nature portfolio

Peer Review File

Anion-mediated approach to overcome oxidation in ether electrolytes for high-voltage sodium-ion batteries

Corresponding Author: Professor Mei Yang

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
In this work, trace amount of sodium nitrate was introduced as the electrolyte additive to significantly enhance the oxidative resistance of G2-based electrolytes. The optimization approach was designed from the direct electrolyte decomposition process during initial cycling, including modification of both solvation behavior and CEI-forming procedure. The use of sodium nitrate, with its high donor number, is shown to induce the formation of novel solvation structures such as CIP-NO3– and AIP-NO3–, which enhance the oxidative resistance of electrolytes. Additionally, the distinct solvation clusters are found to regulate the decomposition process, leading to the formation of an optimized CEI with NaF and NaNxOy species, further prohibiting electrolytes from oxidation. This strategy is suggested to be broadly applicable to various high-voltage cathode materials. However, before acceptance, the following revisions and inquiries should be addressed.
- Can the authors provide a detailed identification of the black decomposition products depicted in Figure 3C? This would enhance the reader's understanding of the decomposition mechanisms.
- Is there any alteration in the structural evolution of the cathode influenced by the formation of the NO3–-derived CEI? If so, how does this impact the overall performance?
- The decomposition of NaOTf is known to increase the NaF content in the CEI. Could the authors explain why this enrichment does not confer sufficient high-voltage endurance?
- Would an increase in the NaNO3 content in the electrolyte further enhance the anti-oxidation performance? If so, is there an optimal concentration that maximizes this effect?
- How does the introduction of the NaNO3 additive affect anode performance, particularly in terms of phenomena such as co-intercalation in graphite? Are there any observable changes that need to be considered?

Reviewer #2

(Remarks to the Author)
The manuscript introduces a straightforward additive approach to bolster the high voltage stability of ether-based electrolytes. The authors have effectively demonstrated a profound connection between solvent-cluster distribution and interphase formation. The incorporation of nitrate ions is shown to regulate both solvation structures and CEI components, thereby inhibiting the continuous decomposition of the electrolyte and the overgrowth of the interphase. This methodology is suggested to have broad applicability in improving the high voltage tolerance of ether-based electrolytes, making them a viable option for SIBs, given their compatibility with both cathode and anode materials. However, the following revisions and clarifications are required before the manuscript can be accepted:
1. The authors should address why the discharge capacity decays in pure G2, as depicted in Figure 1a. Understanding this phenomenon is crucial for the overall context of the study.
2. In Figure 2, the manuscript suggests that diglyme can be protected, yet Figure 4a indicates that NO3- containing clusters would be sacrificed first to form an ideal CEI. The authors need to clarify whether these statements are contradictory and explain the possible discrepancy.
3. Why such a trace amount of NaNO3 can significantly alter solvation structures? The authors should discuss the potential effects of increasing the concentration of NaNO3 and how it might influence the electrolyte's performance.
4. Determining the electron insulation effects of the modified CEI is challenging due to its complex mixture of components. The authors should provide a methodology or rationale for assessing these effects.
5. The authors should explain why there are distinguished GCD curves when LiNO3, NaNO3 and KNO3 are used as additives.
6. The GCD curves of NNM||graphite full batteries show total deformation in G2 and R-G2. The authors should investigate and explain whether the anode reactions have also been altered, which could have significant implications for the battery's performance.

Reviewer #3

(Remarks to the Author)
Dear Editor,
Thank you for inviting me to review this manuscript. After a thorough evaluation, I have summarized my comments and suggestions on this manuscript as follows.
In this work, the authors address the oxidation issue of ether-based electrolytes in the application of sodium-ion batteries. The authors demonstrated the high voltage intolerance and sensitivity of the nucleophilic nature of the ether-based electrolytes, which significantly limits their application for a vast range of high-voltage cathode materials above 3.9 V. The addition of a foreign NO3- was found to suppress the electrolyte oxidation side effect on the cathode surface by forming a passivating cathode electrolyte interphase (CEI), extending the electrochemical voltage window up to 4.8 V. The authors also demonstrated this strategy could be universal across various nitrate salts (such as LiNO3, NaNO3, and KNO3), exhibits excellent compatibility with different cathodes and anodes (hard carbon and graphite), and is effective with other ether-based electrolytes such as TEGDME. Under this reformulated G2 electrolyte system, the modified CEI and enhanced high-voltage stability result in improved battery cyclability over 1000 cycles. To elucidate the mechanism, the authors conducted NMR, Raman, XPS and DFT calculations to further identify the role of the NO3- additive in forming a more stable NaNxOy/NaF interphase and suppressing the dehydrogenation and oxidation of G2 electrolyte.
However, certain ambiguities and issues need to be addressed before the manuscript can be considered for acceptance. Additionally, the reviewer also found several typos and language inconsistencies that the authors should also carefully revise.
1. In the introduction, the authors state, “Carbonate solvents, prevalent in LIBs, are less effective in SIBs due to their tendency to form complex, ion-transport hindering reductive products”. However, this statement may be somehow misleading, as carbonate-based electrolytes are actually more commonly used for SIBs, with higher cut-off voltage such as 4.6 V. Hence, the authors should make a more fair comparison between carbonate and ether-based electrolyte systems. However, the authors can highlight the advantage of ether-based electrolytes, proving to be compatible with commercial graphite via solvent co-intercalation reaction, whereas the conventional carbonate-based solvents exhibit poor Na+ storage in graphite as shown in Fig. S1. Additionally, in Fig. 1 and S1, the electrolyte and Na salt should be written out in the figure caption.
2. The authors state, “we used a pure P3-phase Na2/3Ni1/2Mn1/2O2 (NNM) cathode with a particulate form (Supplementary Fig. 2)”. However, it’s clear that the P3 material is not pure with NiO as impurity.
3. In Fig. 2, the captions of (c) and (d) are reversed.
4. In line 134, please provide more details for characteristic peaks in the Raman spectrum. The reviewer did not find the information provided in ref.16.
5. Why are the data of G2 steel in Fig. 3a and Fig.S7 inconsistent?
6. I overlaid the voltage curves of R-G2 and G2 in Fig. 3c. They appear rather similar in the high-voltage range of 3.25-4.0 V. However, there is an obvious difference in the low-voltage range of 2.0-3.25 V. Intuitively, one would expect electrolyte oxidation at high voltage to result in irreversible charge capacity specifically within the high-voltage range. Can authors explain why this phenomenon happened? A CV curve may be a better way to showcase the voltage-current relationship.
7. The color of the separator-electrolyte of G2 turns black. Could the authors propose a possible byproduct responsible for this change? GC-MS might help to identify the changes involved.
8. In Fig. 4e, the 6 nm CEI layer is not very apparent. Is that possible to validate the thickness with XPS etching depth?
9. In Line 218, the authors state NaNxOy is an excellent Na+ conductor. Could the author provide a reference or explanation to support this statement?
10. The XPS etching profiles demonstrate different CEI chemical species formed between G2 and R-G2 electrolytes. The XPS analysis is crucial for further mechanism explanation in Fig. 5b. The authors proposed the presence of RSO3Na species. However, could the authors also provide the S 2p spectrum to further confirm the presence of RSO3Na species, where the intensity of the S 2p should be proportional to O 1s (RSO3Na) with etching depth? Additionally, the authors did not ascribe lattice oxygen (from NNM), which may be unusual for the cathode even with CEI. However, the author may prove the presence of lattice oxygen with transition metal peaks, such as Ni and Mn.
11. In the method section, the authors are encouraged to provide further details of sample preparation for the XPS etching study, especially whether the cathode was washed and how this was done to make sure there is no NaOTf salt residue.
12.Typo: Line 171 NMM||Na into NNM||Na; stainless||Na steel cell should be stainless steel||Na; Line 265, redundant “the”; Line 271, Supplementary Fig. 11 into Fig. 12.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have well revised the MS that becomes acceptable now.

