference of redshift described at line 195. This redshift is using pure PFPN solvent as a reference, which can be a result of polarization effect Na[+] instead of other solvents

mentioned at line 196. There is no unique peaks arising from anion-dipole and dipole intermolecular interaction. If strong intermolecular interactions exist, it will show up in infrared spectroscopy, which is missing in the manuscript. Similarly, Figure 3b NMR doesn't make a clear distinct from the effect of dielectric constant change; Figure 3c 2D NMR doesn't have any cross peaks beyond two neural solvents PFPN-PC and didn't compare to a simple PFPN/PC mixture. As a minimum requirement for the synergistic stabilization claim, at least three component correlation is required. This work uses Figure 4h to demonstrate the interactions. However, there is no single snapshot captured from molecular dynamics, that has a structure similar to the one drawn in Figure 4h. To remedy these issues, it will need a fundamental change to the manuscript, which is beyond the extent of major revision.

Below are several specific comment regarding technical details:

1) In Figure 4h, Why the anion-dipole interaction dashed line connects to the far end of PC ellipse rather than near end? I can understand that the electrostatic force from Na+ puts a preferred orientation of PC. However, this will prefer a negatively charge a near end, and lead to a repulsive interaction. This is a destabilizing force to the the structure proposed in Figure 4h, contradictory to the synergistic stabilization but it shouldn't be ignored. More likely, this near end repulsive force is stronger than the attractive far end interaction and is expected to be primary force of the anion-dipole interaction. By ignoring stronger force and drawing only the weaker force, Figure 4h is very misleading. I can't be convinced that this solvation structure is stable.

2) The DFT calculation was oversimplified. The equation at 484 ignores the solvation energy of Na[+]-solvent complex and Na[+], which can change the relative order of the computed binding energies.

3) The concept of "no-solvated PFPN" (e.g. the one at line 162) is confusing and needs further explanation. In particular, is it a homogeneous part of the electrolyte solution?

4) What are the dashed lines in Figure 4(d-f)?

Reviewer #3

(Remarks to the Author)
In this manuscript, the authors report a dipolar interaction-mediated and molecular anchoring electrolyte to enable the stable operation of sodium-ion batteries under wide temperatures. Particularly, the electrolyte features intrinsic flame retardancy, oxidative/reductive reliability and electrochemical durability against both cathode and anode. A series of experimental characterizations and theoretical calculations are conducted to reveal the structure-property relationship. In my opinion, this work is interesting, and this manuscript is well organized. So I recommend publishing the manuscript on Nature Communications after addressing the following issues.
1. The authors point out that simple blending of PC and DEE fails to achieve the desired properties and it is difficult to fully utilize their respective advantages. I suggest providing more explanation and discussion on this phenomenon.
2. The concept of dipolar interaction-mediated molecular anchoring effect is crucial in this work, but there is a lack of sufficient explanation on the concept and its function.
3. Compared with ND and NP electrolytes, the NDPP electrolyte exhibits significantly enhanced electrochemical durability according to Fig. 5a-c. Understanding the reasons for the performance improvement is necessary. I suggest the authors further discuss this concern.
4. The sodium layered oxide cathode has also been investigated in Fig. 5e. The corresponding charge-discharge curves should be supplemented.
5. The depth profiles of ion fragments based on TOF-SIMS should also be added.
6. The capacity retention at –40 °C is much lower than at 25 °C. The rate-limiting step should be clearly identified.
7. “For full-cell fabrication, all HC anodes were pre-sodiated chemically, and the N/P ratio was controlled at about 1.2.” The pre-sodiated process should be fully detailed, as it plays a decisive role in determining battery performance.
8. “Consequently, representative high-voltage phosphates, layered oxide cathodes and hard carbon (HC) anode demonstrate extraordinary cycling stability, e.g., 87.6% of reversible capacity after 5000 cycles for Na3V2(PO4)2O2F (NVPOF) model cathode.” The battery performance of hard carbon as the anode is not included in the main manuscript. Figure S14 only shows the HC/Na cell performance, which is hardly extraordinary. Additionally, the poor performance of the HC/Na cell stems from the sodium metal, not the electrolyte or hard carbon. Please correct these issues.
9. Figure 6b requires revision as the XPS fitting demonstrates: (1) non-aligned peaks for identical species, and (2) inconsistent peak broadening. Standardization is needed.
10. “0.8 M NaPF6 in DEE-PC-PFPN (5: 5: 2 by volume ratio).” Given the crucial impact of sodium salt concentration and solvent ratio on battery performance, please justify the selected ratio.

Reviewer #4

(Remarks to the Author)
This manuscript examines the impact of incorporating DEE and PFPN solvents into classical 1M NaPF6 in PC electrolytes, focusing primarily on the performance of half-cells, mainly containing cathode active materials. While the introduction presents some impressive claims, most of them do not align with the results observed with the NDPP electrolyte discussed by the authors. The writing lacks clarity and coherence, and the conclusions drawn do not reflect the observed results. Most importantly, rigorous full-cell data is lacking, and the present data shows that NDPP electrolyte is not stable, leading to capacity loss even when cycled at fast rates (2C) in the full cell.

Below are some specific comments:
1. In the introduction of the manuscript, please note the claim of an "admirable capacity retention of 95.2% over 900 cycles at 70 °C." However, this assertion seems to apply only to low-voltage cathodes. As indicated in Supplementary Fig. 9c, the NVPOF//Na half-cell is unable to complete even a single cycle, suggesting substantial overcharging due to electrolyte oxidation. Could the authors clarify this discrepancy?

2. The authors mention "energy density reduction (e.g., capacity loss in cathodes caused by high-salt systems)" in the introduction. I would appreciate clarification on the meaning of this statement and any supporting literature that may be available.

3. The claim regarding "process economic efficiency deterioration (e.g., skyrocketing costs of fluorinated solvents)", followed by the use of a fluorinated PFPN in the manuscript, raises some questions. It may be helpful for the authors to address this apparent contradiction.

4. The manuscript employs several abbreviations such as DEE, PFPN, NDP, NDPP, NT0102, and NVP without definitions at all!!! Additionally, the electrolyte formulations (NP, ND, NDP, and NDPP) are only outlined at the end of the supplementary information. To enhance clarity for readers, it would be beneficial for the authors to define these terms upon their first use in the text, including common abbreviations like PC.

5. Were all the parameters presented in Fig. 1b measured by the authors? If some were not, I recommend that the authors provide references for this information, apart from the HOMO-LUMO calculations they performed.

6. Fig. 2a presents a schematic of different solvation structures. Citing the source of these solvation structures would strengthen the manuscript, as they are not characterized within the paper.

7. The optimized structures shown in Fig. S2 raise some concerns, particularly the Na+--G2 structures, which differ from reported observations in the literature. For example, the structures presented in DOI: 10.1002/cey2.518 appear more consistent.

8. The CE efficiency of the HC vs. Na cells (supplementary information) is bad for the NDP electrolyte. It may be valuable to include data on the cyclic stability and CE of HC vs. Na cells for the NP, ND, and NDPP electrolytes.

9. The CV data depicted in Fig. 2d and Fig. 2e could benefit from more rigorous experiments. Increasing the sweep rate and using a reference electrode would help clarify the onset potential for oxidation and yield more reliable reduction curves. Additionally, could the authors explain why the open-circuit voltage (OCV) of the cell with NP in Fig. 2e differs significantly from the other cells?

10. What specific message do the authors intend to convey through Fig. 3b? If there is an NMR spectrum for the NDP electrolyte, it may fall between the ND and NP electrolytes and should be discussed.

11. The authors assert in Fig. 3e that the interactions between PC-PFPN and DEE-PFPN are surprisingly stronger than those between PFPN and PF6. Could the authors discuss from HOESY NMR spectra to further illustrate the interactions of PC-PFPN and DEE-PFPN? The interactions of PFPN still remain unclear to me.

12. It would be beneficial to experimentally verify the solvation structures derived from theoretical calculations in order to confirm the calculated hypotheses, particularly since the authors are already utilizing spectroscopic techniques in the manuscript to monitor these interactions.

13. Adjusting the y-axis for CE throughout the manuscript to ranges of 90-101 or 75-102 (considering the lower first cycle CE) may provide a clearer understanding of the CE values for the various electrolyte formulations.

14. The energy efficiency graph shown in Fig. 5c may not be necessary. It could be more effective to incorporate the curves for NT0102 and NVP instead.

15. Fig. 5d appears misleading, as ND actually shows better reductive stability than NDPP, while NP demonstrates better oxidative stability than NDPP. This discrepancy should be addressed.

16. A crucial aspect that seems to be missing from the paper is the full cell cycling data of high-voltage cathodes vs. hard carbon. The full cell illustrated in supplementary Fig. 15 indicates poor performance, suggesting that DEE from the NDPP electrolyte decomposes at high voltage, resulting in capacity loss. It would be beneficial for the authors to include data showing 100 cycles at a C/5 rate for NDPP and NP electrolytes, as NP is known to perform well in this full cell chemistry. Additionally, if the claims regarding safety and high voltage stability of the NDPP electrolyte are accurate, the authors should demonstrate full cells with NVPOF cycling at 55°C, similar to what has been documented in the literature (DOI: 10.1002/aenm.202101490).

17. Finally, the radar plots presented in Fig. 7 appear somewhat misleading concerning oxidative stability, reductive stability, and electrochemical durability, as they seem to contradict the results discussed in the manuscript. It would be helpful if the authors could clarify this aspect.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
This is a revised manuscript. I have carefully read the article and response to the first-round review, finding that the authors have thoroughly explained the issues raised by the reviewers and supplemented the further experimental investigations and discussions in the corresponding sections. In particular, the authors further elaborated on the crucial dipolar interaction-mediated molecular anchoring effect based on a series of additional spectral and theoretical analyses. I think, this work is innovative and systematic, this manuscript is well organized. So I recommend publishing the manuscript on Nature Communications after addressing the following minor issues.
1. The structural diagram of PF6- anion in Fig. 3c is incorrect. The one shown in the current figure represents the PF5- anion, which is wrong. Suggest the authors further check and adjust it.
2. In Fig. 4a-c, the more specific compositions of these three extracted solvation structures should be presented instead of a rough description, such as Na+-DEE-PF6-.
3. The “Ra” mentioned only in Fig. 6c should also be added and explained in the manuscript so that the readers can better understand.
4. In the manuscript, the discussions on some research results should include appropriate references to further support the conclusions drawn, e. g., the highlighted description in yellow background on page 10.
5. Please provide detailed assembly parameters for the pouch cells. In addition, please provide the energy density of the pouch cells to demonstrate the practical value of the electrolyte.

Reviewer #2

(Remarks to the Author)
The revised manuscript has undergone significant improvement. My concerns were addressed by additional figures and discussions. I am satisfied with this version.

Reviewer #3

(Remarks to the Author)
The authors have addressed all my concerns, I would recommend its publication now.

Reviewer #4

(Remarks to the Author)
Thank you to the authors for their response and revisions. Many comments are addressed, however, several key issues remain unresolved or have been selectively avoided. The revised manuscript continues to omit critical analyses necessary to substantiate the claims and improve the overall quality of the work. In its current form, it requires major revision. I disagree with several of the authors’ interpretations and claims, as detailed below.

1. The claim of superior interfacial stability and the associated radar plots (Figures 5 and 7) are misleading. The NP electrolyte exhibits the highest oxidative stability, and the ND electrolyte shows the highest reductive stability, not the NDPP electrolyte (confirmed in the revised version). This interpretation could be verified using three-electrode CV measurements to eliminate cross-talk from Na metal. Importantly, the radar plots should incorporate these results and explicitly highlight the limitations of the NDPP electrolyte.

2. Capacity retention must be rigorously evaluated in full cell format using a hard carbon anode at a lower rate (e.g., C/10–C/5) to assess interfacial (SEI) stability. These full-cell results should form a central part of the main discussion for the electrochemical performance, not remain supplementary.

3. The reported 79.1% capacity retention for NVPOF//HC after 1000 cycles at 2C, presented as good performance, is misleading. Each 2C cycle lasts only about 1 hour, whereas a C/5 cycle requires roughly 10 hours (charge + discharge). Thus, 1000 cycles at 2C correspond to only ~100 cycles at C/5 in total cycling time. Achieving merely 79% capacity retention after the equivalent of ~100 C/5 cycles (~1000 hours of operation) is therefore poor. Cycling at high rates artificially inflates retention values. For reference, NVPF|HC cells (2-4.3V) with conventional carbonate electrolytes [DOI: 10.1149/2.0831802jes] exhibit over 90% retention after 3000 hours (equivalent of 3000 cycles at 2C).

4. The NVPOF|CC cell configuration is conceptually flawed and cannot be generalized to practical Na-ion cells. The role of the carbon cloth (CC) is not defined. Supplementary Figure 23 shows very low CE for the first ~20 cycles, yet capacity appears retained, indicating a substantial sodium reservoir in the CC. If the carbon cloth is presodiated, why its not mentioned in experimental section. Overall, NVPOF|CC cells with unlimited Na inventory from sodiated carbon cloth are representative for NVPOF|HC full cells.

5. The revised manuscript still lacks NVPOF|HC full-cell data at elevated temperature (55 °C) and low C-rate (C/5) without

carbon cloth trick or presodiation. Such baseline data are essential for comparison and are standard in the quality literature [DOI: 10.1002/aenm.202101490; 10.1002/aenm.201901431; 10.1149/1945-7111/ad47da].

6. It is unclear why ionic conductivity, 19F NMR, and related properties of NDP are not presented in the main text when NDP is compositionally closest to NDPP.

7. The authors acknowledge in their response to Q1 that the electrolyte shows poor stability at 70 °C due to oxidative decomposition and parasitic reactions. Yet, the abstract still claims “superior high-temperature stability at 70 °C” based on data limited to 3.9 V with NVP. To satisfy this claim, high temperature performance data for layered oxide or polyanionic compounds full cell at high voltage of at least 4.2V is necessary.

8. The response to Q11 is inadequate. The authors claim stronger PC–PFPN and DEE–PFPN interactions than PFPN–PF6, yet HOESY NMR shows only PFPN–PF6 interactions, with no cross-peaks for PC–PFPN or DEE–PFPN. The authors must clarify Figure 3e interpretations related to NMR observations.

9. Similarly, the claim of low-temperature performance is not well supported. The abstract mentions operation under extreme temperatures down to –60 °C, but this is valid only for NVP|Na half cells, and even then, only when the upper cutoff is increased to 4.2 V (instead of 3.9 V) to recover capacity lost due to polarization. Meanwhile, NFNMO|HC pouch cells present only discharge curves at –25 °C and –40 °C. Why is the complete charge–discharge profile of the full cell not compared in the same plot for room temperature and –40 °C/–60 °C conditions inline with the claims?