Reviewer #2

(Remarks to the Author)
Previous comments have been well addressed. The present version is ready to be accepted.

Reviewer #3

(Remarks to the Author)
The authors have addressed all my comments adequately, and the revised manuscript is significantly improved. I recommend the paper to be considered for publication.

南京理工大学
NANJING UNIVERSITY OF SCIENCE & TECHNOLOGY

4 November, 2024

Dear Reviewers,

We greatly appreciate your efforts and the comments on our manuscript "*Overcoming Oxidation Challenges in Ether Electrolytes: An Anion-Mediated Approach for High-Voltage Sodium-Ion Batteries*" submitted to the *Nature Communications*. We are particularly encouraged by the positive comments. Following the reviewers' suggestions, we have made additions, revisions, and clarifications to the manuscript.

In this response letter, we itemized the comments/suggestions followed by our responses and revisions that we have made. For your convenience, the changes were highlighted in yellow color in the revised manuscript.

We hope that this revision could answer your questions and comments.

Sincerely yours,

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E-mail: bayberry616@163.com

Response to Reviewers' Comments

Reviewer #1:

In this work, trace amount of sodium nitrate was introduced as the electrolyte additive to significantly enhance the oxidative resistance of G2-based electrolytes. The optimization approach was designed from the direct electrolyte decomposition process during initial cycling, including modification of both solvation behavior and CEI-forming procedure. The use of sodium nitrate, with its high donor number, is shown to induce the formation of novel solvation structures such as CIP-NO_3^- and AIP-NO_3^-, which enhance the oxidative resistance of electrolytes. Additionally, the distinct solvation clusters are found to regulate the decomposition process, leading to the formation of an optimized CEI with NaF and NaN_xO_y species, further prohibiting electrolytes from oxidation. This strategy is suggested to be broadly applicable to various high-voltage cathode materials. However, before acceptance, the following revisions and inquiries should be addressed.

Response: We appreciate the reviewer for the positive comments and critical questions, which help us further improve the quality of our manuscript. We have made careful clarifications and revisions based on reviewer's suggestions and comments.

1. Can the authors provide a detailed identification of the black decomposition products depicted in Figure 3c? This would enhance the reader's understanding of the decomposition mechanisms.

Response: We appreciate this insightful question. We have attempted multiple testing methods on the separator, including XPS and inductively coupled plasma atomic emission spectroscopy (ICP-AES), but these attempts have regrettably fallen short of yielding any valuable data. This could be attributed to the fact that the quantity of the black substance is relatively scant compared to the entire separator, falling below the detectable concentration threshold. By carefully comparing the ^{1}H NMR spectroscopy data with the reference materials from LibreTexts (Figure R1, Table R1), the decomposition products observed in Figure 3c are likely attributed to a series of R_xCH_{3-x} or ROH species, aligning with the decomposition pathways depicted in Figure 5b. The black product is likely from this extensive decomposition, which might be similar to the CEI composition. However, precisely identification of the products and pathways remains a formidable challenge due to the intricate chemistry involved in the decomposition of organic electrolytes. Thank you for your valuable suggestion; we have modified relative discussion in the revised manuscript.

The separator subjected to cycling in the G2 electrolyte exhibited a darkened appearance, as shown in the inset of Fig. 3c, which is perhaps the detached CEI components or other byproducts resulting from electrolyte decomposition. In marked contrast, the R-G2 separator retained its pristine cleanliness. (In page 9)

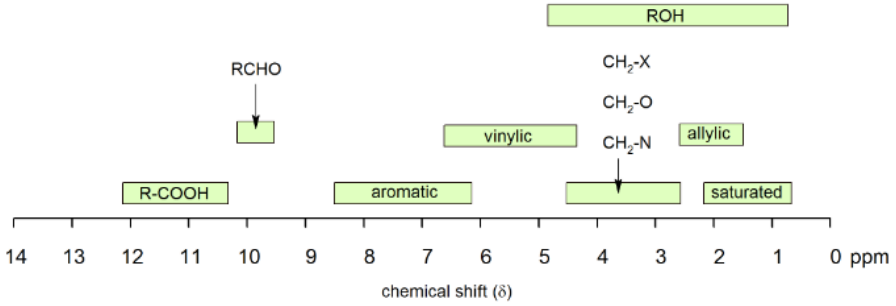
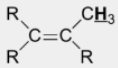
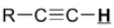
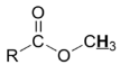
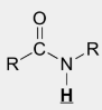


Figure R1. ^{1}H NMR spectroscopy data sourced from LibreTexts. (Accessed via https://chem.libretexts.org/).

Table R1. Comparative Analysis of ^{1}H NMR Spectroscopy Data from LibreTexts. (Data accessed via https://chem.libretexts.org/)

Hydrogen type	Chemical shift (ppm)
RCH_3	0.9 - 1.0
RCH_2R	1.2 - 1.7
R_3CH	1.5 – 2.0
	2.0 – 2.3
	1.5 – 1.8
RNH_2	1 - 3
$ArCH_3$	2.2 – 2.4
	2.3 – 3.0
$ROCH_3$	3.7 – 3.9
	3.7 – 3.9
ROH	1 - 5
	3.7 – 6.5
	5 - 9
ArH	6.0 – 8.7
	9.5 – 10.0

2. Is there any alteration in the structural evolution of the cathode influenced by the formation of the NO_3^--derived CEI? If so, how does this impact the overall performance?

Response: We cycled NNM electrodes using both G2 and R-G2 electrolytes and subsequently disassembled the cathodes for XRD analysis. As shown in Figure R2, the overall diffraction intensity of the NNM electrode cycled with G2 electrolyte was diminished, suggesting a reduction in crystallinity due to significant structural degradation. Notably, the markedly reduced intensity of the (002) peak (indicated by a gray dashed line) signifies interlayer collapse, which compromises the sodium storage capacity of the NNM cathode, aligning with the observed decline in electrochemical performance. This degradation is likely due to overcharging and/or side reactions involving electrolyte corrosion. In contrast, the NNM electrode cycled with R-G2-electrolyte exhibited minimal lattice distortion, indicating that the NO_3^--derived CEI layer not only protected the electrolyte but also shielded the cathode from side reactions. We appreciate this insightful question and have incorporated an evaluation of the cathode evolution into the revised manuscript.

We further conducted XRD analysis on the cathode materials after cycling. As displayed in Supplementary Figure 11, the NNM electrode cycled with R-G2 electrolyte exhibited minimal crystallinity loss and structural degradation, suggesting that the NO_3^--derived CEI layer effectively protected both the electrolyte and the cathode from side reactions. (In page 9)

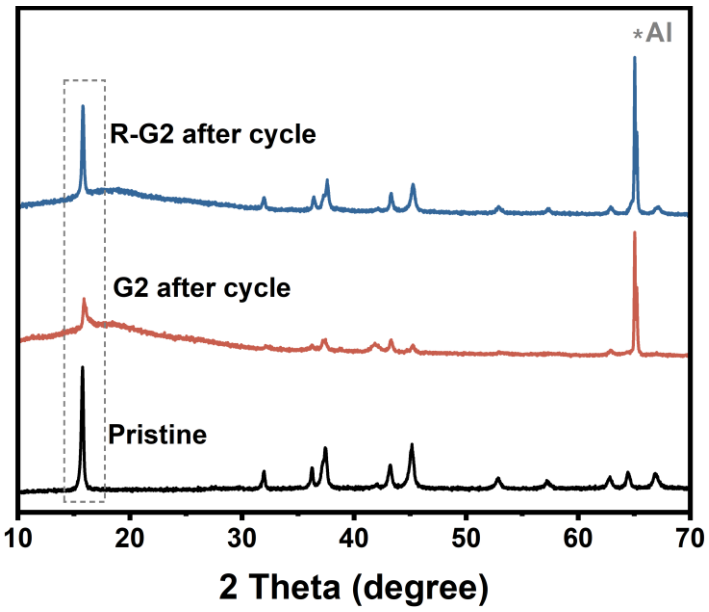


Figure R2. XRD patterns of the NNM electrodes after 5 cycles with G2 and R-G2 electrolytes.