Version 2:

Reviewer comments:

Reviewer #4

(Remarks to the Author)
I thank the authors for their rigorous revision and response to the comments. Only one point I want to highlight is that the cell capacity cannot go to 0 mAh/g directly from ~100 mAh/g for NP and ND electrolyte in Fig. 5i. I strongly believe this is from the cell balancing or cell assembly issue and not representative of the electrolyte. I would advise to remove the 0 mAh/g capacity data point from both the curves. If authors believe that what they observe is real and reproducible then it will be raising more questions behind the reasons for the same: its even worse than roll over cell failure. If the 0 mAh/g data point are removed the manuscript is in perfect state for publications without further review process.

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We would like to thank the four reviewers for their profound and insightful comments, which help us to improve the manuscript effectively. The relevant parts of the manuscript have been modified according to the reviewers' comments. Below is our point-by-point response to each of the comments. All changes in the revised manuscript have been highlighted in yellow background.

For Reviewer #1:

Overall assessment: This work reports a molecular anchoring electrolyte to construct a dynamic hierarchical solvation network for safe sodium-ion batteries. The designed NDPP electrolyte showed compatibility with HC negative electrode and NVPOF positive electrode. Multiscale characterizations and theoretical insights reveal the unique interface stabilization mechanism towards robust interphases. While the proposed mechanism involving dipole-mediated SEI/CEI formation is conceptually valuable, substantive concerns regarding methodological rigor and scientific advancement preclude its current suitability for publication in Nature Communications. The key limitations are outlined as follows:

***Response*:** We sincerely thank the Reviewer 1 for the thoughtful evaluation of the conceptual value of the dipole-mediated interface stabilization mechanism we proposed. We acknowledge there are still deficiencies in the methodological rigor and scientific advancement.

In response, we have conducted additional multiscale experiments for verification and provided elaborate explanations. For instance, NMR, Raman techniques and MD simulations have been further investigated to disclose the dipolar interaction-mediated solvation characteristic (**Q2**). Furthermore, in situ Raman spectroscopy has also been employed to reveal the evolution of the solvation during the charge/discharge cycle (**Q3**). Additionally, the NFNMO//HC pouch cells are assembled to substantiate the great adaptability of the NDPP electrolyte (**Q7**).

In addition, the Reviewer 1 also mentioned prior works have extensively explored weak-solvation electrolytes employing analogous solvent systems (DEE/PFPN) (**Q4**). Specifically, (1) Wang et al. systematically investigated the terminal groups of linear ethers (DME, DEE, DBE) and their impacts on solvation effect and interface chemistry, ultimately leading to distinct electrochemical properties and deposition morphologies (Angew. Chem. Int. Ed. 2023, 62, e202313447). Among them, DEE

stands out with its middle-length ethoxy terminal groups (0.5 M $NaPF_6$ DEE) and demonstrates the moderate Na^+ solvation and stable cycling of sodium metal batteries. (2) Zhang et al. designed and synthesized a multifunctional additive (PQA-NO_3, PN) for ether-based electrolytes (1 M LiFSI DEE/DME, DEE is diethyl ether, which is distinct from ethylene glycol diethyl ether in our work), where PN preferentially participates in the formation of SEI on the anode side, while optimizing the solvation configuration and enhancing the electric double layer at the cathode/electrolyte interface, promoting the comprehensive electrochemical performance of lithium metal batteries (Nat. Commun. 2025, 16, 3344). (3) Zou et al. designed a novel all-fluorinated electrolyte ($LiPF_6$ in MDFA/PFPN/FEC) by regulating the Li^+ solvation-coordination environment for high-voltage NCM811//graphite lithium-ion batteries with good electrochemical stability, high power density and wide-temperature operation capability from -50 to 60 ℃, providing new insights into the electrolyte behavior at the molecular scale including the bulk solution and electrode/electrolyte interface (Angew. Chem. 2023, 135, e202216189). (4) Although similar solvents have been applied in previous literature, our current work still demonstrates the following novelty: we developed a dipolar interaction-mediated molecular anchoring electrolyte engineering, which integrates strongly solvated ester (PC), weakly solvated ether (DEE) and anti-solvent (PFPN) for safe and durable SIBs under extreme conditions. Multiscale characterizations and theoretical insights revealed a dynamic hierarchical solvation network constructed by multiple dipolar interactions among PF_6^- anions and solvent molecules, ultimately the prominent electrochemical improvements can be achieved in sodium-ion batteries even under a wide temperature range (-60~70 ℃) with the dipolar interaction-mediated solvation-interface synergistic stabilization mechanism. Therefore, our current work differs fundamentally from previous studies in terms of core scientific issues, electrolyte design concepts and mechanism explanations.

Based on the above points, we have strived to address the issues raised by the Reviewer 1 to ensure the methodological rigor and scientific advancement of our work. The specific revision details are presented below.

Q1: The LSV profiles in Fig. 2d-e inadequately characterize the redox thresholds of NDPP electrolyte. The absence of distinctive PFPN decomposition peaks in both anodic and cathodic scans raises questions about the actual decomposition pathways and potential parasitic reactions.

***Response*:** Thanks for the reviewer's valuable suggestion. We have further adjusted the LSV curves

in Figs. 2d, e and Supplementary Figure 5, the sequence of electrochemical oxidation stability of these electrolytes is ND < NDP < NDPP < NP, while the sequence of their reduction stability is as follows: NP < NDP < NDPP < ND. Among them, the NDPP electrolyte demonstrates the comprehensive electrochemical stability to sustain the stable operation of the cathodes and anodes. Despite the presence of complementary PC and DEE solvents, the NDP electrolyte fails to exhibit the desired electrochemical redox stability. This phenomenon further confirms the indispensable role of PFPN, while the decomposition peaks of PFPN may not have been clearly identified, especially at the increased scanning rate. **Please refer to Figs. 2d, e in Page 8 in the revised manuscript and Supplementary Figure 5 in Page 6 in the revised Supporting information.**

Q2: Although molecular dynamics (MD) simulations propose specific solvation configurations, the experimental validation remains fragmentary. NMR and vibrational spectroscopy data currently focus solely on identifying selected molecular interactions, rather than systematically correlating with MD-predicted coordination structures.

***Response*:** Thank you for your insightful suggestion. Specific solvation configurations have been demonstrated in Supplementary Figure 10 based on molecular dynamics simulations. (1) The variation of PF_6^- anions in the Na^+ solvation structures was further analyzed by the chemical shift in the ^{19}F NMR spectra. We further demonstrated the ^{19}F NMR spectrum of NDP electrolyte. As displayed in Fig. 3b and Supplementary Figure 8, there is an upfield shift of P-F peaks in PF_6^- when the electrolyte changes from ND to NDPP, and NP, manifesting the increased electron cloud density around F and enhanced shielding effect (Adv. Funct. Mater. 2023, 33, 2305974; Nat. Commun. 2024, 15, 8866). This might be attributed to the weak interaction force between Na^+ and PF_6^- in NP electrolyte, while the relatively strong interaction in ND electrolyte, and the moderate interaction in NDP and NDPP electrolytes. This phenomenon is in agreement with the subsequent theoretical calculation results, specifically, in the ND electrolyte, a relatively greater number of anions are involved in the Na^+ coordination than those of NP and NDPP electrolytes, and the NDPP electrolyte demonstrates a balanced coordination of anions and dipoles. **Please refer to Page 10 in the revised manuscript.** (2) The Raman analysis of salt, solvents and electrolytes were executed to identify the solvation and intermolecular interactions among various electrolyte components (Fig. 3a and Supplementary Figure 7). The peaks around 430 and 807 cm^{-1} correspond to the free DEE molecules, and their weakening in the NDPP electrolyte indicates the reduced free DEE. Additionally, the blue shift of the coordinated PC and DEE peaks can be observed in NDPP electrolyte, further implying

the reduction of free solvents. Furthermore, there is a strong peak at 728.1 cm^{-1} in NDPP, assigned to PFPN. Meanwhile, this peak exhibits a red shift compared to pure PFPN solvent, indicating the presence of interactions between PFPN and other electrolyte components (e. g., PF_6^-, PC and DEE). The peak appears at 729~744 cm^{-1} can be attributed to coordinated PF_6^-. **Please refer to Pages 9-10 in the revised manuscript.**

Q3: The manuscript lacks in situ/operando analyses (e.g., in situ Raman, in situ FTIR) to probe the potential-dependent evolution of solvation structure and desolvation kinetics during battery operation.

***Response*:** We appreciate the kind reminding of reviewer. As shown in Fig. 6e, in situ Raman analysis of the NVPOF//Na cell was executed to study the evolution of solvation during the charge/discharge process. The cathode surface exhibits characteristic vibration bands around 710, 850 and 950 cm^{-1}, corresponding to the PC and DEE solvents. And the peaks at ~727 and 739 cm^{-1} can be assigned to PFPN and PF_6^-, respectively. The peak shift indicates the changes in the solvation structure, the reversible peak shift demonstrates the reversibility of (de-)solvation during the cycle. **Please refer to Page 17 Line 30 and Page 18 Lines 1-5 in the revised manuscript.**

Q4: Prior works (Angew. Chem. Int. Ed. 2023, 62, e202313447; Nat Commun 16, 3344 (2025); Angew. Chem. 2023, 135, e202216189) have extensively explored weak-solvation electrolytes employing analogous solvent systems (DEE/PFPN), thereby diminishing the novelty of the current approach.

***Response*:** We are grateful to the reviewer for providing the above highly relevant and important references. We have carefully read and studied these advanced works.

(1) Wang et al. systematically investigated the terminal groups of linear ethers (DME, DEE, DBE) and their impacts on solvation effect and interface chemistry, ultimately leading to distinct electrochemical properties and deposition morphologies (Angew. Chem. Int. Ed. 2023, 62, e202313447). Among them, DEE stands out with its middle-length ethoxy terminal groups (0.5 M $NaPF_6$ DEE) and demonstrates the moderate Na^+ solvation and stable cycling of sodium metal batteries.

(2) Zhang et al. designed and synthesized a multifunctional additive (PQA-NO_3, PN) for ether-based electrolytes (1 M LiFSI DEE/DME, DEE is diethyl ether, which is distinct from ethylene glycol diethyl ether in our work), where PN preferentially participates in the formation of SEI on the anode side, while optimizing the solvation configuration and enhancing the electric double layer at the cathode/electrolyte interface, promoting the comprehensive electrochemical performance of lithium

metal batteries (Nat. Commun. 2025, 16, 3344).

(3) Zou et al. designed a novel all-fluorinated electrolyte ($LiPF_6$ in MDFA/PFPN/FEC) by regulating the Li^+ solvation-coordination environment for high-voltage NCM811//graphite lithium-ion batteries with good electrochemical stability, high power density and wide-temperature operation capability from -50 to 60 ℃, providing new insights into the electrolyte behavior at the molecular scale including the bulk solution and electrode/electrolyte interface (Angew. Chem. 2023, 135, e202216189).

(4) Although similar solvents have been applied in previous literature, our current work still demonstrates the following novelty: we developed a dipolar interaction-mediated molecular anchoring electrolyte engineering, which integrates strongly solvated ester (PC), weakly solvated ether (DEE) and anti-solvent (PFPN) for safe and durable SIBs under extreme conditions. Multiscale characterizations and theoretical insights revealed a dynamic hierarchical solvation network constructed by multiple dipolar interactions among PF_6^- anions and solvent molecules, ultimately the prominent electrochemical improvements can be achieved in sodium-ion batteries even under a wide temperature range (-60~70 ℃) with the dipolar interaction-mediated solvation-interface synergistic stabilization mechanism.

Based on the above points, our current work differs fundamentally from previous studies in terms of core scientific issues, electrolyte design concepts and mechanism explanations. Therefore, I think our work is highly innovative and has certain guiding significance for the electrolyte design for safe and durable electrochemical systems under extreme conditions.

Q5: The purported "molecular anchoring-solvation-interfacial dynamics" relationship remains conjectural, as no quantitative descriptors or mechanistic models explicitly link these hierarchical processes to the observed electrochemical behaviors.

***Response*:** We are very grateful for the valuable and profound suggestions made by the Reviewer, and we also fully agree that establishing accurate and quantitative descriptors or models is crucial to thoroughly clarify the proposed “molecular anchoring-solvation configuration-interfacial dynamics” structure-property relationship. We have investigated the relevant literature and found that it remains a very challenging and significant task (Nat. Commun. 2024, 15, 2033; Angew. Chem. Int. Ed. 2024, 63, e202412703; Angew. Chem. Int. Ed. 2025, 64, e202506395). This further indicates the direction of our future work. In this study, we have proposed a fundamental mechanism framework to integrate the multiscale experimental and theoretical findings. As illustrated in Fig. 7, we have strived to clarify

the relationship between the hierarchical processes and electrochemical behaviors. Specifically, the dipolar interaction-mediated molecular anchoring engineering regulates the solvation configuration and effectively restricts the reactive PC/DEE solvent molecules (Fig. 3 and 4, Supplementary Figure 10), further modulating the subsequent interface formation (Fig. 6), ultimately exerting the crucial influence on the electrochemical properties (Fig. 5). Compared to conventional ND and NP electrolytes, the introduction of PFPN enables the NDPP electrolyte to demonstrate abundant intermolecular dipolar interactions, alleviating the unfavorable decomposition process of organic solvents, and is conducive to the interfacial stability and long-term cycling stability with high CEs.

Please refer to Page 19 Lines 17-20 in the revised manuscript.

Q6: The authors highlighted the thin, uniform and robust organic-inorganic coupling interface on NVPOF. While the continued use of NVP cathodes for extreme-temperature evaluations (despite emphasizing NVPOF's CEI advantages) creates a methodological paradox that undermines the mechanistic conclusions regarding interfacial stability.

***Response*:** We thank the reviewer for the insightful suggestion. First of all, we discovered the thin, uniform and robust organic-inorganic coupling interface can be constructed on the NVPOF cathode, which is primarily responsible for remarkable electrochemical durability conferred by the integrated NDPP electrolyte design. Furthermore, the feasibility assessment of the electrolyte under extreme temperatures is crucial to prove its practicality. Generally, apart from the electrolyte, the electrode material also exerts a significant impact on the low-temperature performance (Carbon Energy. 2024, 6, e546; Chem. Rev. 2024, 124, 4778-4821). To ensure the objectivity of the assessment, the limitations from the electrode should be excluded. Unfortunately, poor electronic conductivity of NVPOF cathode material makes it difficult to accomplish the tests at extremely low temperatures. Specifically, the NVPOF material, without being combined with carbon, exhibits significantly lower electronic conductivity than that of NVP (carbon-coated), hindering its low-temperature properties (Adv. Energy Mater. 2025, 2500471). In contrast, NVP is commonly used as a representative cathode material to reasonably evaluate the temperature adaptability of the electrolyte, as reported in most literature (Proc. Natl. Acad. Sci. U.S.A. 2024, 121, e2316914121; Angew. Chem. Int. Ed. 2024, 63, e202401051; Energy Environ. Sci. 2025, 18, 7669-7679).

Q7: The absence of large-format pouch cell data substantially weakens the translation potential assessment of this electrolyte technology.

***Response*:** Thanks for the reviewer's valuable suggestion. The NFNMO//HC pouch cells have been

assembled for the further electrochemical evaluation of the electrolyte. Specifically, Fig. 5h shows their low-temperature performances (charging at room temperature and subsequently discharging at low temperatures). The discharge capacity of 1.05 Ah can be obtained at -25 °C. Even at -40 °C, the discharge capacity still reaches 0.66 Ah, substantiating the great adaptability of the NDPP electrolyte.

Please refer to Fig. 5h in Page 14 and Page 15 Lines 18-21 in the revised manuscript.

For Reviewer #2:

Overall assessment: This work developed a new electrolyte, NDPP, by mixing PC, DEE and PFPN with the $NaPF_6$ salt, to enhance safety and durability of sodium ion battery (SIB). SIB is a promising solution for energy storage and as such the scope of this work addresses a contemporary and highly demanded topic.

I like the concept of "dipolar interaction-mediated solvation-interface synergistic stabilization mechanism". However, this mechanism is short of evidence in the current version of the manuscript. The Raman spectrum of NDPP is almost simply a linear combination of individual solvent molecules, with only difference of redshift described at line 195. This redshift is using pure PFPN solvent as a reference, which can be a result of polarization effect Na[+] instead of other solvents mentioned at line 196. There is no unique peaks arising from anion-dipole and dipole intermolecular interaction. If strong intermolecular interactions exist, it will show up in infrared spectroscopy, which is missing in the manuscript. Figure 3c 2D NMR doesn't have any cross peaks beyond two neural solvents PFPN-PC and didn't compare to a simple PFPN/PC mixture. As a minimum requirement for the synergistic stabilization claim, at least three component correlation is required. This work uses Figure 4h to demonstrate the interactions. However, there is no single snapshot captured from molecular dynamics, that has a structure similar to the one drawn in Figure 4h. To remedy these issues, it will need a fundamental change to the manuscript, which is beyond the extent of major revision.

Below are several specific comment regarding technical details:

***Response*:** We are very grateful to the Reviewer 2 for the in-depth and meticulous evaluation of our current manuscript. Thanks for your acceptance of the proposed concept of “dipolar interaction-mediated solvation-interface synergistic stabilization mechanism”. We also acknowledge the deficiencies in the mechanism study, and have made the following detailed supplements in response to the raised questions.

(1) As shown in Fig. 3a and Supplementary Figure 7, Raman analysis of salt, solvents and electrolytes

were executed to identify the solvation and intermolecular interactions among various electrolyte components. The peaks around 430 and 807 cm^{-1} correspond to free DEE molecules, and their weakening in the NDPP electrolyte indicates the reduced free DEE. Additionally, the blue shift of the coordinated PC and DEE peaks can be observed in NDPP electrolyte, further implying the reduction of free solvents. Furthermore, there is a strong peak at 728.1 cm^{-1} in NDPP, assigned to PFPN. Meanwhile, this peak exhibits a red shift compared to pure PFPN solvent, indicating the presence of interactions between PFPN and other electrolyte components (e. g., PF_6^-, PC and DEE), considering the negligible coordination effect between Na^+ and PFPN. The peak appears at 729~744 cm^{-1} can be attributed to coordinated PF_6^-. **Please refer to Pages 9-10 in the revised manuscript.**

(2) According to the FTIR spectra, the characteristic absorption peaks at 2800-3000 and 1350-1490 cm^{-1} correspond to the stretching and bending vibrations of C-H bonds in the solvents (PC, DEE, PFPN), respectively. The stretching vibrational peak of C=O in PC is observed at 1792.32 and 1794.02 cm^{-1} in NDPP and NP electrolytes, respectively, implying the reduced free PC solvent. The peak at 1116.60 cm^{-1} represents the C-O-C stretching vibration. The stronger vibrational peaks around 846.01 cm^{-1} are assigned to P-F bonds in PF_6^-. Additionally, the weak and broad absorption bands around 3500-3600 cm^{-1} can be attributed to the intermolecular hydrogen bond interactions. (J. Am. Chem. Soc. 2025, 147, 8024−8031; Angew. Chem. Int. Ed. 2025, 64, e202425507). **Please refer to Supplementary Figure 6 in Page 7 in the revised Supporting information.**

(3) In Fig. 3c, there are several distinct cross singles between PC and PF_6^-, between PFPN and PF_6^-, between PFPN and PFPN, respectively, verifying their intermolecular interactions via δ^+H-δ^-F, consistent with the results in Fig. 3e. In addition, 2 D ^{1}H-^{19}F HOESY NMR spectra of a simple PFPN/PC mixture have been provided in **Supplementary Figure 9 in Page 10 in the revised Supporting information**. There are the cross singles between PFPN and PFPN, indicating the intermolecular interactions via δ^+H-δ^-F.

(4) The electrochemical improvements in this work are attributed to the synergistic stabilization mechanism: both hierarchical solvation with dipolar interactions and interfacial reinforcement through molecular anchoring engineering.

(5) We further elaborated on Fig. 4h, as mentioned in **Q1** below.

In conclusion, the integrated NDPP electrolyte demonstrates a hierarchical solvation with abundant

dipolar interactions among anions and solvent molecules, which activates the PFPN molecules that are hardly involved in Na^+ solvation and restricts the free PC/DEE molecules. This further alleviates the solvent degradation, facilitating the construction of robust electrode-electrolyte interfaces on the electrodes and ultimately promoting the electrochemical improvements.

Q1: In Figure 4h, Why the anion-dipole interaction dashed line connects to the far end of PC ellipse rather than near end? I can understand that the electrostatic force from Na^+ puts a preferred orientation of PC. However, this will prefer a negatively charge a near end, and lead to a repulsive interaction. This is a destabilizing force to the structure proposed in Figure 4h, contradictory to the synergistic stabilization but it shouldn't be ignored. More likely, this near end repulsive force is stronger than the attractive far end interaction and is expected to be primary force of the anion-dipole interaction. By ignoring stronger force and drawing only the weaker force, Figure 4h is very misleading. I can't be convinced that this solvation structure is stable.

***Response*:** Thanks for the reviewer's valuable suggestion. We apologize for the confusion caused by Fig. 4h. Whereas it is merely a schematic diagram to simplify the intricate intermolecular interactions present in the NDPP electrolyte, and does not represent any specific solvation structure. Particularly, there are the cation-anion coordination interaction between Na^+ and PF_6^-, cation-dipole interaction between Na^+ and PC or DEE, anion-dipole interaction between PF_6^- and PC or DEE or PFPN, and dipole-dipole interaction among PC, DEE, PFPN molecules. Fig. 2a and Supplementary Figure 10 clearly demonstrate its specific solvation configuration with intermolecular interactions. **Please refer to Page 11 in the revised Supporting information.**

Q2: The DFT calculation was oversimplified. The equation at 484 ignores the solvation energy of Na[+]-solvent complex and Na[+], which can change the relative order of the computed binding energies.

***Response*:** We thank the reviewer for the insightful suggestion. Generally, the calculation of binding energy between two components (A and B) was defined as: $E_b = E_{A\text{-}B} - E_A - E_B$, where $E_{A\text{-}B}$ is the total energy of the A-B complex, E_A is the energy of the A component and E_B is the energy of the B component, A and B can be the cation, anion, and solvent. The intricate and variable interactions exist in the electrolyte (e. g., Supplementary Figure 10), which can decrease the absolute value of binding energies while the order of binding energies between different components hardly changes (Batteries & Supercaps 2019, 2, 128-131; Energy Storage Materials 2025, 81, 104467).

Q3: The concept of "no-solvated PFPN" (e.g. the one at line 162) is confusing and needs further

explanation. In particular, is it a homogeneous part of the electrolyte solution?

***Response*:** We appreciate the kind reminding of reviewer. In the NDPP electrolyte system, PFPN hardly coordinates with Na^+, implies its non-solvated characteristic. And, it is homogeneous in the electrolyte solution through intermolecular interactions.

Q4: What are the dashed lines in Figure 4(d-f)?

***Response*:** Thanks for the reviewer's valuable suggestion. The dashed lines in Fig. 4d-f represent the coordination numbers (CNs) for different Na^+-anion and Na^+-solvent complexes.

For Reviewer #3:

Overall assessment: In this manuscript, the authors report a dipolar interaction-mediated and molecular anchoring electrolyte to enable the stable operation of sodium-ion batteries under wide temperatures. Particularly, the electrolyte features intrinsic flame retardancy, oxidative/reductive reliability and electrochemical durability against both cathode and anode. A series of experimental characterizations and theoretical calculations are conducted to reveal the structure-property relationship. In my opinion, this work is interesting, and this manuscript is well organized. So I recommend publishing the manuscript on Nature Communications after addressing the following issues.

***Response*:** We are very grateful to Reviewer 3 for the positive evaluation of our present work and the recommendation for publishing after modification. We would also like to thank Reviewer 3 for the following revision suggestions.

Q1: The authors point out that simple blending of PC and DEE fails to achieve the desired properties and it is difficult to fully utilize their respective advantages. I suggest providing more explanation and discussion on this phenomenon.

***Response*:** Thanks for the reviewer's valuable suggestion. We have further discussed the phenomenon in Supplementary Figure 3. Specifically, by simply blending PC and DEE, the obtained NDP electrolyte exhibited unsatisfactory electrochemical stability with insufficient CEs for both NVPOF cathode and HC anode, which may be attributed to the presence of abundant free solvents and the instability of electrode/electrolyte interfaces. **Please refer to Page 4 in the revised Supporting information.**

Q2: The concept of dipolar interaction-mediated molecular anchoring effect is crucial in this work, but there is a lack of sufficient explanation on the concept and its function.

***Response*:** Thank you for your insightful suggestion. We have further discussed the concept of dipolar interaction-mediated molecular anchoring effect. The intricate intermolecular interactions in the integrated solvating electrolyte NDPP have been demonstrated through molecular dynamics simulations (Supplementary Figure 10). Apart from anion-dipole interactions between PF_6^- and PC or DEE and dipole-dipole interactions between PC and DEE, the dipolar interactions related to PFPN are also involved, which increases the disorder of the electrolyte system and diversity of solvation, facilitating ionic conductivity and the formation of uniform interfaces. Additionally, the participation of PFPN in the solvation shell further stabilizes the reactive organic solvents through dipolar interaction-mediated molecular anchoring effect, conducive to interfacial and electrochemical stability. **Please refer to Page 11 in the revised Supporting information.**

Q3: Compared with ND and NP electrolytes, the NDPP electrolyte exhibits significantly enhanced electrochemical durability according to Fig. 5a-c. Understanding the reasons for the performance improvement is necessary. I suggest the authors further discuss this concern.

***Response*:** We appreciate the kind reminding of reviewer. Further discussion on the aforementioned concern has been supplemented. As shown in Fig. 5a-c, compared with ND and NP electrolyte, the modified NDPP electrolyte demonstrates significantly improved electrochemical stability, which mainly stems from the restricted PC/DEE free molecules and robust F/N-based electrode/electrolyte interfaces through the introduction of PFPN. **Please refer to Page 13 Lines 8-9 in the revised manuscript.**

Q4: The sodium layered oxide cathode has also been investigated in Fig. 5e. The corresponding charge-discharge curves should be supplemented.

***Response*:** Thanks for the reviewer's valuable suggestion. We have supplemented the corresponding charge-discharge curves of the sodium layered oxide cathode. **Please refer to Fig. 5d in Page 14 in the revised manuscript.**

Q5: The depth profiles of ion fragments based on TOF-SIMS should also be added.

***Response*:** Thank you for your suggestion. We have added the corresponding depth profiles of ion fragments based on TOF-SIMS. **Please refer to Supplementary Figure 30 in Page 31 in the revised Supporting information.**

Q6: The capacity retention at −40 °C is much lower than at 25 °C. The rate-limiting step should be clearly identified.

***Response*:** Thanks for the reviewer's valuable suggestion. We have further elaborated on the rate-

limiting step at low temperatures. The Na^+ transportation on the anode side during the charging process is mainly divided into the following steps: (i) solvated Na^+ transports in the bulk electrolyte, (ii) Na^+ de-solvation at the surface of the SEI, (iii) Na^+ migrates into the anode across the SEI, (iv) electrochemical reduction reactions of the electrode occur. The relatively poor electrochemical properties at low temperatures compared to those at room temperature (e. g., reduced capacity, insufficient rate capability and lifespan) may be attributed to the sluggish ion diffusion kinetics during one or several of the above processes. The de-solvation step is considered to be the rate-determining step for the interfacial ion transfer process, demonstrating a crucial influence on the electrochemical stability. **Please refer to Page 20 in the revised Supporting information.**

Q7: "For full-cell fabrication, all HC anodes were pre-sodiated chemically, and the N/P ratio was controlled at about 1.2." The pre-sodiated process should be fully detailed, as it plays a decisive role in determining battery performance.

***Response*:** We appreciate the kind reminding of reviewer. We have made a detailed supplement to the pre-sodiated process of HC anodes in the Methods section. Specifically, drop ~60 μL electrolyte on the sodium metal, and then cover sodium metal on the HC anode to ensure the metallic sodium is in complete contact with the HC anode, keeping this state for 3-7 h to complete the pre-sodiation of HC anode. **Please refer to Page 21 Lines 28-29 and Page 22 Lines 1-2 in the revised manuscript.**

Q8: "Consequently, representative high-voltage phosphates, layered oxide cathodes and hard carbon (HC) anode demonstrate extraordinary cycling stability, e.g., 87.6% of reversible capacity after 5000 cycles for $Na_3V_2(PO_4)_2O_2F$ (NVPOF) model cathode." The battery performance of hard carbon as the anode is not included in the main manuscript. Figure S14 only shows the HC/Na cell performance, which is hardly extraordinary. Additionally, the poor performance of the HC/Na cell stems from the sodium metal, not the electrolyte or hard carbon. Please correct these issues.