3. The decomposition of NaOTf is known to increase the NaF content in the CEI. Could the authors explain why this enrichment does not confer sufficient high-voltage endurance?

Response: The NaF component is well-established in the literature as a beneficial constituent of the SEI/CEI layers, and the decomposition of NaOTf has been demonstrated to substantially boost the NaF concentration within these protective films. The NaF-enriched interphase is recognized for its role in enhancing rapid ionic diffusion and achieving uniform anode deposition, which are among its several beneficial effects. However, it has been noted that this interphase does not sufficiently prevent electron leakage or control the relentless growth of the interphase layer (as discussed in Angew. Chem. Int. Ed. 2023, 62, e202216354). Furthermore, beyond the compositional elements, the structural design of the CEI in our study is also crucial for attaining robust antioxidant properties.

4. Would an increase in the $NaNO_3$ content in the electrolyte further enhance the anti-oxidation performance? If so, is there an optimal concentration that maximizes this effect?

Response: That's a thought-provoking inquiry. Regrettably, enhancing the solubility of $NaNO_3$ in the G2 electrolyte at room temperature without altering its composition presents a challenge. However, the successful integration of a more concentrated $NaNO_3$ into our electrolyte is expected to yield substantial enhancements in anti-oxidative performance and electrochemical stability. To delve deeper into potential optimizations, we have conducted the following experiments for your consideration:

1. A 10% mass ratio of $NaNO_3$ was blended with NNM during the electrode preparation process and then assembled with the R-G2 electrolyte (referred to as R-NNM-G2).
2. The separator was immersed in a 1 M $NaNO_3$ solution in DMSO for 12 hours, followed by drying under vacuum for another 12 hours, before being assembled with the R-G2 electrolyte (referred to as R-Sep-G2).

As depicted in Figure R3, the cycling stability of NNM with the R-Sep-G2 electrolyte has been notably enhanced, attributed to the sustained release and replenishment of $NaNO_3$. In the case of R-NNM-G2, there was an initial rapid decline in capacity, likely due to the dissolution of $NaNO_3$ leading to the stripping of the NNM cathode. And a stable performance could be obtained in the following cycling. To sum up, the continuous supplementation of $NaNO_3$ within the battery system during cycling could further enhance cycling stability. We are also committed to exploring additional methods to refine the electrolyte formulation and maximize these benefits.

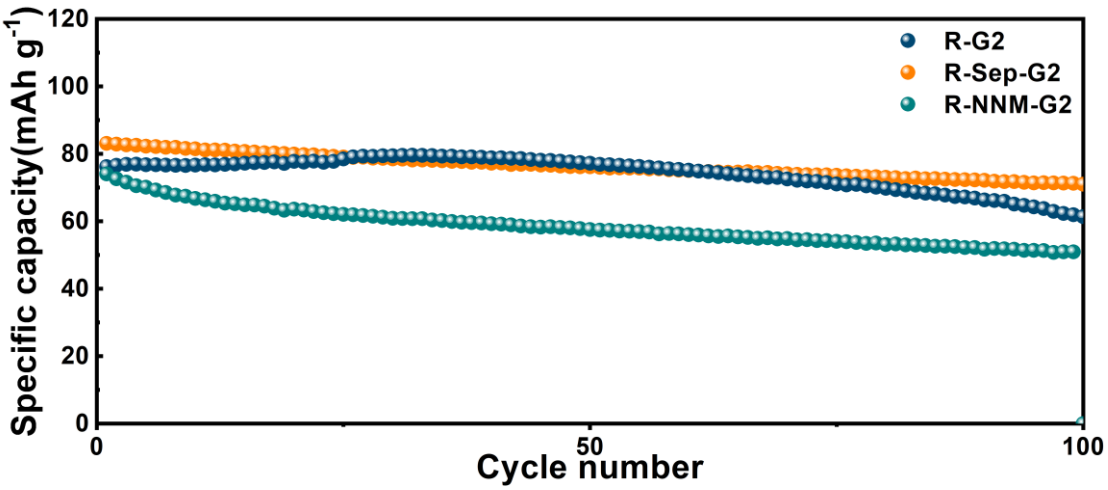


Figure R3. Comparative cycling performance of NNM electrodes under three different conditions.

5. How does the introduction of the $NaNO_3$ additive affect anode performance, particularly in terms of phenomena such as co-intercalation in graphite? Are there any observable changes that need to be considered?

Response: Thank you for your constructive suggestion to assess the impact of the additive from both cathodic and anodic perspectives. Figure R4 illustrates that the GCD curves of graphite electrodes with G2 and R-G2 electrolytes exhibit minimal differences under elevated current densities, suggesting that the co-intercalation behavior remains largely unaffected. The rate performance experiences a very slight decline with the addition of $NaNO_3$, potentially due to the formation of a reformative SEI layer and the enlargement of Na-solvent/anion clusters, which marginally increase the co-intercalation barriers. However, in the context of full-cell assessments, the anodic influence is found to be minimal.

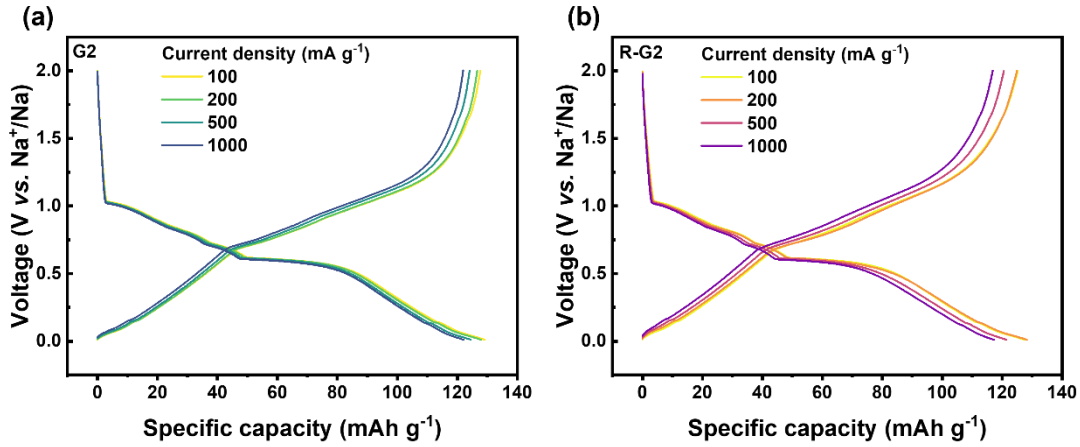


Figure R4. GCD curves of graphite anodes with (a) G2 and (b) R-G2 electrolytes under elevated current densities.

Reviewer #2:

The manuscript introduces a straightforward additive approach to bolster the high voltage stability of ether-based electrolytes. The authors have effectively demonstrated a profound connection between solvent-cluster distribution and interphase formation. The incorporation of nitrate ions is shown to regulate both solvation structures and CEI components, thereby inhibiting the continuous decomposition of the electrolyte and the overgrowth of the interphase. This methodology is suggested to have broad applicability in improving the high voltage tolerance of ether-based electrolytes, making them a viable option for SIBs, given their compatibility with both cathode and anode materials. However, the following revisions and clarifications are required before the manuscript can be accepted:

Response: We appreciate a lot for the approval of our study. Also, we would like to thank the reviewer for the positive comments and the very constructive suggestions to help us further improve the quality of our manuscript.