***Response*:** We appreciate the kind reminding of reviewer. We have corrected the issues mentioned above. **Please refer to Page 3 Lines 29-30 in the revised manuscript.**

Q9: Figure 6b requires revision as the XPS fitting demonstrates: (1) non-aligned peaks for identical species, and (2) inconsistent peak broadening. Standardization is needed.

***Response*:** Thanks for the reviewer's valuable suggestion. All values of binding energy were referenced to the C 1s peak of carbon located at 284.8 eV.

Q10: "0.8 M $NaPF_6$ in DEE-PC-PFPN (5: 5: 2 by volume ratio)." Given the crucial impact of sodium salt concentration and solvent ratio on battery performance, please justify the selected ratio.

***Response*:** Thanks for the reviewer's valuable suggestion. The various integrated NDPP electrolytes have been prepared with different solvent ratios (DEE/PC = 4/6, 5/5, 6/4, in volume). Considering the weak salt solubility in PFPN, 0.8 M was chosen as an appropriate concentration. They all demonstrated the prominent electrochemical reversibility and stability, indicating the effectiveness of the dipolar interaction-mediated molecular anchoring engineering. The NDPP (0.8 M $NaPF_6$ in DEE-PC-PFPN, 5: 5: 2 in volume) sample was applied as a representative electrolyte model to further study the solvation and working mechanism. **Please refer to Supplementary Figure 4 in Page 5 in the revised Supporting information.**

For Reviewer #4:

Overall assessment: This manuscript examines the impact of incorporating DEE and PFPN solvents into classical 1M $NaPF_6$ in PC electrolytes, focusing primarily on the performance of half-cells, mainly containing cathode active materials. While the introduction presents some impressive claims, most of them do not align with the results observed with the NDPP electrolyte discussed by the authors. The writing lacks clarity and coherence, and the conclusions drawn do not reflect the observed results. Most importantly, rigorous full-cell data is lacking, and the present data shows that NDPP electrolyte is not stable, leading to capacity loss even when cycled at fast rates (2C) in the full cell. Below are some specific comments:

***Response*:** We sincerely thank the Reviewer 4 for the profound and constructive comments on our current manuscript. In response to the deficiencies in the clarity, coherence and rigor of the introduction and results sections in the current manuscript, we have carefully examined and thoroughly revised the relevant sections. Specifically, considering some of the potentially misleading claims and descriptions presented in the introduction, we have provided detailed explanations for them, such as **Q1**, **Q2** and **Q3** below. Additionally, the concerns regarding the full cell data have also been properly addressed, as demonstrated in **Q16**. As shown in Supplementary Figure 22, the NDPP electrolyte can sustain the stable operation of NVPOF//HC full cells with 79.1% of capacity retention after 1000 cycles at 2 C. Generally, the irreversible decomposition of the electrolyte leads to poor CEs. While flat CEs during the cycle can be observed, which further indicates the electrochemical durability of this electrolyte. In addition, the NVPOF//HC full cell in NDPP electrolyte demonstrated relatively lower electrochemical stability, compared to the NVPOF//Na half cell (87.6% of capacity retention after 5000 cycles at 2 C in Fig. 5b), which might mainly be attributed to the matching degree

of the cathode and anode as well as the assembly technology of the full cell. Furthermore, we have studied the relevant literature, and it can be observed that the electrochemical stability of NVPOF//HC full cells we obtained is not poor (Adv. Mater. 2022, 34, 2110108; Adv. Funct. Mater. 2024, 34, 2315318; Adv. Mater. 2024, 36, 2310051). In conclusion, we have made efforts to address the issues raised by the Reviewer 4 to enhance the clarity, coherence and rigor of our manuscript. Below are the specific revision suggestions and response details.

Q1: In the introduction of the manuscript, please note the claim of an "admirable capacity retention of 95.2% over 900 cycles at 70 °C." However, this assertion seems to apply only to low-voltage cathodes. As indicated in Supplementary Fig. 9c, the NVPOF//Na half-cell is unable to complete even a single cycle, suggesting substantial overcharging due to electrolyte oxidation. Could the authors clarify this discrepancy?

***Response*:** Thanks for the reviewer's valuable suggestion. We have mentioned "the electrolyte also sustains successful operation under wide temperatures (-60 ~ 70 °C) with admirable capacity retention of 95.2% over 900 cycles at 70 °C and 51.2 mAh g^{-1} of reversible capacity at -60 °C for $Na_3V_2(PO_4)_3$ (NVP)" in the introduction of the manuscript. For the NVPOF//Na half cell under extreme high-temperature condition (70 °C), it demonstrates poor electrochemical behavior with irreversible side reactions during the charging process, which originates from the oxidation decomposition of the electrolyte, as well as the parasitic interfacial reactions between the electrolyte and active electrode material in a highly charged state. Considering rational selection of the electrode material system is also crucial for evaluating the suitability of the electrolyte. In order to conduct a more comprehensive assessment of high-temperature adaptability of the electrolyte, another representative sodium-based cathode system (NVP) was further studied. As expected, the NVP//Na half cells exhibit prominent electrochemical stability at high temperatures.

Q2: The authors mention "energy density reduction (e.g., capacity loss in cathodes caused by high-salt systems)" in the introduction. I would appreciate clarification on the meaning of this statement and any supporting literature that may be available.

***Response*:** Thank you for your suggestion. Generally, the high concentrated electrolytes have higher viscosity, which leads to a decrease in ionic conductivity and thus adversely affects the kinetics of the battery. In addition, their poor wettability towards the electrodes and separators is also unfavorable for ionic migration, resulting in capacity loss (Mater. Futures 2023, 2, 012101; ACS Energy Lett. 2024, 9, 373-380).

Q3: The claim regarding "process economic efficiency deterioration (e.g., skyrocketing costs of fluorinated solvents)", followed by the use of a fluorinated PFPN in the manuscript, raises some questions. It may be helpful for the authors to address this apparent contradiction.

***Response*:** We appreciate the kind reminding of reviewer. Fluorinated solvents face trade-offs. Most of the literature use fluorinated molecules as the main solvents, especially weakly solvating electrolytes, which leads to an increase in costs (Adv. Funct. Mater. 2024, 34, 2401868; J. Am. Chem. Soc. 2025, 147, 16107-16118). While in this work, we designed an electrolyte system (0.8 M $NaPF_6$ PC/DEE/PFPN, 5/5/2, in volume), where conventional carbonate and ether (PC and DEE) as the main solvents, and a small amount of PFPN was further utilized to achieve flame retardancy and regulate the solvation environment.

Q4: The manuscript employs several abbreviations such as DEE, PFPN, NDP, NDPP, NT0102, and NVP without definitions at all!!! Additionally, the electrolyte formulations (NP, ND, NDP, and NDPP) are only outlined at the end of the supplementary information. To enhance clarity for readers, it would be beneficial for the authors to define these terms upon their first use in the text, including common abbreviations like PC.

***Response*:** We sincerely thank the Reviewer for the thoughtful comment. These abbreviations have been summarized in Supplementary Table 1 and 3 in the Supporting information. Furthermore, we have also added them in the corresponding places within the revised manuscript.

Q5: Were all the parameters presented in Fig. 1b measured by the authors? If some were not, I recommend that the authors provide references for this information, apart from the HOMO-LUMO calculations they performed.

***Response*:** Thank you for your valuable suggestion. Fig. 1b summarized the basic physicochemical properties of representative carbonate and ether solvent molecules. We conducted the HOMO/LUMO and binding energy calculations with details in the Supplementary Figure 1 and 2. While the other parameters including dielectric constant, DN value, melting and boiling points are introduced from the previous literature (Adv. Mater. 2023, 2308484; Chem. Soc. Rev., 2023,52, 5255-5316). **Please refer to Page 4 Lines 23-24 in the revised manuscript.**

Q6: Fig. 2a presents a schematic of different solvation structures. Citing the source of these solvation structures would strengthen the manuscript, as they are not characterized within the paper.

***Response*:** We sincerely thank you for your valuable suggestion. The corresponding solvation structures with intricate intermolecular interactions (e. g., ion-ion, ion-dipole and dipole-dipole) have

been demonstrated through theoretical calculations (Supplementary Figure 10). Specifically, in the weakly solvated electrolyte ND, the first solvation shell forms due to the strong electrostatic forces between the Na^+ cation and the PF_6^- anions, DEE solvent molecules (dipole). For the secondary solvation shell, it is less compact and contains the partially restricted solvent molecules, which interact with anions and solvent molecules through anion-dipole (δ^-F in PF_6^- and δ^+H in DEE) and dipole-dipole (δ^+H in DEE and δ^-O in DEE). In the strongly solvated electrolyte NP, the first solvation shell consists of closely arranged PC solvent molecules and PF_6^- anion coordinated with Na^+. And the secondary solvation shell is formed due to the intermolecular interactions between PC and PC via δ^+H-δ^-O, as well as PC and PF_6^- via δ^+H-δ^-F. In the integrated solvating electrolyte NDPP, the PC, DEE and PF_6^- all participate in the Na^+ coordination in the first solvation shell. In contrast, PFPN hardly undergoes the coordination with Na^+ in this electrolyte system. In the secondary solvation shell, PFPN can interact with PC and DEE via δ^+H-δ^-O and δ^+H-δ^-N, respectively. In addition, the PF_6^- anion interacts with PC or DEE via δ^-F-δ^+H, and the δ^+H-δ^-O dipolar interaction exists between PC and PC, DEE and DEE, PC and DEE. **Please refer to Supplementary Figure 10 in Page 11 in the revised Supporting information.**

Q7: The optimized structures shown in Fig. S2 raise some concerns, particularly the Na^+--G2 structures, which differ from reported observations in the literature. For example, the structures presented in DOI: 10.1002/cey2.518 appear more consistent.

***Response*:** Thanks for the reviewer's valuable suggestion. The optimized structure for Na^+-G2 complex has been corrected. **Please refer to Supplementary Figure 2 in Page 3 in the revised Supporting information.**

Q8: The CE efficiency of the HC vs. Na cells (supplementary information) is bad for the NDP electrolyte. It may be valuable to include data on the cyclic stability and CE of HC vs. Na cells for the NP, ND, and NDPP electrolytes.

***Response*:** Thank you for your suggestion. The cyclic stability and CE of HC//Na half cells with different electrolytes (NP, ND and NDPP) have been further added, as shown in Supplementary Figure 21. As expected, the HC anode suffers from poor specific capacity and electrochemical stability in the conventional carbonate-based electrolyte (NP), while the ND electrolyte maintains the stable operation of HC//Na half cell. Particularly, the integrated NDPP electrolyte also demonstrates enhanced cyclic stability accompanied by steady CEs, which could be comparable to ND electrolyte. **Please refer to Supplementary Figure 21 in Page 22 in the revised Supporting information.**

Q9: The CV data depicted in Fig. 2d and Fig. 2e could benefit from more rigorous experiments. Increasing the sweep rate and using a reference electrode would help clarify the onset potential for oxidation and yield more reliable reduction curves. Additionally, could the authors explain why the open-circuit voltage (OCV) of the cell with NP in Fig. 2e differs significantly from the other cells?

***Response*:** We sincerely thank the Reviewer for the thoughtful comment. We have further investigated the electrochemical oxidation and reduction stability of various electrolytes by their LSV measurements at 2 mV s^{-1}, as displayed in Supplementary Figure 5. Specifically, the sequence of electrochemical oxidation stability of these electrolytes is ND < NDP < NDPP < NP, while the sequence of their reduction stability is as follows: NP < NDP < NDPP < ND. Among them, the NDPP electrolyte demonstrates the comprehensive electrochemical stability to sustain the stable operation of the cathodes and anodes. Despite the presence of complementary PC and DEE solvents, the NDP electrolyte fails to exhibit the desired electrochemical stability. This phenomenon further confirms the indispensable role of PFPN. In addition, the significantly different OCV of the stainless steel//Na cell with ND in Fig. 2e could be attributed to the electrolyte itself, based on multiple repeated experiments. **Please refer to Supplementary Figure 5 in Page 6 in the revised Supporting information.**

Q10: What specific message do the authors intend to convey through Fig. 3b? If there is an NMR spectrum for the NDP electrolyte, it may fall between the ND and NP electrolytes and should be discussed.

***Response*:** Thank you for your suggestion. The variation of PF_6^- anions in the Na^+ solvation structures was further analyzed by the chemical shift in the ^{19}F NMR spectra. We further demonstrated the ^{19}F NMR spectrum of NDP electrolyte. As displayed in Fig. 3b and Supplementary Figure 8, there is an upfield shift of P-F peaks in PF_6^- when the electrolyte changes from ND to NDPP, NDP, and NP, manifesting the increased electron cloud density around F and enhanced shielding effect (Adv. Funct. Mater. 2023, 33, 2305974; Nat. Commun. 2024, 15, 8866). This might be attributed to the weak interaction force between Na^+ and PF_6^- in NP electrolyte, while the relatively strong interaction in ND electrolyte, and the moderate interaction in NDP and NDPP electrolytes. The difference in the chemical shift of NDP and NDPP electrolytes mainly stems from the addition of PFPN, which can regulate the solvation environment. **Please refer to Page 10 Lines 6-14 in the revised manuscript and Supplementary Figure 8 in Page 9 in the revised Supporting information.**

Q11: The authors assert in Fig. 3e that the interactions between PC-PFPN and DEE-PFPN are

surprisingly stronger than those between PFPN and PF_6^-. Could the authors discuss from HOESY NMR spectra to further illustrate the interactions of PC-PFPN and DEE-PFPN? The interactions of PFPN still remain unclear to me.

***Response*:** We sincerely thank you for the insightful suggestion. As displayed in Fig. 3c, there are several distinct cross singles between PC and PF_6^-, between PFPN and PF_6^-, between PFPN and PFPN, respectively, verifying their intermolecular interactions via δ^+H-δ^-F. This phenomenon is consistent with Fig. 3e. The interactions of PC-PFPN and DEE-PFPN (dominated by δ^+H-δ^-O) may require the further ^{1}H-^{17}O 2 D NMR measurements.

Q12: It would be beneficial to experimentally verify the solvation structures derived from theoretical calculations in order to confirm the calculated hypotheses, particularly since the authors are already utilizing spectroscopic techniques in the manuscript to monitor these interactions.

***Response*:** Thank you for your valuable suggestion. According to the FTIR spectra in Supplementary Figure 6, the characteristic absorption peaks at 2800-3000 and 1350-1490 cm^{-1} correspond to the stretching and bending vibrations of C-H bonds in the solvents (PC, DEE, PFPN), respectively. The stretching vibrational peak of C=O in PC is observed at 1792.32 and 1794.02 cm^{-1} in NDPP and NP electrolytes, respectively, implying the reduced free PC solvent. The peak at 1116.60 cm^{-1} represents the C-O-C stretching vibration. The stronger vibrational peaks around 846.01 cm^{-1} are assigned to P-F bonds in PF_6^-. Additionally, the weak and broad absorption bands around 3500-3600 cm^{-1} can be attributed to the intermolecular hydrogen bond interactions. (J. Am. Chem. Soc. 2025, 147, 8024−8031; Angew. Chem. Int. Ed. 2025, 64, e202425507). Raman analysis of salt, solvents and electrolytes were executed to identify the solvation and intermolecular interactions among various electrolyte components (Fig. 3a and Supplementary Figure 7). The peaks around 430 and 807 cm^{-1} correspond to the free DEE molecules, and their weakening in the NDPP electrolyte indicates the reduced free DEE. Additionally, the blue shift of the coordinated PC and DEE peaks can be observed in NDPP electrolyte, further implying the reduction of free solvents. Furthermore, there is a strong peak at 728.1 cm^{-1} in NDPP, assigned to PFPN. Meanwhile, this peak exhibits a red shift compared to pure PFPN solvent, indicating the presence of interactions between PFPN and other electrolyte components (e. g., PF_6^-, PC and DEE). The peak appears at 729~744 cm^{-1} can be attributed to coordinated PF_6^-. Furthermore, Fig. 3b presents ^{19}F NMR spectra of different electrolytes. There is an upfield shift of P-F peaks in PF_6^- when the electrolyte changes from ND to NDPP, and NP, manifesting the increased electron cloud density around F and enhanced shielding effect (Adv. Funct.

Mater. 2023, 33, 2305974; Nat. Commun. 2024, 15, 8866). This might be attributed to the weak interaction force between Na^+ and PF_6^- in NP electrolyte, while the relatively strong interaction in ND electrolyte, and the moderate interaction in NDP and NDPP electrolytes. This phenomenon is in agreement with the subsequent theoretical calculation results, specifically, in the ND electrolyte, a relatively greater number of anions are involved in the Na^+ coordination than those of NP and NDPP electrolytes, and the NDPP electrolyte demonstrates a balanced Na^+ coordination with anions and dipoles. **Please refer to Pages 9-10 in the revised manuscript.**

Q13: Adjusting the y-axis for CE throughout the manuscript to ranges of 90-101 or 75-102 (considering the lower first cycle CE) may provide a clearer understanding of the CE values for the various electrolyte formulations.

***Response*:** Thank you for your valuable suggestion. We have adjusted the relevant figures in the manuscript (e. g., Figs. 5b and c, Supplementary Figure 21).

Q14: The energy efficiency graph shown in Fig. 5c may not be necessary. It could be more effective to incorporate the curves for NT0102 and NVP instead.

***Response*:** We sincerely thank you for the insightful suggestion. We have made adjustments to Fig. 5. The further charge-discharge curves for NT0102 and NVP have also been demonstrated in the Fig. 5d and Supplementary Figure 13.

Q15: Fig. 5d appears misleading, as ND actually shows better reductive stability than NDPP, while NP demonstrates better oxidative stability than NDPP. This discrepancy should be addressed.

***Response*:** Thank you for your valuable suggestion. As discussed in **Q9**, the ND and NP electrolytes stand out in terms of electrochemical reduction and oxidation stability, respectively. We have further adjusted the radar plots, as shown in Fig. 5e. The integrated electrolyte has demonstrated significant advantages from the following perspectives: ionic conductivity, cyclic life, interfacial stability, energy efficiency and safety, compared with ND and NP electrolytes. **Please refer to Fig. 5e in Page 14 in the revised manuscript.**

Q16: A crucial aspect that seems to be missing from the paper is the full cell cycling data of high-voltage cathodes vs. hard carbon. The full cell illustrated in supplementary Fig. 15 indicates poor performance, suggesting that DEE from the NDPP electrolyte decomposes at high voltage, resulting in capacity loss. It would be beneficial for the authors to include data showing 100 cycles at a C/5 rate for NDPP and NP electrolytes, as NP is known to perform well in this full cell chemistry. Additionally, if the claims regarding safety and high voltage stability of the NDPP electrolyte are

accurate, the authors should demonstrate full cells with NVPOF cycling at 55°C, similar to what has been documented in the literature (DOI: 10.1002/aenm.202101490).

***Response*:** Thank you for your insightful suggestion. (1) As shown in Supplementary Figure 22, the NDPP electrolyte can sustain the stable operation of NVPOF//HC full cells with 79.1% of capacity retention after 1000 cycles at 2 C. Generally, the irreversible decomposition of the electrolyte leads to poor CEs. While flat CEs during the cycle can be observed, which further indicates the electrochemical durability of this electrolyte. In addition, the NVPOF//HC full cell in NDPP electrolyte demonstrated relatively lower electrochemical stability, compared to the NVPOF//Na half cell (87.6% of capacity retention after 5000 cycles at 2 C in Fig. 5b), which might mainly be attributed to the matching degree of the cathode and anode as well as the assembly technology of the full cell. Furthermore, we have studied the relevant literature, and it can be observed that the electrochemical stability of NVPOF//HC full cells we obtained is not poor (Adv. Mater. 2022, 34, 2110108; Adv. Funct. Mater. 2024, 34, 2315318; Adv. Mater. 2024, 36, 2310051).

(2) The electrochemical properties of the NVPOF//CC full cells with different electrolyte (ND, NP and NDPP) have been investigated at C/5 for 100 cycles. The NDPP electrolyte enables the cell to operate stably with higher CEs during the charge-discharge process, compared to those of ND and NP electrolytes. Additionally, the full cell with NDPP electrolyte sustains the stable operation at 50 ℃ and 5 C with 95.3% of capacity retention over 1000 cycles. These results further substantiate the interfacial stability derived from the integrated NDPP electrolyte. **Please refer to Supplementary Figure 23 in Page 24 in the revised Supporting information.**

Q17: Finally, the radar plots presented in Fig. 7 appear somewhat misleading concerning oxidative stability, reductive stability, and electrochemical durability, as they seem to contradict the results discussed in the manuscript. It would be helpful if the authors could clarify this aspect.

***Response*:** Thank you for your valuable suggestion. We have further adjusted the radar plots in Fig. 7. According to LSV measurements of these electrolytes, the sequence of electrochemical oxidation stability is ND < NDPP < NP, while the sequence of their reduction stability is as follows: NP < NDPP < ND (**Q9**). The NDPP electrolyte demonstrates the comprehensive electrochemical stability to sustain the stable operation of the cathodes and anodes. Fig. 7 schematically illustrates comprehensive assessments of conventional ND, NP and our designed NDPP electrolytes. Through multiscale experimental and theoretical investigations, NDPP has demonstrated remarkable merits in the following aspects: enhanced ionic conductivity, prominent cyclic life, improved energy efficiency

during the cycle, great interfacial stability with both electrodes, and mitigated safety threat from non-flammability (**Q15**). **Please refer to Page 19 Lines 3-7 in the revised manuscript.**

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We would like to thank the four reviewers for their profound and insightful comments, which help us to improve the manuscript effectively. The relevant parts of the manuscript have been modified according to the reviewers' comments. Below is our point-by-point response to each of the comments. All changes in the revised manuscript have been highlighted in yellow background.

For Reviewer #1:

Overall assessment: This is a revised manuscript. I have carefully read the article and response to the first-round review, finding that the authors have thoroughly explained the issues raised by the reviewers and supplemented the further experimental investigations and discussions in the corresponding sections. In particular, the authors further elaborated on the crucial dipolar interaction-mediated molecular anchoring effect based on a series of additional spectral and theoretical analyses. I think, this work is innovative and systematic, this manuscript is well organized. So I recommend publishing the manuscript on Nature Communications after addressing the following minor issues.

***Response*:** We sincerely thank the Reviewer 1 for the positive evaluation of our present work and the recommendation for publishing after modification. We would also like to thank Reviewer 1 for the following revision suggestions.

Q1: The structural diagram of PF_6^- anion in Fig. 3c is incorrect. The one shown in the current figure represents the PF_5^- anion, which is wrong. Suggest the authors further check and adjust it.

***Response*:** Thanks for the reviewer's careful checks. We are sorry for our carelessness. Based on your comment, we have further corrected the structural diagram of PF_6^- anion in Fig. 3c. **Please refer to Fig. 3c in Page 10 in the revised manuscript.**

Q2: In Fig. 4a-c, the more specific compositions of these three extracted solvation structures should be presented instead of a rough description, such as Na^+-DEE-PF_6^-.

***Response*:** Thank you for your insightful suggestion. The specific compositions of these three extracted solvation structures have been supplemented in Figs. 4a-c, namely Na^+-2DEE-PF_6^-, Na^+-5PC-PF_6^- and Na^+-3PC-DEE-PF_6^-. **Please refer to Figs. 4a-c in Page 12 in the revised manuscript.**

Q3: The "R_a" mentioned only in Fig. 6c should also be added and explained in the manuscript so that the readers can better understand.

***Response*:** We appreciate the kind reminding of reviewer. We have added the corresponding description for R_a mentioned in Fig. 6c. Specifically, R_a represents the surface average roughness. **Please refer to Page 18 Line 11 in the revised manuscript.**

Q4: In the manuscript, the discussions on some research results should include appropriate references to further support the conclusions drawn, e. g., the highlighted description in yellow background on page 10.

***Response*:** Thanks for the reviewer's valuable suggestion. We have supplemented the relevant reference in the corresponding results and discussion sections. **Please refer to Page 9 Line 16 (Ref. 50) in the revised manuscript.**

Q5: Please provide detailed assembly parameters for the pouch cells. In addition, please provide the energy density of the pouch cells to demonstrate the practical value of the electrolyte.

***Response*:** We are very grateful for the valuable and profound suggestions made by the reviewer, and we have supplemented the detailed fabrication parameters of the 1 Ah NNFMO//HC pouch cells. **Please refer to Supplementary Table 5 in Page 41 in the revised Supporting information.** It is also presented as follows. The NNFMO//HC pouch cells delivered 1.25 Ah of reversible capacity and 102.8 Wh kg^{-1} of energy density at RT. Fig. 5k also shows their discharge curves at LTs (charging at RT and subsequently discharging at LTs). The discharge capacities of 1.05, 0.66 and 0.49 Ah and energy densities of 77.1, 43.1 and 32.3 Wh kg^{-1} can be obtained at -25, -40 and -60 °C, respectively. **Please refer to Page 16 Lines 6-10 in the revised manuscript.**

Cathode	Active material	NaNiFeMnO
	Active material percentage (wt%)	95.3
	Area weight (each side, mg cm^{-2})	20.0
	Area capacity (each side, mAh cm^{-2})	1.93
	Length (mm)	80
	Width (mm)	60
	Thickness (μm)	140
	Compact density (g cm^{-3})	3
Anode	Active material	Hard carbon
	Active material percentage (wt%)	94.5
	Area weight (each side, mg cm^{-2})	8.0

	Area capacity (each side, mAh cm^{-2})	2.12
	Length (mm)	84
	Width (mm)	64
	Thickness (μm)	170
	Compact density (g cm^{-3})	0.97
Layer of cathodes	8	
Layer of anodes	9	
Negative to positive capacity ratio		1.1
Thickness of separator (μm)		12
Thickness of packing foil (μm)		113
Electrolyte to capacity ratio (g Ah^{-1})		5

For Reviewer #2:

Overall assessment: The revised manuscript has undergone significant improvement. My concerns were addressed by additional figures and discussions. I am satisfied with this version.

***Response*:** We are very grateful to Reviewer 2 for the positive evaluation of our present work and the recommendation for publication.

For Reviewer #3:

Overall assessment: The authors have addressed all my concerns, I would recommend its publication now.

***Response*:** We are very grateful to Reviewer 3 for the positive evaluation of our present work and the recommendation for publication.

For Reviewer #4:

Overall assessment: Thank you to the authors for their response and revisions. Many comments are addressed, however, several key issues remain unresolved or have been selectively avoided. The revised manuscript continues to omit critical analyses necessary to substantiate the claims and improve the overall quality of the work. In its current form, it requires major revision. I disagree with several of the authors' interpretations and claims, as detailed below.

***Response*:** We sincerely thank the Reviewer 4 for taking the time to review our revised manuscript

again and pointing out the parts of our argument that need to be further strengthened. We understand your deep concern regarding the critical analysis. In this revision, we are committed to directly addressing these issues by supplementing the full cell data. We hope these amendments will adequately address your concerns and strengthen the robustness of our conclusions. Below are the specific revision suggestions and response details.

Q1: The claim of superior interfacial stability and the associated radar plots (Figures 5 and 7) are misleading. The NP electrolyte exhibits the highest oxidative stability, and the ND electrolyte shows the highest reductive stability, not the NDPP electrolyte (confirmed in the revised version). This interpretation could be verified using three-electrode CV measurements to eliminate cross-talk from Na metal. Importantly, the radar plots should incorporate these results and explicitly highlight the limitations of the NDPP electrolyte.

***Response*:** Thanks for the reviewer's valuable suggestion regarding the stability analysis of the electrolytes. We have provided the following detailed explanations and revisions on the aforementioned issues.

(1) Interfacial stability can be affected by several key factors: i) the properties of electrolyte, including composition and solvation; ii) the characteristics of electrode, such as structural and morphological evolution; iii) external operating conditions like voltage, current and temperature; iv) the properties of interface layer, e. g., chemical composition and mechanical properties. The interfacial stability is manifested macroscopically in electrochemical properties of the battery, including cycle life and efficiency. Therefore, based on the electrochemical assessment in our manuscript, it can be concluded that the NDPP electrolyte sustains stable operation with high Coulombic efficiency and energy efficiency, compared to other control electrolytes. This can mainly be attributed to the optimized interfacial stability. Furthermore, postmortem investigations through XPS, SEM, TEM, AFM, TOF-SIMS can confirm the superiority of the interfaces derived from NDPP electrolyte.