1. The authors should address why the discharge capacity decays in pure G2, as depicted in Figure 1a. Understanding this phenomenon is crucial for the overall context of the study.

Response: Thanks for the valuable suggestion. Indeed, the ionic conductivity of the interphase plays a crucial role in regulating the diffusion of Na^+ ions, thereby exerting a substantial influence on the electrochemical performance (Adv. Energy Mater. 2021, 11, 2001455). In our specific case, the pronounced oxidation of electrolyte components leads to an overgrowth of the CEI layer within the G2 electrolyte. As a result, the intercalation of Na^+ ions would also be hindered by interfacial barrier, leading to capacity decay during discharge. To enrich the overall context of the research, the correlative discussion has been integrated into the revised manuscript.

We suspect that the high irreversible charge capacity is the result of severe electrolyte decomposition at the electrode-electrolyte interface, which impedes the intercalation of Na^+ ions. Scanning electron microscopy (SEM) analysis of NNM particles both prior to cycling and after five cycles, as depicted in Figs. 1c and 1d, revealed the formation of a thick layer of byproducts on the NNM cathode surface. Notably, the presence of substantial C-containing species in Fig. 1e suggests uncontrollable parasitic reactions at the electrode-electrolyte interface, leading to uneven deterioration of the CEI layer. (In page 4)

2. In Figure 2, the manuscript suggests that diglyme can be protected, yet Figure 4a indicates that NO_3^- containing clusters would be sacrificed first to form an ideal CEI. The authors need to clarify whether these statements are contradictory and explain the possible discrepancy.

Response: In fact, the principal distinction between these two statements is which components are targeted for initial decomposition. As shown in Figure 2b and Figure 4a, the HOMO level of NO_3^- is far higher than other electrolyte constituents, making it the most susceptible to oxidation. In Figure 2, the diglyme was protected due to the electron donating ability of NO_3^-. While in Figure 4a, although the NO_3^- containing clusters would be sacrificed first, the NO_3^- ions within these clusters serve as the vulnerable sites for initial decomposition, which means a transition in the decomposition process from diglyme molecules to NO_3^- ions. Besides, before the decomposition of solvated clusters, the dissolved OTf^- and NO_3^- anions would sacrifice first, constructing the dense inner regions of the CEI.

We appreciate your insightful suggestions and have emphasized the following clarifications into the revised manuscript.

"Specifically, the oxidation sites are mostly located on the NO_3^- of solvation clusters while the C-O bonds of the G2 solvent are thus protected." (In page 10)

3. Why such a trace amount of $NaNO_3$ can significantly alter solvation structures? The authors should discuss the potential effects of increasing the concentration of $NaNO_3$ and how it might influence the electrolyte's performance.

Response: Although 0.04 M represents a minor concentration, the NO_3^- anion to diglyme molecule ratio is approximately 1:100, which is sufficient to alter solvation structures. To substantiate this, we constructed a simulation box containing 525 atoms and employed molecular dynamics (MD) studies to simulate the radial distribution functions (RDF). The resulting snapshots and corresponding RDF results indicate that NO_3^- ions penetrate the first solvation shell, with a coordination distance of Na^+-$O(NO_3^-)$ around 2.1 Å, as depicted in Figure R5. Concurrently, there is a reduction in the overall coordination number of OTf^-, suggesting that some OTf^- are released from the solvation shell, which aligns with our earlier discussion on Raman spectroscopy and NMR data. Additionally, several publications have demonstrated the modification of solvation or interfacial behavior through the addition of trace amounts of additives (Nano-Micro Lett. 2023, 15: 81; Nature Energy, 2024, https://doi.org/10.1038/s41560-024-01638-z).

For the second question, 0.04 M $NaNO_3$ is nearly saturated in G2 electrolyte. To delve deeper into potential optimizations, we have conducted the following experiments for your consideration:

1. A 10% mass ratio of $NaNO_3$ was blended with NNM during the electrode preparation process and then assembled with the R-G2 electrolyte (referred to as R-NNM-G2).
2. The separator was immersed in a 1 M $NaNO_3$ solution in DMSO for 12 hours, followed by drying under vacuum for another 12 hours, before being assembled with the R-G2 electrolyte (referred to as R-Sep-G2).

As depicted in Figure R3, the cycling stability of NNM with the R-Sep-G2 electrolyte has been notably enhanced, attributed to the sustained release and replenishment of $NaNO_3$. In the case of R-

NNM-G2, there was an initial rapid decline in capacity, likely due to the dissolution of $NaNO_3$ leading to the stripping of the NNM cathode. And a stable performance could be obtained in the following cycling. To sum up, the continuous supplementation of $NaNO_3$ within the battery system during cycling could further enhance cycling stability.

We thank the Reviewer for their perceptive inquiry. We have now included the relevant content within the section discussing the solvation structure.

A molecular dynamics (MD) study reveals that NO_3^- ions are integrated into the primary solvation shell, featuring a Na^+-O(NO_3^-) coordination distance of around 2.1 Å, as shown in Supplementary Fig. 6. Simultaneously, there is an observed reduction in the total coordination number of OTf^-, indicating the release of some OTf^- ions from the solvation shell. These findings are consistent with the outcomes of Raman spectroscopy and the NMR data. (In page 12)

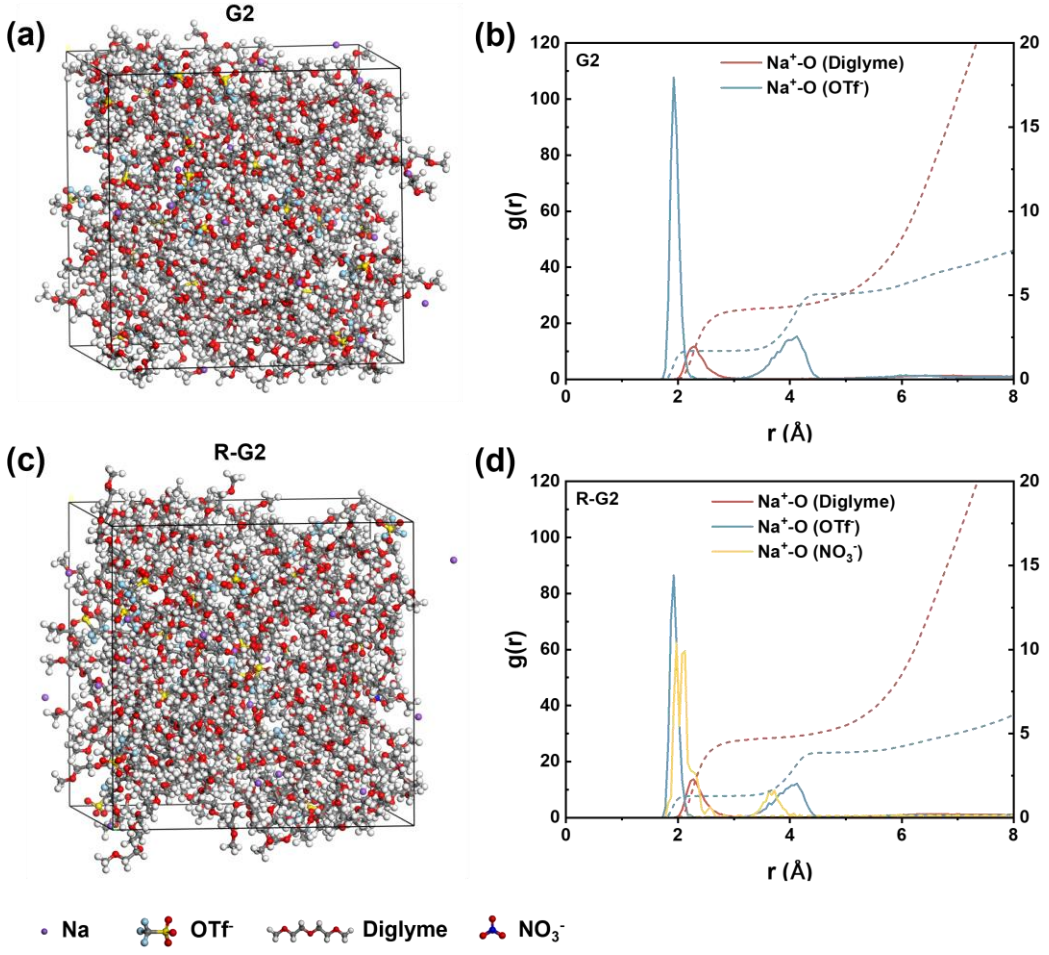


Figure R5. Snapshots of simulated (a) G2 electrolyte and (c) R-G2 electrolyte, together with (b) and (d) corresponding RDF distributions.

4. Determining the electron insulation effects of the modified CEI is challenging due to its complex mixture of components. The authors should provide a methodology or rationale for assessing these effects.

Response: Thanks a lot for your kind advice. It is indeed challenging to ascertain the enhancement of electron insulation effects within a modified CEI, given the intricate composition and delicate structure of CEI, which complicates both experimental characterization and theoretical analysis. As shown in Figure 4c, we pre-cycled the NNM cathode in R-G2 electrolyte, subsequently removed the cathode, reassembled it with G2 electrolyte, and proceeded with the LSV test. The enhanced high voltage tolerance capability confirmed the improved electron insulation effects with modified CEI in real operating environment. Additionally, we reviewed relevant literature and discovered successful instances of enhancing battery reversibility by engineering a NaF/NaN_xO_y-rich interphase. (Refer to Adv. Mater. 2024, 36, 2307645; Angew. Chem. Int. Ed. 2024, e202406277; Mater. Today Energy 2022, 23, 100898). This represents a challenging yet significant research avenue that we are actively pursuing.

5. The authors should explain why there are distinguished GCD curves when $LiNO_3$, $NaNO_3$ and KNO_3 are used as additives.

Response: Upon examining the GCD curves, we observed that the most significant differences occurred at the open-circuit voltage (OCV) of the batteries. Consequently, we immersed the NNM electrodes in G2 electrolytes with varying additives and performed XRD analysis, as illustrated in Figure R6. The result indicates that the NNM went through lattice structural alterations with varying degrees of change, especially in the presence of $LiNO_3$ additive, which corresponded to the most significant GCD curve distortion. Based on these findings, we assumed that the changes of GCD curves are intimately connected to the spontaneous ion-exchange between electrolyte additives and bulk materials before cycling. This opens up a fascinating pathway for deeper investigation in our future research initiatives. Nevertheless, the noticeable improvement in antioxidant properties is a consistent finding, which can be ascribed to the development of CEI layers from anion-derived CEI and the reconfiguration of solvation structures.

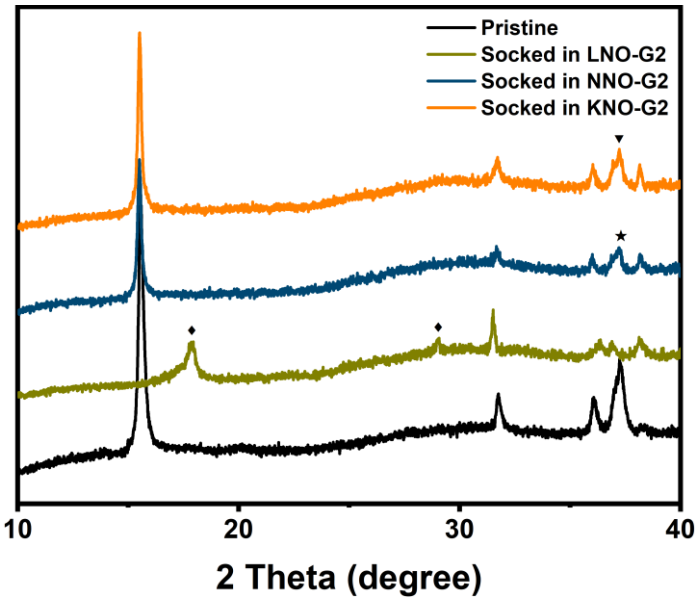


Figure R6. XRD patterns of NNM cathodes socked in G2 electrolytes with $LiNO_3$ additive (LNO-G2), $NaNO_3$ additive (NNO-G2) and KNO_3 additive (KNO-G2).

6. The GCD curves of NNM||graphite full batteries show total deformation in G2 and R-G2. The authors should investigate and explain whether the anode reactions have also been altered, which could have significant implications for the battery's performance.

Response: Thanks for your considerable advice. The GCD curves of graphite anode in G2 and R-G2 electrolytes under elevated current densities indicate that the co-intercalation process was not fundamentally changed, as shown in Figure R4. The only notable difference is a slight reduction in the rate capabilities of the graphite anode with the R-G2 electrolyte, likely due to increased interfacial barriers for Na-solvent cluster intercalation, a result of the similar film-forming process observed on the anode side. However, the impact of the anode reaction on the overall battery performance is minimal, suggesting that the distortion of the GCD curves is primarily attributed to the decomposition of the G2 electrolyte during charging. It should be noted that overcharging in full batteries can also cause a mismatch in the cathode/anode voltage range, leading to the deformation of GCD curves. Thanks again for your insightful comment. We have clarified this issue in the revised manuscript.

Reviewer #3:

After a thorough evaluation, I have summarized my comments and suggestions on this manuscript as follows.

In this work, the authors address the oxidation issue of ether-based electrolytes in the application of sodium-ion batteries. The authors demonstrated the high voltage intolerance and sensitivity of the nucleophilic nature of the ether-based electrolytes, which significantly limits their application for a vast range of high-voltage cathode materials above 3.9 V. The addition of a foreign NO_3^- was found to suppress the electrolyte oxidation side effect on the cathode surface by forming a passivating cathode electrolyte interphase (CEI), extending the electrochemical voltage window up to 4.8 V. The authors also demonstrated this strategy could be universal across various nitrate salts (such as $LiNO_3$, $NaNO_3$, and KNO_3), exhibits excellent compatibility with different cathodes and anodes (hard carbon and graphite), and is effective with other ether-based electrolytes such as TEGDME. Under this reformulated G2 electrolyte system, the modified CEI and enhanced high-voltage stability result in improved battery cyclability over 1000 cycles. To elucidate the mechanism, the authors conducted NMR, Raman, XPS and DFT calculations to further identify the role of the NO_3^- additive in forming a more stable NaN_xO_y/NaF interphase and suppressing the dehydrogenation and oxidation of G2 electrolyte.

However, certain ambiguities and issues need to be addressed before the manuscript can be considered for acceptance. Additionally, the reviewer also found several typos and language inconsistencies that the authors should also carefully revise.

Response:

We thank the reviewer for his/her acknowledgement of the novelty and significance of our work. We also thank the reviewer for raising several important points that help us improve our manuscript. In light of the reviewer's valuable suggestions and comments, we have carried out necessary experiments to address the reviewer's questions, and made clarifications and revisions to our manuscript.