(2) Regarding oxidative and reductive stability of the electrolytes, conventional two-electrode LSV test is conducted through the SS//Na half cell to simply determine the apparent stability of the electrolyte. We also fully agree with the reviewer's opinion that three-electrode measurements should be performed to identify the intrinsic electrochemical stability of the electrolyte by eliminating the cross-talk from Na metal. Specifically, three-electrode cells with different electrolyte systems were assembled using stainless steel as the working electrode and sodium as the counter and reference electrodes, as illustrated in **Fig. R1-1**. These findings are consistent with the conclusion based on the

two-electrode method. ND and NP respectively show the highest reductive and oxidative stability, while NDPP achieves a delicate balance rather than a single extreme. Compared to NDP, NDPP electrolyte exhibits enhanced anti-oxidative capacity and reduction stability due to the synergy effect involved in PFPN, verifying the effectiveness of PFPN and thus compatibility with both high-voltage cathodes and anodes. **Please refer to Page 7 Lines 24-29 in the revised manuscript and Supplementary Fig. 5 in Page 6 in the revised Supporting information.**

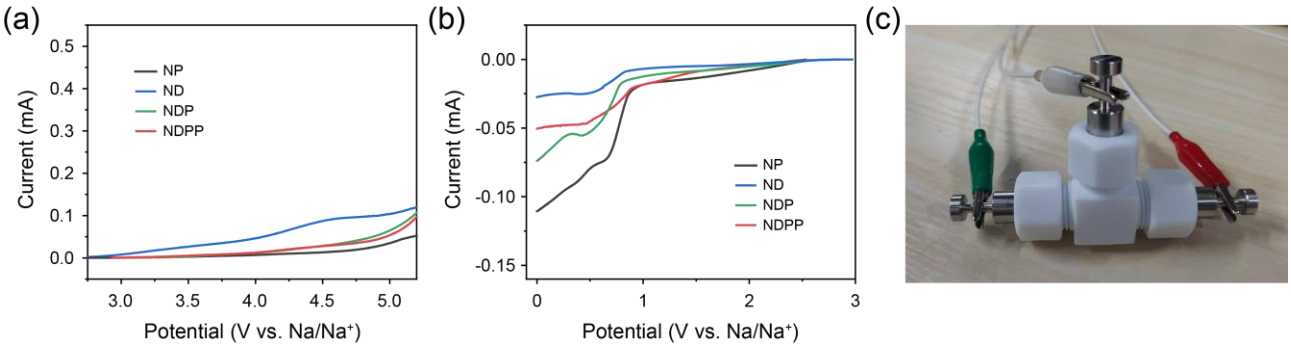

Fig. R1-1 (a, b) Three-electrode LSV measurements at 2.0 mV s^{-1}. (c) Optical photograph of the three-electrode battery system.

(3) The radar plots are further adjusted to integrate the characteristics of the electrolytes (i. e., ionic conductivity, oxidation stability, reduction stability, cyclic life, interfacial stability and safety), as shown in **Fig. R1-2**. Specifically, i) ionic conductivity: ND < NP < NDPP (**Fig. 2c**); ii) oxidation stability: ND < NDPP < NP (**Fig. 2d**); iii) reduction stability: NP < NDPP < ND (**Fig. 2e**); iv) cyclic life: ND < NP < NDPP (**Fig. 5b**); v) interfacial stability: NP < ND < NDPP (**Fig. 6**); vi) safety: ND < NP < NDPP (**Fig. 2f**). **Please refer to Fig. 7 in Page 19 in the revised manuscript.**

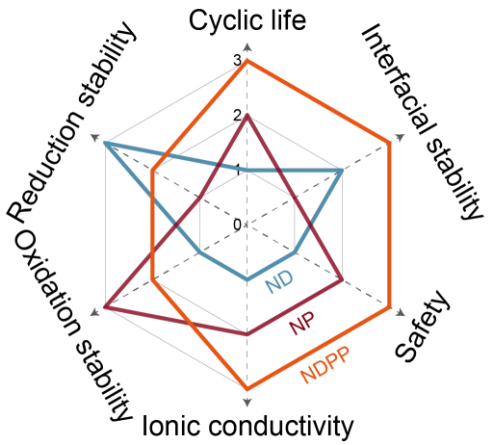

Fig. R1-2 Radar plot evaluating the fundamental properties of three electrolytes.

Once again, we would like to express our gratitude to the reviewer for their professional and meticulous comments, which have greatly enhanced the rigor of our paper.

Q2: Capacity retention must be rigorously evaluated in full cell format using a hard carbon anode at

a lower rate (e.g., C/10–C/5) to assess interfacial (SEI) stability. These full-cell results should form a central part of the main discussion for the electrochemical performance, not remain supplementary.

***Response*:** Thank you for your highly constructive suggestion. You pointed out that a full cell configuration with hard carbon anode must be adopted and the capacity retention should be evaluated at a low rate to strictly assess the interfacial stability. We fully agree with the above viewpoint and apologize for placing the crucial part in the Supporting information in the previous version. Specifically, we have made the following major revisions: The electrochemical performance of NVPOF//HC full cells at a low rate (0.2 C) has been demonstrated in **Fig. R2**. Note that the aforementioned cyclic tests are still ongoing. However, due to time constraints, only 80 cycles of data have been collected so far. Compared with ND and NP, NDPP electrolyte ensures the stable operation during the 0.2 C cycle at RT and 50 ℃—about 98.5% and 91.0% of capacity retention after 80 cycles (~761 and 698 h), proving the effectiveness of the optimized electrolyte through the synergistic interface regulation. **Please refer to Figs. 5h and i in Page 14 and Page 15 Lines 26-29 in the revised manuscript.** In conclusion, after these fundamental revisions, the current manuscript centers on the compelling full-cell data, which demonstrates the desired performance of NDPP electrolyte in terms of interfacial stability. Your feedback has significantly enhanced the quality and impact of our work. We once again express our heartfelt gratitude.

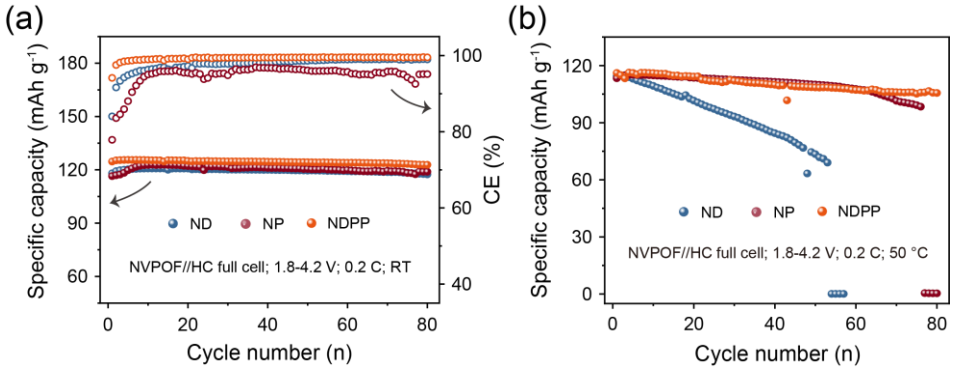

Fig. R2 Electrochemical investigations of NVPOF//HC full cells at 0.2 C.

Q3: The reported 79.1% capacity retention for NVPOF//HC after 1000 cycles at 2 C, presented as good performance, is misleading. Each 2 C cycle lasts only about 1 hour, whereas a C/5 cycle requires roughly 10 hours (charge + discharge). Thus, 1000 cycles at 2C correspond to only ~100 cycles at C/5 in total cycling time. Achieving merely 79% capacity retention after the equivalent of ~100 C/5 cycles (~1000 hours of operation) is therefore poor. Cycling at high rates artificially inflates retention values. For reference, NVPF|HC cells (2-4.3 V) with conventional carbonate electrolytes [DOI: 10.1149/2.0831802jes] exhibit over 90% retention after 3000 hours (equivalent of 3000 cycles at 2

C).

***Response*:** Thank you for the profound and professional suggestion regarding the evaluation of cycling stability of NVPOF//HC cells in our study. The viewpoint you pointed out that the cycle performance needs to be combined with the total running time and high-rate cycling to overestimate the capacity retention is highly constructive and accurately points out the key dimensions that should be considered in the evaluation of battery performance. We fully agree with this scientific judgment and have conducted a detailed review and supplementary explanation. The specific reply is as follows:

(1) We accept that 1000 cycles at 2 C correspond to approximately 100 cycles at 0.2 C in total cycle time. Although their electrochemical behaviors are not equivalent, this revelation indicates that when evaluating the cycle life at high rates, we need to take into account both the number of cycles and the total operating time. Therefore, we have adjusted the corresponding descriptions to make them more objective and accurate. **Please refer to Page 15 Line 30 and Page 16 Line 1 in the revised manuscript.**

(2) Considering the significantly different electrochemical behaviors at high and low rates, the evaluation of cycle life at low rates is also crucial. We have further supplemented the cycling performance of NVPOF//HC full cells with these electrolytes at 0.2 C to explore the application possibilities in low-rate scenarios, as shown in **Fig. R2**. **Also, please refer to Figs. 5h and i in Page 14 and Page 15 Lines 26-29 in the revised manuscript.**

(3) Regarding the reference the reviewer provided, we acknowledge that the NVPF//HC full cells with conventional carbonate electrolytes indeed demonstrated excellent cycling stability at 1 C. It is worth noting that the cathode material used in the NVPF//HC full-cell system is $Na_3V_2(PO_4)_2F_3$ (NVPF), which is different from the $Na_3V_2(PO_4)_2O_2F$ (NVPOF) cathode used in our research. Although both belong to sodium-based polyanion compounds, they exhibit significantly different electrochemical properties. For instance, from the perspective of cycle stability of full cells matched with HC, considering that the M-F (i. e., V-F) bond is usually stronger than the M-O bond, the crystal structure of NVPF is considered to be more robust, resulting in smaller volume changes during the repeated Na^+ insertion and extraction processes, and thus having a longer cycle life.

(4) Based on the above discussion, we believe that the specific NVPOF//HC system exhibits competitive cycle stability at 2 C high rate compared to the reported similar NVPOF-based cathode systems under similar rates. We will clarify this point in the revised version and select more literature working under similar rates for comparison to provide a more fair reference background. **Please refer**

to Supplementary Table 4 in Page 40 in the revised Supporting information. It is also presented as follows:

Configuration description	Current density	Cycling number, retention	Ref.
$Na_3V_{1.85}Fe_{0.15}(PO_4)_2O_2F$//HC	0.4 C	100, 82.3%	1
NVOPF//HC	1 C	500, ~ 80%	2
$Na_3V_2(PO_4)_{1.95}(SO_4)_{0.05}O_2F$//SbSn/NPC	3 C	100, 75.0%	3
NVPOF-$Zn_{0.05}$//a-Se	10 C	900, 77.6%	4
$N(VO)_{1.8}Fe_{0.2}PF_{1.2}$//HC	500 mA g^{-1}	200, 94.7%	5
$Na_{3-y}VPO_{2-x}Br_xF$//HC	5 C	1000, 84.9%	6
NVPOF-HE//HC	5 C	1000, ~93.8%	7
NVOPF-PE//HC	3 C	750, ~91%	8
NVPOF//HC	**0.2 C** **2 C**	**80, 98.5%** **1000, 79.1%**	**This work**

We are very grateful for your assistance in helping us further clarify the positioning and value of our work more clearly.

Q4: The NVPOF|CC cell configuration is conceptually flawed and cannot be generalized to practical Na-ion cells. The role of the carbon cloth (CC) is not defined. Supplementary Figure 23 shows very low CE for the first ~20 cycles, yet capacity appears retained, indicating a substantial sodium reservoir in the CC. If the carbon cloth is presodiated, why its not mentioned in experimental section. Overall, NVPOF|CC cells with unlimited Na inventory from sodiated carbon cloth are representative for NVPOF|HC full cells.

***Response*:** We are extremely grateful for your insightful and constructive comment. We sincerely apologize for the inappropriate response to **Q16**, which was based on the electrochemical analysis of NVPOF//CC cells rather than NVPOF//HC full cells. We fully accepted the reviewer's criticism and are aware of the underestimated issues and unrigorous experimental results present in the NVPOF//CC system. Therefore, we have removed the relevant descriptions (i. e., Supplementary Figure 23) in the revised manuscript to ensure the overall coherence and logic. Furthermore, in order to make up for the aforementioned deficiencies, we have supplemented detailed electrochemical investigations on the NVPOF//HC full cells at 0.2 C. Specifically, **please refer to the responses to Q2, Q3 and Q5.**

Q5: The revised manuscript still lacks NVPOF|HC full-cell data at elevated temperature (55 °C) and low C-rate (C/5) without carbon cloth trick or presodiation. Such baseline data are essential for comparison and are standard in the quality literature [DOI: 10.1002/aenm.202101490; 10.1002/aenm.201901431; 10.1149/1945-7111/ad47da].

***Response*:** Thank you for your valuable suggestion. We have further supplemented the electrochemical properties of NVPOF//HC full cells at high temperatures (50 and 60 °C) and a low C-rate (0.2 C), as shown in **Fig. R5**. In this context, we mainly chose the test temperatures of 50 and 60 °C to be consistent with the other parts of the manuscript. Note that the aforementioned cyclic tests at 50 ℃ are still ongoing. However, due to time constraints, only 80 cycles of data have been collected so far. Compared to ND and NP, NDPP electrolyte ensures the more stable operation during the 0.2 C cycle and 50 ℃—about 91.0% of capacity retention after 80 cycles (~698 h). **Also, please refer to Fig. 5i in Page 14 and Page 15 Lines 26-29 in the revised manuscript.**

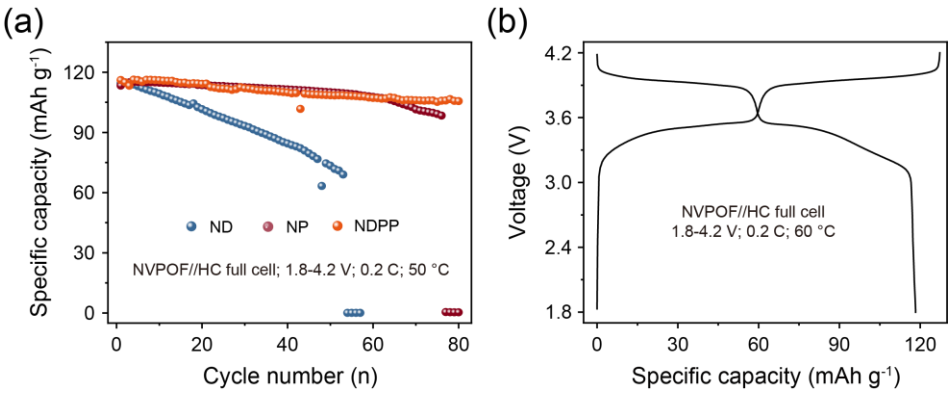

Fig. R5 Electrochemical investigations of NVPOF//HC full cells at 0.2 C and HTs.

Q6: It is unclear why ionic conductivity, ^{19}F NMR, and related properties of NDP are not presented in the main text when NDP is compositionally closest to NDPP.