1. In the introduction, the authors state, "Carbonate solvents, prevalent in LIBs, are less effective in SIBs due to their tendency to form complex, ion-transport hindering reductive products". However, this statement may be somehow misleading, as carbonate-based electrolytes are actually more commonly used for SIBs, with higher cut-off voltage such as 4.6 V. Hence, the authors should make a more fair comparison between carbonate and ether-based electrolyte systems. However, the authors can highlight the advantage of ether-based electrolytes, proving to be compatible with commercial graphite via solvent co-intercalation reaction, whereas the conventional carbonate-based solvents exhibit poor Na^+ storage in graphite as shown in Fig. S1. Additionally, in Fig. 1 and S1, the electrolyte and Na salt should be written out in the figure caption.

Response: We thank the reviewer for carefully reading our manuscript and provide this important suggestion. In the revised version, we have revised the corresponding part to clarify our point in the introduction.

"Unlike the poor Na^+ storage in carbonate-based electrolyte system that is prevalent in SIBs, commercial graphite demonstrates high capacity in ether-based electrolytes through a solvent co-intercalation reaction, as illustrated in Supplementary Fig. 1. Further, ether electrolytes show good compatibility with various SIB anodes, mainly owing to its capability of forming a thin and robust solid-electrolyte interphase (SEI) layer that promotes sodium ion transport and enhances electrochemical properties regarding specific capacity, rate capability, life span and initial Coulombic efficiency, as detailed in Supplementary Table 1. Nevertheless, the use of conventional ether-based electrolytes still struggles with high-voltage requirement of SIBs due to their ease of degradation at the oxidizing potential of cathode materials."

2. The authors state, "we used a pure P3-phase $Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ (NNM) cathode with a particulate form (Supplementary Fig. 2)". However, it's clear that the P3 material is not pure with NiO as impurity.

Response: We thank the reviewer for raising this important point. It is true that P3-phase $Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ (NNM) cathode contains minor NiO that are not easy to eliminate, for which we labeled in the figure but did not mention in the text. Since we use this NNM in both experimental and control electrolytes, this does not affect the conclusion of our work. In the revised version, we have made revision to the wording.

"To evaluate high-voltage stability, we employed a P3-phase $Na_{2/3}Ni_{1/2}Mn_{1/2}O_2$ (NNM) cathode material with a particulate morphology, as shown in Supplementary Fig. 2." (In page 4)

3. In Fig. 2, the captions of (c) and (d) are reversed.

Response: We thank the reviewer for carefully reading our paper and bringing this up. We have revised Figure 2 in the new version.

4. In line 134, please provide more details for characteristic peaks in the Raman spectrum. The reviewer did not find the information provided in ref.16.

Response: We appreciate the reviewer's comments and understand his/her concern. We are sorry that the reviewer has missed this information because of our wrongly labeled citation. The FI-OTf species of G2 electrolyte is identified by the characteristic peaks at 1034 cm^{-1} in the Raman spectrum, which is consistent with OTf species identified in the previous reports (Energy Storage Mater. 2022, 47, 203-210; Adv. Mater. 2020, 32, 1904427) Typically, the shift of Raman peaks towards higher energy indicates a transformation in solvation structures, i.e. the transition to more tightly packed ion pairs,

such as CIP or AIP (Electrochimica Acta 2019, 321, 134600). This led us to assign the peak at 1039 cm^{-1} to the feature of CIP-OTf. Thanks again for pointing out this important point. We have corrected and added these citations to our revised manuscript

"The G2 electrolyte contains two characteristic peaks at 1034 and 1039 cm^{-1} in the Raman spectra (Supplementary Fig. 5). [Energy Storage Mater. 2022, 47, 203-210; Adv. Mater. 2020, 32, 1904427] The former corresponds to the FI-OTf species and the latter implies the formation of the CIP-OTf, the downshift of Raman peaks signifies a transition in solvation structures to more tightly packed ion pairs." [Electrochimica Acta 321 (2019) 134600] (In page 7)

5. Why are the data of G2 steel in Fig. 3a and Fig.S7 inconsistent?

Response: We thank the reviewer for bring up this important question. The darker blue curve actually belongs to the LSV of the ester electrolyte (1.0 M NaOTf in EC/DEC/FEC), which we used, in our original experiment, to show that oxidation tolerance of R-G2 electrolyte is comparable to that of ester electrolyte. This was mislabeled as G2 electrolyte. In the revision, we have corrected the Figure S9 (attached as Figure R7 here). We apologize for causing this confusion and thank the reviewer's scrutiny.

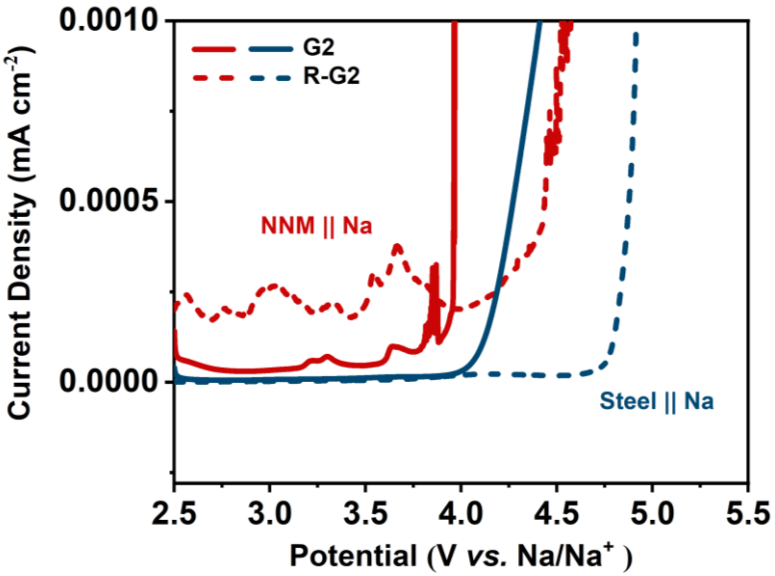


Figure R7. Enlarged detail from the LSV curves of Figure 3a, highlighting the current peak associated with Na^+ intercalation in NMM||Na cells.

6. I overlaid the voltage curves of R-G2 and G2 in Fig. 3c. They appear rather similar in the high-voltage range of 3.25-4.0 V. However, there is an obvious difference in the low-voltage range of 2.0-3.25 V. Intuitively, one would expect electrolyte oxidation at high voltage to result in irreversible charge capacity specifically within the high-voltage range. Can authors explain why this phenomenon happened? A CV curve may be a better way to showcase the voltage-current relationship.

Response: We thank the reviewer for raising this interesting question and understand his/her point. Advised by the reviewer, we conducted CV measurements for NNM in R-G2 and G2, shown in Figure R8b. For the purpose of comparison, we also re-plotted the GCD curve of NNM in R-G2 and G2, shown here in Figure R8a. Treating GCD curves as a whole, NNM electrode operated in G2 electrolyte shows much higher charging capacity than that of NNM electrode in R-G2, due to the electrolyte degradation, which happens both in the low and high voltage range. The more appropriate dissection point of high and low voltage is 3.0 V, i.e. half-way potential of the GCD test, above which electrochemical reaction of NNM took place. In the low-voltage range of 2.0-3.0 V (vs. Na^+/Na), the charging curves shows a very small capacity difference (1.63 mAh/g). This implies the decomposition of G2 at early charging stage, which is verified by the irreversible anodic peak below 2.15 V (vs. Na^+/Na, red trace). In the high-voltage range of 3.0-4.5 V, the two charging curves show much larger gap, contributing to the majority of the capacity difference (20.33 mAh/g), as also evidenced by the higher anodic peaks in CV curves. Given that there is no individual peak associated with the oxidation of electrolyte, the degradation of electrolyte likely happens along with the de-intercalation of Na^+ from NNM electrodes, particularly at the high-voltage range, which is consistent with the common knowledge noted by the reviewer. We have added the CV results in the related part of our revised version

This finding is further supported by the GCD profiles (Fig. 3b) and the cyclic voltammetry curves (CV, Supplementary Fig. 8), which showed large irreversible capacities and an average CE of 51.72% for the NNM||Na cell with G2 electrolyte. (In page 8)

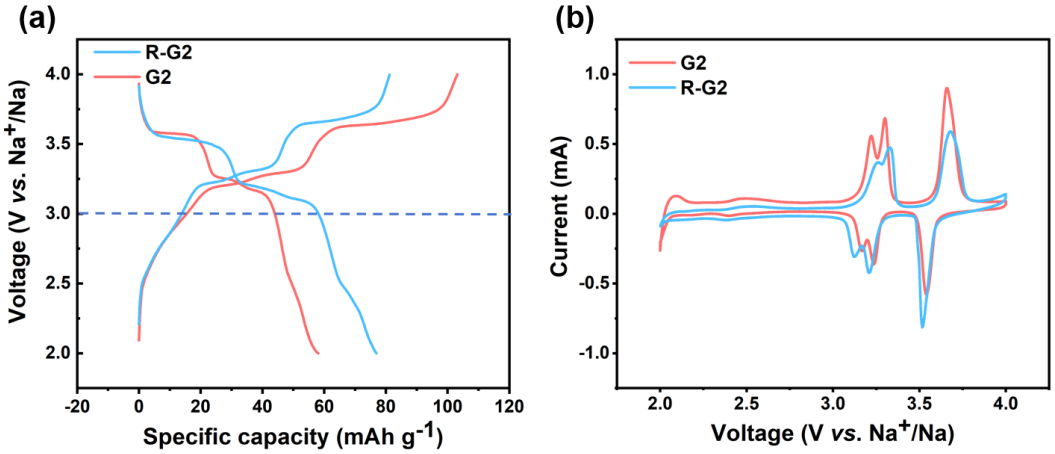


Figure R8. (a) GCD curves and (b) CV curves of NNM||Na cells for the second cycle with G2 and R-G2 electrolytes.

7. The color of the separator-electrolyte of G2 turns black. Could the authors propose a possible byproduct responsible for this change? GC-MS might help to identify the changes involved.

Response: We thank the reviewer for raising this interesting question. Following the reviewer's suggestion, we have conducted gas chromatography/mass spectrometry test (GC-MS) seeking to identify the byproduct. As shown in Figure R9a, the dominating peak is ascribed to the diglyme (G2) molecule while other low-intensity peaks likely belong to some Si-contained compounds. The latter could come from the separator debris (glass fiber, major component SiO_2) or background components inside the instrument. We are not surprised by this result since the decomposition only occurs to the G2 electrolyte at electrode surface while the bulk electrolyte, which is the majority, remain unchanged. This phenomenon is also reported by Johansson et al. (ACS Appl. Energy Mater. 2018, 1, 2671-2680), where only diglyme and the soak solvent acetonitrile were detected for the cycled separator. This is perhaps why identifying the exact composition of the byproduct is so challenging in this area. Having said those, we note that ^{1}H NMR spectroscopy could be potentially used for byproduct identification, which is enlightened by reviewer 1 (results are shown in Figure R1 and Table R1, also attached here as Figure R9b). After compared to the reference materials from LibreTexts, we ascribed the decomposition products of G2 electrolyte to a series of R_xCH_{3-x} or ROH while the black residue remaining on separator is perhaps the detached CEI components or other byproducts resulting from electrolyte decomposition. Still, we have to admit that accurately identifying the byproduct is challenging but interesting, which is not the focus but will be the scope of our future work. We have integrated these discussion in the proper section of the revised manuscript.

The separator subjected to cycling in the G2 electrolyte exhibited a darkened appearance, as shown in the inset of Fig. 3c, which is perhaps the detached CEI components or other byproducts resulting from electrolyte decomposition. In marked contrast, the R-G2 separator retained its pristine cleanliness. (In page 9)

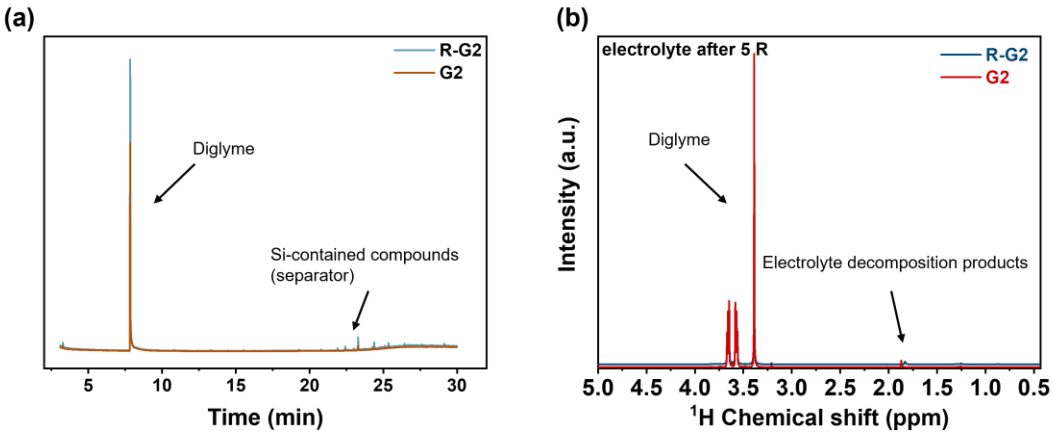


Figure R9. (a) GC and (b) ^{1}H NMR spectrum of cycled G2 and R-G2 electrolytes.

8. In Fig. 4e, the 6 nm CEI layer is not very apparent. Is that possible to validate the thickness with XPS etching depth?

Response: We appreciate this insightful suggestion. The precise quantification of CEI thickness remains a challenge to date, while TEM being one of the most used techniques (Nat Energy, 2023, 8, 1345–1354; Adv. Functional Mater., 2020, 30, 2002824). We agree with the reviewer that there are certain limitations associated with this technique. To address the reviewer's concern, we have conducted depth-dependent XPS analysis. We estimate the CEI thickness using the Mn element as a marker. As illustrated in Figure R10, we detect a minimal concentration of Mn at an etching depth of around 20 nm for the NNM electrode cycled in the G2 electrolyte, which suggests a substantial CEI layer with a thickness over 20 nm. By comparison, for the NNM electrode cycled in the R-G2 electrolyte, Mn exists in the very surface even before etching. Given the probing depth of XPS is less than 10 nm, we believe the thickness of CEI here is smaller than 10 nm, which is consistent with the TEM results. We have included the results in the revised manuscript.