***Response*:** We sincerely thank the reviewer for pointing out this crucial issue. We fully agree with your viewpoint. For the NDP electrolyte that is highly similar to the components of NDPP, its ionic conductivity, ^{19}F NMR and related properties are of crucial importance for a thorough understanding of the performance differences between them. We apologize for not adequately presenting and discussing these data in the main text. In the revised version, we have further demonstrated the ionic conductivity, redox stability, flammability, ^{19}F NMR spectrum of NDP electrolyte, as summarized in **Fig. R6**. Through a simple combination of strongly solvated PC and weakly solvated DEE, the prepared electrolyte exhibited a high ionic conductivity, moderate redox stability and obvious flammability. Furthermore, the NVPOF cathode and HC anode with NDP electrolyte displayed

unsatisfactory electrochemical stability, which can be attributed to the presence of abundant free solvents and unstable electrode/electrolyte interfaces. These findings verify that simple ester-ether mixing design strategy is insufficient to achieve the desired properties and cannot make full use of their advantages. Ultimately, we conceived an integrated solvating electrolyte (NDPP) to effectively address the existing problems. To maintain the conciseness of the discussion and highlight the key points, we did not include the above data in the main text in the initial version. **Please refer to Figs. 2c-f and 3b in the revised manuscript and Supplementary Figure 3 in Page 4 in the revised Supporting information.**

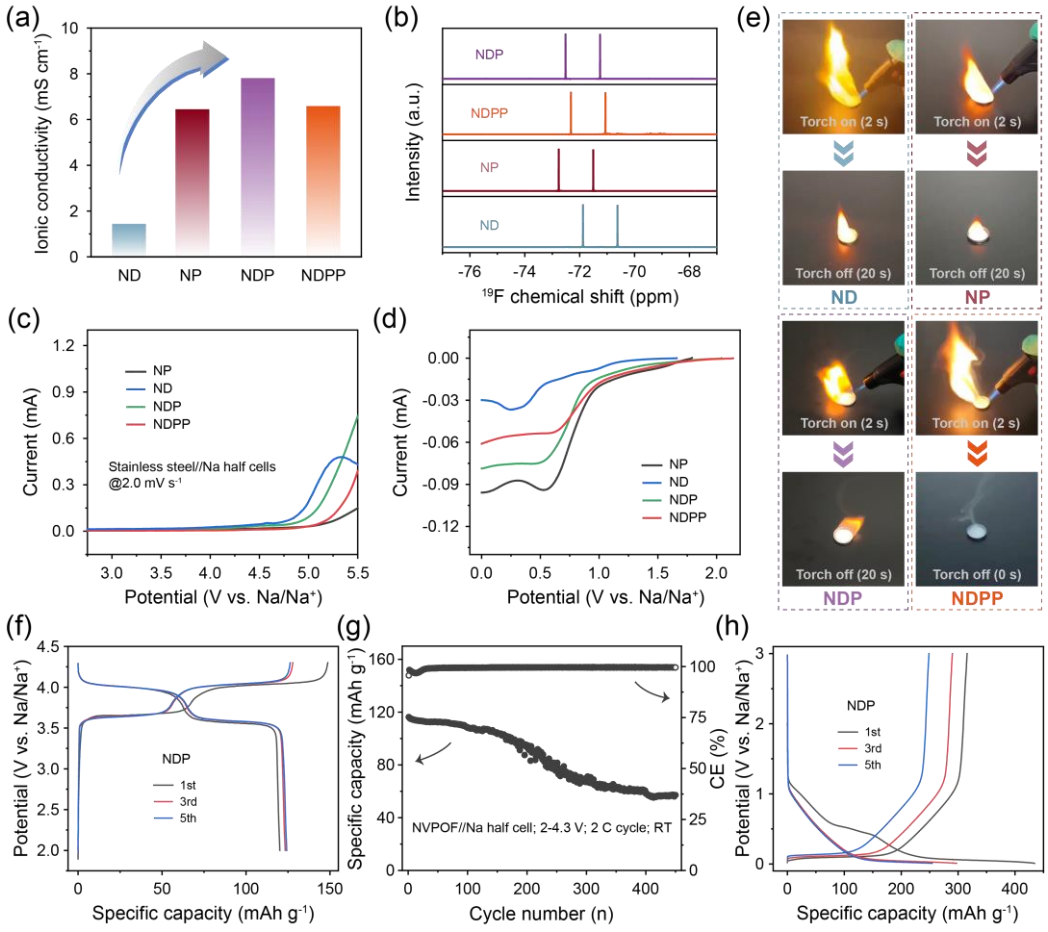

Fig. R6 (a) Ionic conductivity of the electrolytes at 25 °C, (b) ^{19}F NMR spectra, (c, d) electrochemical oxidation and reduction stability of different electrolytes as evaluated by LSV measurements at 2.0 mV s^{-1}, (e) flammability tests of the electrolytes, (f) GCD curves of the sodium-ion half cells with NVPOF cathode at 0.1 C, (g) cycling stability of NVPOF//Na half cells with NDP at 2 C, (h) GCD curves of the sodium-ion half cells with HC anode at 25 mA g^{-1} in the NDP electrolyte.

Q7: The authors acknowledge in their response to Q1 that the electrolyte shows poor stability at 70 °C due to oxidative decomposition and parasitic reactions. Yet, the abstract still claims "superior high-temperature stability at 70 °C" based on data limited to 3.9 V with NVP. To satisfy this claim, high

temperature performance data for layered oxide or polyanionic compounds full cell at high voltage of at least 4.2 V is necessary.

***Response*:** Thanks for the reviewer's thoughtful and professional suggestion. We acknowledge that the mentioned high-temperature stability at 70 °C is limited to a specific material system (NVP), which results in the current conclusion lacking in rigor. To substantiate this statement, we have further supplemented the following experimental investigations on the high-voltage polyanionic compound and layered oxide systems.

(1) $Na_4Fe_3(PO_4)_2P_2O_7$ (NFPP) material is used as the cathode to verify the high-temperature stability of NDPP electrolyte. Initially, the electrochemical stability of NFPP//Na and NFPP//HC cells with NDPP electrolyte was investigated at RT (**Fig. R7-1**). NFPP//Na half cells demonstrated the initial reversible specific capacity of ~104 mAh g^{-1} at 0.1 C and stable cycling performance at 0.5 C and 1.8-4.2 V. For the NFPP//HC full cells, there were ~97 mAh g^{-1} of discharge specific capacity at 0.2 C and ~89.3% of capacity retention over 100 cycles at 0.5 C and 1.6-4.2 V. Furthermore, we carried out the electrochemical evaluation of NFPP//Na and NFPP//HC cells with NDPP electrolyte at 70 °C (**Fig. R7-2**). Specifically, NFPP//Na half cells demonstrated the stable reversible capacity of ~107 mAh g^{-1} over 200 cycles at a 5 C rate and within a voltage range of 1.8 to 4.2 V. For the NFPP//HC full cells, there was a capacity retention of 71.7% during the 100-cycle process at a 5 C rate and within a voltage range of 1.6 to 4.2 V. **Please refer to Supplementary Figures 26-27 in Pages 27-28 in the revised Supporting information.** It is also presented as follows:

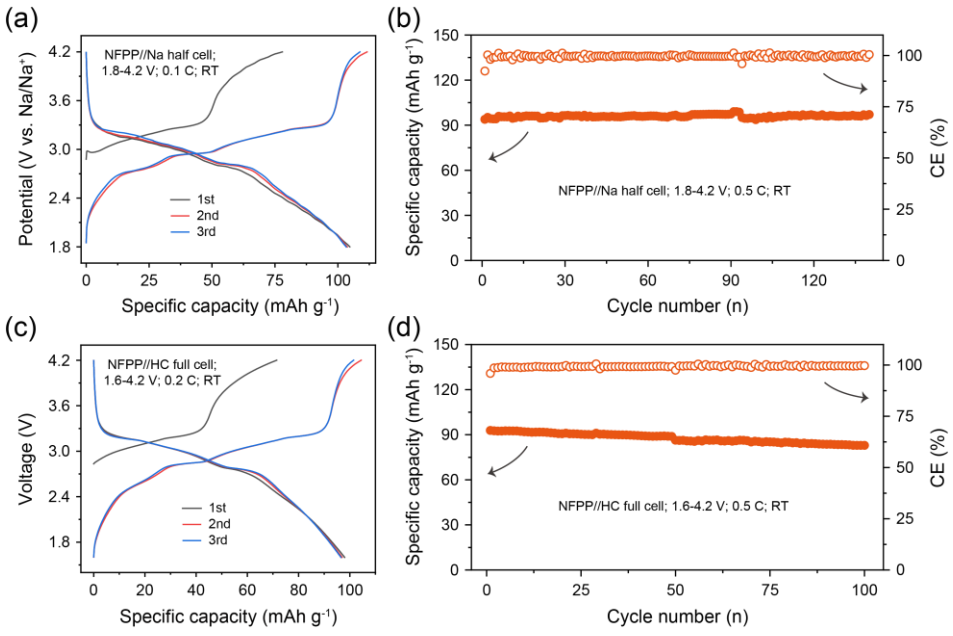

Fig. R7-1 Electrochemical evaluation of NFPP//Na and NFPP//HC cells with NDPP electrolyte at RT. (a) GCD

curves at 0.1 C, (b) cycling performance at 0.5 C of NFPP//Na half cells. (c) GCD curves at 0.2 C, (d) cycling performance at 0.5 C of NFPP//HC full cells. 1 C = 129 mA g^{-1}.

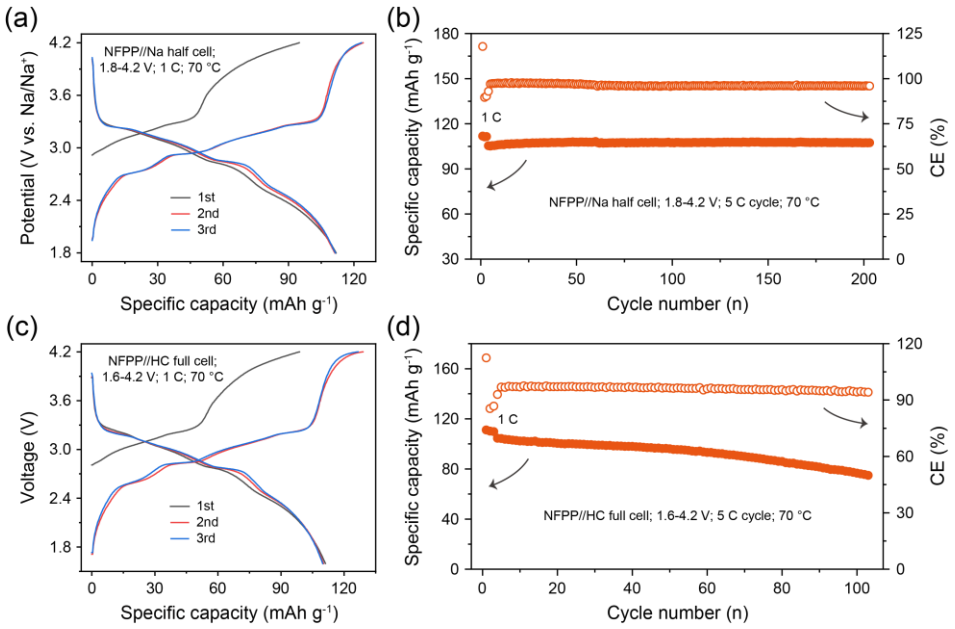

Fig. R7-2 Electrochemical evaluation of NFPP//Na and NFPP//HC cells with NDPP electrolyte at 70 ℃. (a) GCD curves at 1 C, (b) cycling performance at 5 C of NFPP//Na half cells. (c) GCD curves at 1 C, (d) cycling performance at 5 C of NFPP//HC full cells.

(2) In addition, a representative layered oxide cathode material $Na_{0.67}Ni_{0.33}Mn_{0.67}O_2$ (NNMO) is also utilized to verify the high-temperature applicability of NDPP electrolyte. Initially, the electrochemical stability of NNMO//Na half cells was investigated at RT. **Fig. R7-3a** shows their charge-discharge curves at 0.25 C and cycling stability over 450 cycles at 2 C. When the temperature rose to 70 ℃, the NNMO//Na half cells demonstrated 91.9% of capacity retention over 200 cycles at 5 C and 2-4.1 V (**Fig. R7-3b**). Furthermore, the electrochemical stability of NNMO//HC full cells at RT and 70 ℃ was displayed in **Fig. R7-3c**. Specifically, there is 91.4% of capacity retention over 250 cycles at RT and 2 C, while 80.9% for 120 cycles at 70 ℃ and 5 C. Their voltage window is between 1.8 and 4.1 V. **Also, please refer to Figs. 5c, d and j in Page 14 in the revised manuscript.**

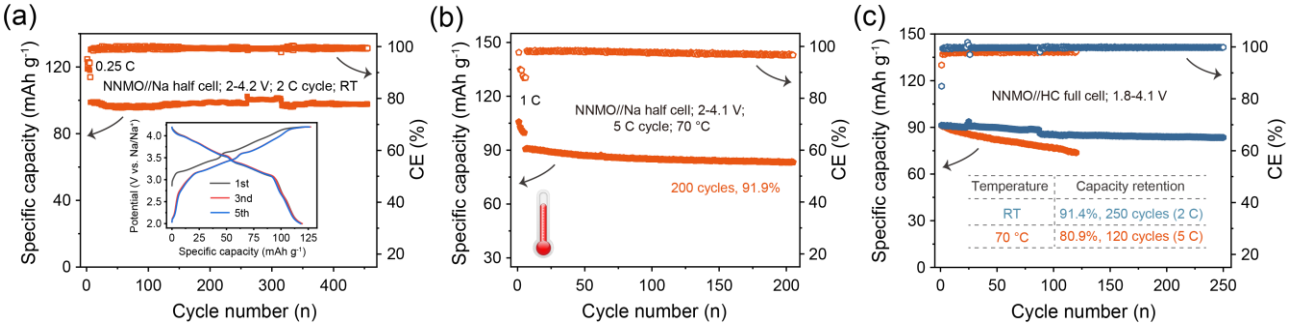

Fig. R7-3 (a, b) Cyclic stability of NNMO//Na half cells with NDPP electrolyte at RT and 70 ℃. (c) Cycling performance of NNMO//HC full cells.

Once again, we would like to express our gratitude to the reviewer for helping us improve the quality of this work.

Q8: The response to Q11 is inadequate. The authors claim stronger PC–PFPN and DEE–PFPN interactions than PFPN–PF_6, yet HOESY NMR shows only PFPN–PF_6 interactions, with no cross-peaks for PC–PFPN or DEE–PFPN. The authors must clarify Figure 3e interpretations related to NMR observations.