This ultrathin CEI layer, further corroborated by the Mn XPS signal observed on the cathode surface (Supplementary Fig. 14), not only ensures stability but also facilitates interfacial charge transfer, as evidenced by electrochemical impedance spectroscopy (EIS) (Supplementary Fig. 15). (In page 11)

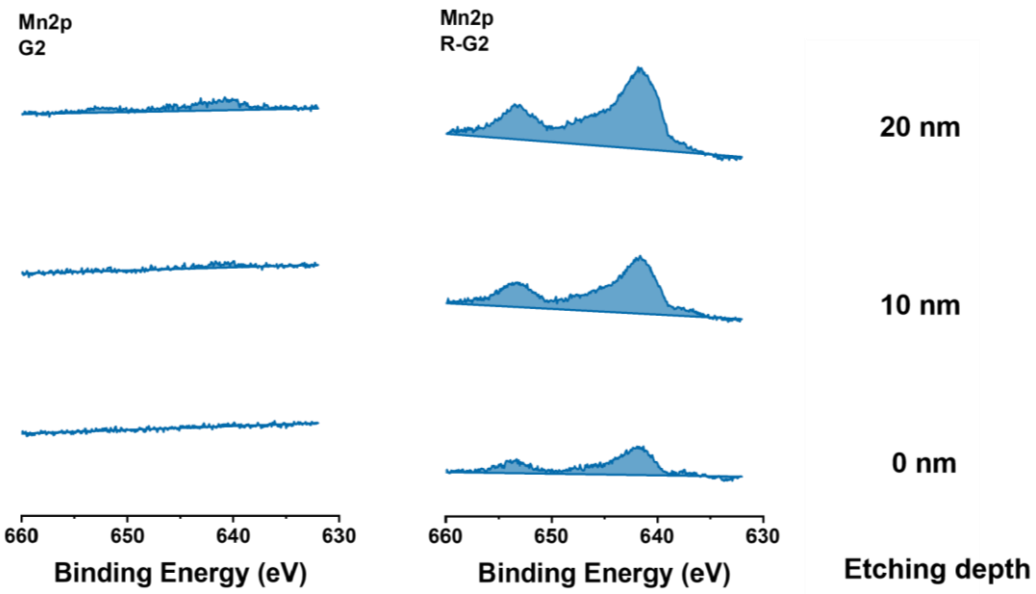


Figure R10. Mn2p XPS spectra of the NNM electrodes cycled with G2 and R-G2 electrolytes.

9. In Line 218, the authors state NaN_xO_y is an excellent Na^+ conductor. Could the author provide a reference or explanation to support this statement?

Response: We appreciate the reviewer's comment. There are several reported literatures highlight the excellent ion conductivity of the NaN_xO_y component within the SEI layer (*Adv. Energy Mater.* 2024, 14, 2303791; *Nano Energy* 2021, 89, 106396). In the revised version, we have added these citations.

10. The XPS etching profiles demonstrate different CEI chemical species formed between G2 and R-G2 electrolytes. The XPS analysis is crucial for further mechanism explanation in Fig. 5b. The authors proposed the presence of RSO_3Na species. However, could the authors also provide the S 2p spectrum to further confirm the presence of RSO_3Na species, where the intensity of the S 2p should be proportional to O 1s (RSO_3Na) with etching depth? Additionally, the authors did not ascribe lattice oxygen (from NNM), which may be unusual for the cathode even with CEI. However, the author may prove the presence of lattice oxygen with transition metal peaks, such as Ni and Mn.

Response: We appreciate the reviewer's insightful suggestions. To address the reviewer's concern, we showed the S 2p spectra along with O 1s spectra in Figure R11 On the surface of NNM electrodes in both G2 and R-G2 electrolytes, tiny RSO_3Na were detected in S spectra but not in O spectra. This is due to the interference from other overwhelming O-associated species with high intensity. However, after a 20-nm sputtering, we noticed the apparent existence of RSO_3Na on NNM electrode in R-G2 electrode (J. Electrochem. Soc. 2022, 169, 050515; Adv. Functional Mater., 2023, 33, 2303667), which reconciles O and S spectra.. By contrast, CEI of NNM electrode in G2 electrolyte at the depth of 20 nm consists of dominating Na_2CO_3 species (O spectra) with nearly zero RSO_3Na (S spectra). These results corroborate that RSO_3Na is one of the major inner CEI species in R-G2 electrolyte. Moreover, our observation suggests that scaling relationship between S 2p and O 1s only applied when RSO_3Na is in a fairly high intensity.

We further checked Mn 2p spectra for identification of lattice O (Figure R10). Mn signal is weak even after 20 nm sputtering for NNM in G2 electrode because of thick CEI on the surface. While for NNM in R-G2, the Mn 2p peaks are evident, with intensity increase with the depth, which suggests the existence of lattice oxygen. Upon checking the O 2p spectrum at depth of 20 nm (NNM in R-GO), we note that the peak around 528 eV in Figure 4f points to the metal-O bonding, according to previous report (J. Electrochem. Soc., 2020, 167, 120534). Further, it is likely overlaps with the feature Na_2O in CEI, another important inorganic species prevalent in the interphase. We have revised the relevant text and figure in the revision.

With NNO electrolyte addition, the inner layer of CEI displayed significantly reduced Na_2CO_3/Na_2CO_2R content and introduced oxidative products such as NaN_xO_y and RSO_3Na/RSO_2Na, which is also confirmed by the S 2p spectra displayed in Supplementary Fig. 11. (In page 11)

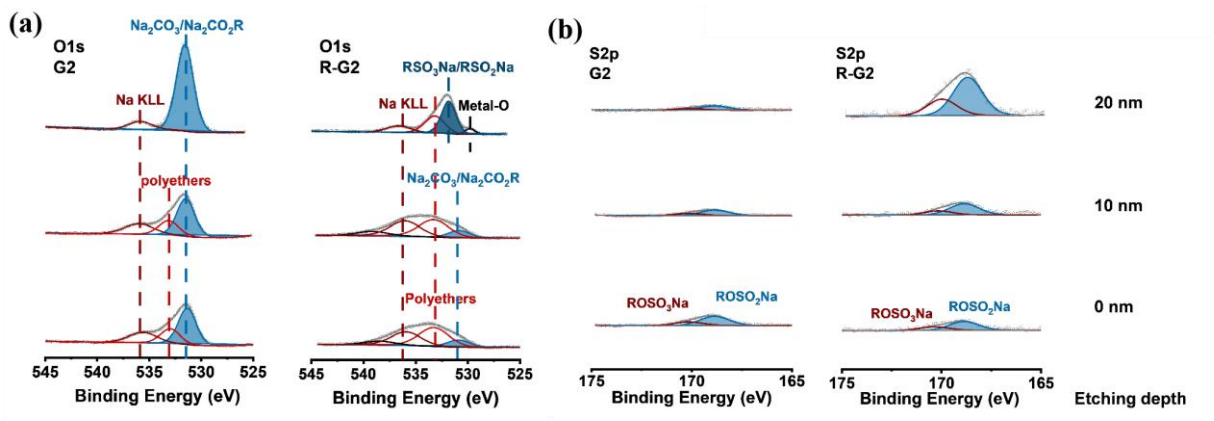


Figure R11. (a) O 1s and (b) S 2p XPS spectra of the NNM electrodes cycled with G2 and R-G2 electrolytes.

11. In the method section, the authors are encouraged to provide further details of sample preparation for the XPS etching study, especially whether the cathode was washed and how this was done to make sure there is no NaOTf salt residue.

Response: During our XPS sample preparation, the cathode was carefully collected from the cycled coin cell, rinsed and washed each 3 times by the diglyme (G2) solvent and fully dried to remove any residual electrolytes. The entire preparation process was carried out in a glove box with the water and oxygen level less than 0.1 ppm. Since NaOTf salt is very soluble in G2 solvent, we believe NaOTf in the residue electrolyte and adsorbed NaOTf could be all wash away from the electrode. The electrode was then sealed and transported to the XPS system through a vacuum chamber for further test. We have added this experimental detail in the revised manuscript.

"During our XPS etching study, the cathode was meticulously extracted from the cycled coin cell, rinsed and washed with the G2 solvent each three times to eliminate residual electrolytes, and then fully dried. This procedure was conducted in a glove box with water and oxygen levels below 0.1 ppm. The electrodes were sealed and vacuum-transferred to the XPS instrument for further analysis." (In page 16)

12.Typo: Line 171 NMM||Na into NNM||Na; stainless||Na steel cell should be stainless steel||Na; Line 265, redundant "the"; Line 271, Supplementary Fig. 11 into Fig. 12.

Response: Thank you for pointing out our typo. We have made the correction to these lines and proofread the manuscript to avoid such errors.