***Response*:** Thank you for the profound and professional suggestion regarding the intricate intermolecular interactions. In order to clarify this phenomenon, we have provided the following detailed explanations and revisions on the aforementioned issues. Initially, as delineated in **Fig. R8a**, the 2 D ^{1}H-^{19}F HOESY NMR spectra of NDPP electrolyte demonstrate several distinct cross signals, indicating the $\delta^{+}H$-$\delta^{-}F$ interactions between PF_6^- anions and PC or PFPN solvents as well as PFPN and PFPN. However, the relatively strong interaction between PC and PFPN as well as the moderate interaction between DEE and PFPN are difficult to observe in the 2 D NMR spectra, which may mainly be attributed to the interaction sites ($\delta^{+}H$-$\delta^{-}O$) and the competitive intermolecular interactions in the integrated electrolyte system with complex components. Furthermore, we have also supplemented the ^{19}F NMR spectra of pure PFPN, PC/PFPN and DEE/PFPN mixtures to reveal the interactions between PFPN and PC or DEE by the NMR peak shifts of PFPN after adding PC or DEE to pure PFPN (**Fig. R8b**). Compared to DEE/PFPN, the more obvious peak shift occurs in the PC/PFPN, indicating the stronger interaction between PC and PFPN. In addition, the intermolecular dipolar interactions among various electrolyte components can be in-depth investigated through theoretical calculations. Note that we have conducted the more precise calculations using Gaussian 16 software to analyze these dipolar interactions. **Fig. R8c, d** and **Supplementary Figure 10** demonstrate their binding energy calculations with the corresponding optimized structures. Among them, there are relatively strong interactions between PF_6^- and PFPN or PC through $\delta^{+}H$-$\delta^{-}F$ as well as PC---PFPN through $\delta^{+}H$-$\delta^{-}O$, moderate interactions between DEE and PFPN or PF_6^- through $\delta^{+}H$-$\delta^{-}F$ as well as PC---PC through $\delta^{+}H$-$\delta^{-}O$, PFPN---PFPN through $\delta^{+}H$-$\delta^{-}F$, relatively weak interactions between DEE and DEE or PC. Consequently, non-coordinated PFPN in NDPP system can be activated via dipolar interactions with vulnerable PC and DEE can be anchored, which ameliorates the solvation environment and interfacial chemistry, conductive to electrochemical improvements. **Also, please refer to Figs. 3d-e in Page 10, Page 9 Lines 26-30, Page 10 Line 1 and Page 11 Lines 1-2 in the revised manuscript and Supplementary Figures 9-10 in Pages 10-11 in the revised**

Supporting information.

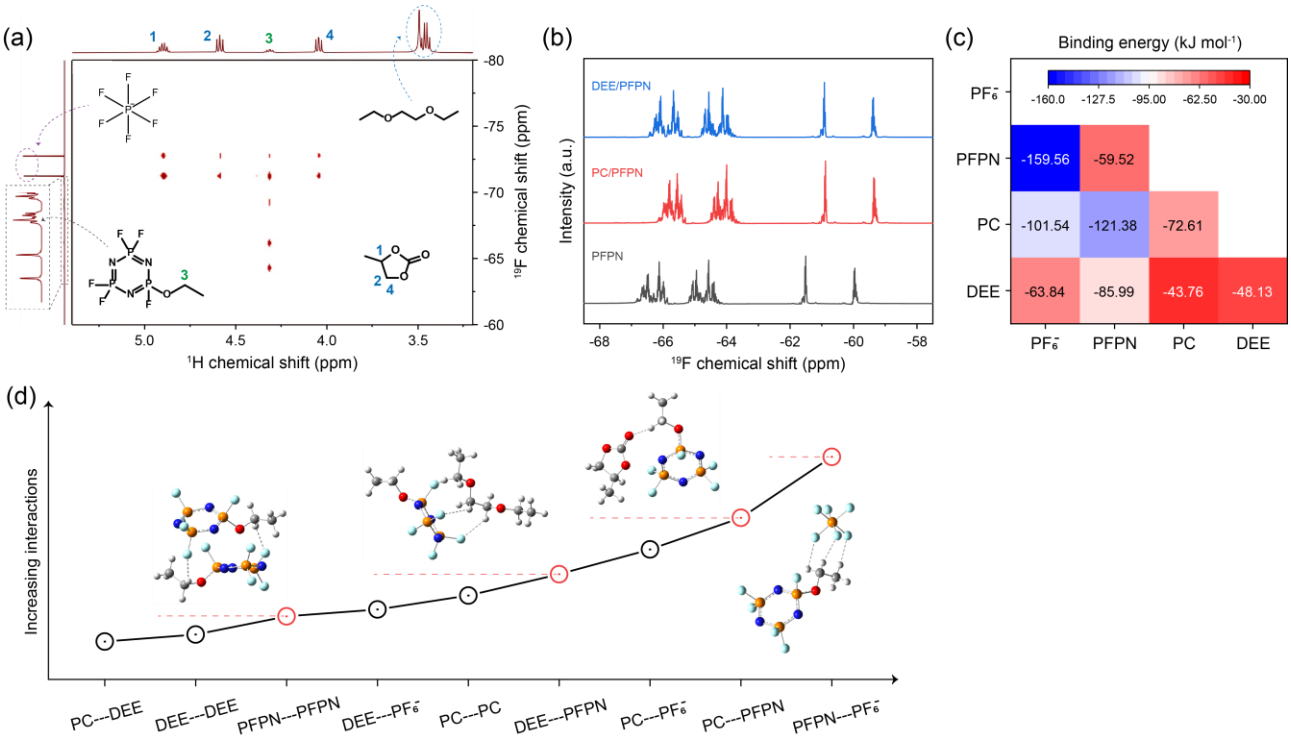

Fig. R8 (a) 2 D ^{1}H-^{19}F HOESY NMR spectra of NDPP electrolyte. (b) ^{19}F NMR spectra of the pure PFPN, PC/PFPN and DEE/PFPN mixtures. (c) Matrix diagram of intermolecular interactions among various electrolyte components. (d) Evolution of interactions with optimized structures of different complexes.

Q9: Similarly, the claim of low-temperature performance is not well supported. The abstract mentions operation under extreme temperatures down to −60 °C, but this is valid only for NVP|Na half cells, and even then, only when the upper cutoff is increased to 4.2 V (instead of 3.9 V) to recover capacity lost due to polarization. Meanwhile, NFNMO|HC pouch cells present only discharge curves at −25 °C and −40 °C. Why is the complete charge–discharge profile of the full cell not compared in the same plot for room temperature and −40 °C/−60 °C conditions inline with the claims?

***Response*:** We sincerely thank the reviewer for the thoughtful comment they made regarding the low-temperature performance section.

(1) We acknowledge that the successful operation at an extreme temperature of -60 °C was only verified in the NVP//Na half cells, and was accomplished by raising the upper cutoff voltage to 4.2 V to compensate for the polarization. This result demonstrates the fundamental low-temperature capability of NDPP electrolyte. We have provided supplementary explanations in the corresponding sections. **Please refer to Page 15 Lines 16-18 in the revised manuscript.** In addition, expanding the voltage window is a common practice when conducting the low-temperature test (Nat. Commun. 2025, 16, 3344; Angew. Chem. Int. Ed. 2025, e202516984).

(2) To further substantiate the proposed low-temperature capability, we conducted the additional electrochemical investigations on other material systems (e. g., NNMO) in the NDPP electrolyte at -40 and -60 °C. Specifically, the NNMO//Na half cells can demonstrate a reversible capacity of 83.4 mAh g^{-1} at 10 mA g^{-1} and -40 °C within the voltage range of 2-4.3 V (**Fig. R9-1a, b**). When the temperature is further reduced to -60 °C, the capacity is still 68.1 mAh g^{-1}. Note that their cyclic tests are still ongoing. However, due to time constraints, about 30 cycles of data have been collected so far. Furthermore, the NNMO//HC full cells have also been investigated and **Fig. R9-1c** is charge-discharge curves of NNMO//HC full cells at -40 and -60 ℃, which respectively illustrate the capacities of ~76.9 and 59.5 mAh g^{-1}. **Please refer to Fig. 5e in Page 14 and Page 15 Lines 9-10 in the revised manuscript and Supplementary Figure 25 in Page 26 in the revised Supporting information.**

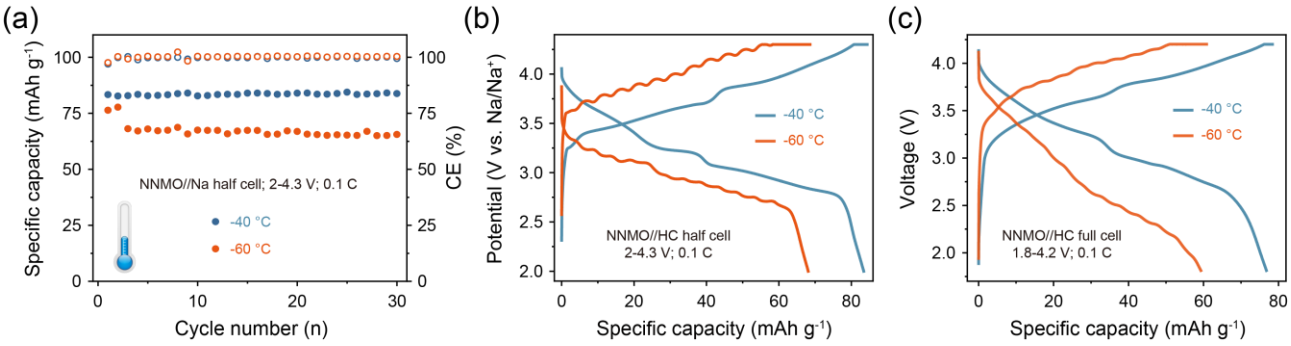

Fig. R9-1 (a) Cyclic stability and (b) representative GCD curves of NNMO//Na half cells at 0.1 C and LTs, (c) GCD curves of NNMO//HC full cells at 0.1 C and LTs.

(3) For the evaluation of the low-temperature performance of NNFMO//HC pouch cells, their tests were conducted by charging at room temperature and subsequently discharging at low temperature. The charge/discharge protocol was employed specifically to simulate the practical scenario where a device is fully charged under benign conditions before being used in a cold environment (DOI: 10.19799/j.cnki.2095-4239.2024.0379). This method allows us to isolate and evaluate the intrinsic discharge capability of the electrode materials and the electrolyte at low temperatures, without the complicating factor and safety concerns associated with low-temperature charging, such as metal plating (J. Power Sources, 2003, 115, 137-140; Nat. Commun. 2025, 16, 10188; Energy Environ. Sci. 2025, https://doi.org/10.1039/D5EE05191F). In addition, we also recognize the limitations of the current methods and the significance of complete charging and discharging at low temperatures. This is also the focus of our ongoing research, and we have provided the relevant explanations in the manuscript.

(4) We have also added the electrochemical curves of NNFMO//HC pouch cells at room temperature and -60 ℃. They delivered 1.25 Ah of reversible capacity and 102.8 Wh kg^{-1} of energy density at RT. **Fig. R9-2** also shows their discharge curves of (charging at RT and subsequently discharging at LTs). The discharge capacities of 1.05, 0.66 and 0.49 Ah can be obtained at -25, -40 and -60 °C, respectively. **Also, please refer to Fig. 5k in Page 14 and Page 16 Lines 6-11 in the revised manuscript.**

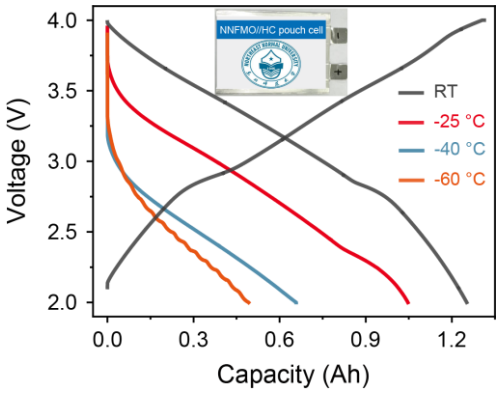

Fig. R9-2 The electrochemical curves for NNFMO//HC pouch cells.

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We would like to thank the reviewers for their profound and insightful comments, which help us to improve the manuscript effectively. The relevant parts of the manuscript have been modified according to the reviewers' comments. Below is our point-by-point response to each of the comments. All changes in the revised manuscript have been highlighted in yellow background.

For Reviewer #4:

Overall assessment: I thank the authors for their rigorous revision and response to the comments. Only one point I want to highlight is that the cell capacity cannot go to 0 mAh/g directly from ~100 mAh/g for NP and ND electrolyte in Fig. 5i. I strongly believe this is from the cell balancing or cell assembly issue and not representative of the electrolyte. I would advise to remove the 0 mAh/g capacity data point from both the curves. If authors believe that what they observe is real and reproducible then it will be raising more questions behind the reasons for the same: its even worse than roll over cell failure. If the 0 mAh/g data point are removed the manuscript is in perfect state for publications without further review process.

***Response*:** We sincerely thank the Reviewer 4 for taking the time to carefully review our revised manuscript again and providing the highly constructive comment. We fully agree with your viewpoint that the sudden drop of the cell capacity from ~100 mAh g^{-1} to 0 mAh g^{-1} in Fig. 5i for ND and NP electrolytes is very likely caused by the cell balancing or cell assembly issue, and does not represent the general electrochemical behaviors of the electrolyte systems. After rechecking several sets of parallel cycling data, we confirmed the aforementioned conjecture. Following your suggestion, we have removed the abnormal end data points of 0 mAh g^{-1} for the ND and NP electrolyte curves to more accurately reflect the cycling performance of the cell with these electrolytes, as shown in Fig. 5i. This revision does not affect the core conclusion of this work, which is the superiority of NDPP electrolyte we designed in terms of cycling stability. **Please refer to Fig. 5i in Page 14 in the revised manuscript.**

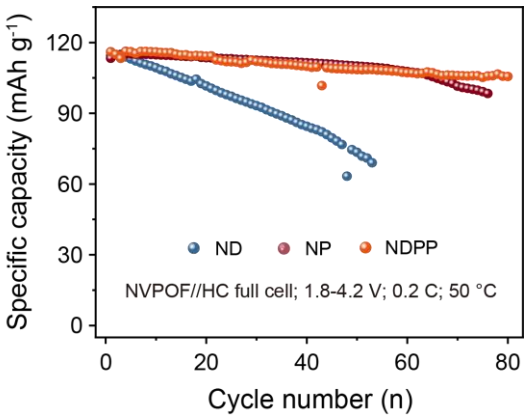

Fig. 5i Cycling performance of NVPOF//HC full cells at 0.2 C and 50 ℃

Once again, we apologize for the presence of this potentially misleading abnormal data points included in the original figure. We also would like to express our gratitude to the reviewers for their professional and insightful analysis, which has helped us further enhance the rigor of the data and the quality of the paper.