

Rational electrolyte solvent screening for high-energy lithium metal batteries at low temperatures

Corresponding Author: Professor Qifeng Zheng

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)

In this paper, the authors evaluate the electrochemical properties, solvation environment, and performance of asymmetric fluorinated solvents for lithium-ion batteries. The primary focus is to improve the low temperature operation of liquid electrolytes for lithium metal batteries through fluorinated solvents. They also performed theoretical calculations to offer possible explanations for the observed electrochemical trends and behavior. They identified 3,3,3-trifluoropropyl-1-methyl ether (TFPM) as the top performing solvent for low temperature operation with a 2M LiFSI salt.

My primary concern with this paper is the lack of novelty for their research approach. There are countless papers and reviews describing the enhanced low temperature performance of fluorinated and/or asymmetric solvents for lithium ion batteries in this and similar journals. These reports use a similar approach to this work by understanding how to control the solvation/coordination of lithium with fluorinated solvents to impact factors such as ionic conductivity, kinetics, oxidation stability, and stable SEI formation. This also includes prior work by the authors from 2023 (Angew. Chem. Int. Ed. 2023, 62, e202218151) in which they look at a structurally similar 1,1,2,2-tetrafluoro-3-methoxypropane (TFMP) solvent. They use a 7:1 mix of TFMP with DME with 1 m LiFSI. They showed cycling at -40 oC with NMC811 for 100 cycles with the electrolyte in coin cell format. This work and general conclusions are very similar to this current study.

In the current work, the authors also present a thorough characterization of the system across multiple time and length scales with a variety of analytical techniques as they previously did for TFMP from 2023. They show improvement in coin cell cycling at -40 oC with NMC811 for 200 cycles with minimal loss in capacity for the TFPM solvent compared to the TFMP solvent. They also expand the practical use of the TFPM solvent by demonstration of 6.0 Ah pouch cells that can operate at low temperature (-40 oC) with good capacity retention and coulombic efficiency. They also demonstrate -60 oC operation in a coin cell with good performance for 150 cycles. The use of lean electrolyte conditions and low N/P ratio in these cells and comparison of its ambient and low temperature performance with current literature highlights the potential utility of the electrolyte solvent. However, is this enough to overcome the lack of novelty in their approach compared to prior work from their group and others which should be addressed? If addressed, it could be accepted. Aside from this issue, the following points should also be considered:

1. Figure 2 only shows the coordination environment for a single lithium cation and solvent molecule. While this highlights the point the authors are trying to make regarding the differences in energies and bond distances for Li-O and F-O, it does not provide a real picture of the solvation environment. How do the bond distances and coordination environment change as the number of solvent molecules is increased? Additionally, where is the anion in the solvation structure? This can be extracted from the MD simulations and further optimized via DFT to show the "true" Li⁺ coordination in the solvent. This will provide a much more accurate representation of the bonding energies and distances in the electrolyte system.

2. Why was LiFSI chosen rather than other electrolyte salts (i.e. LiTFSI, LiClO₄, LiPF₆)? Comment on if you would expect similar or different behavior for other common Li salts with these solvents.

3. Was the impact of LiFSI concentration on any of the electrochemical properties evaluated since it appears that only 2M solution was evaluated?

4. While the radar chart is a visually nice figure (7f), it does not appear that there was a true qualitative methodology for

assessing the designed electrolytes since 4 out of the 5 aspects show the electrolyte has the ideal properties. This makes it appear to readers as if these aspects have been solved, which I do not think that is the case since it is only a qualitative assessment. This could be deceiving to readers and should have some qualitative figures of merit for the rankings. If not, it should be removed from the main text.

5. I think there is a typo in line 275, should it be “PM, TFPM, and TFBM” rather than “BM, TFPM, and TFBM” since the BM shows Al corrosion in Figure S21b while the PM, TFPM, and TFBM electrolytes do not.

6. There are also multiple typos and grammar errors in the paper with the following words misused: line 40 “demanding”; line 46 “wakening”; line 88 “enhances”; line 111 “facial”; lines 117-118 sentence is very difficult to understand; and line 349 “slighter”

Reviewer #2

(Remarks to the Author)

Zehao et al. introduced a promising approach for screening electrolyte solvents for lithium-metal batteries operating under ultra-low temperatures and high voltages using the RESPO- μ principle. As a result, the fluorinated ethers TFPM and TFBM demonstrate superior electrochemical performance compared to their non-fluorinated counterparts, PM and BM. However, it should be noted that a conceptually similar strategy involving rational solvent tuning was previously proposed in a diethyl ether (DEE)-based system by Zhiao et al. (Nat. Energy 7, 94–106, 2022), where improvements in oxidation stability and low-temperature performance were achieved by manipulating the solvation structure. While the present manuscript is thorough, methodically executed, and well-organized, the central concept remains insufficiently substantiated. How solvents with moderate dipole moment (μ) contribute to interphase stability? This mechanism warrants further clarification through either direct or indirect experimental validation. Given the high standards of Nature Communications, the authors are encouraged to address the following concerns before the manuscript can be considered for publication.

Some detailed comments are attached below.

1. In the ^7Li NMR spectra, the observed downfield shift (de-shielding) of Li^+ in LiFSI/BM and LiFSI/PM suggests weaker solvation compared to LiFSI/TFPM and LiFSI/TFBM. However, molecular dynamics (MD) simulations indicate that TFPM and TFBM electrolytes exhibit highly similar solvation structures, as stated in the manuscript: $\text{Li}^+(\text{FSI})_3.03(\text{TFPM})_{0.99}$, and $\text{Li}^+(\text{FSI})_2.93(\text{TFBM})_{1.08}$. How can the significantly lower de-solvation energy observed for LiFSI/TFPM be rationalized relative to the other systems?
2. In both ^{17}O and ^{19}F NMR spectra, the addition of Li salt results in an upfield shift for oxygen and a downfield shift for fluorine. This suggests that fluorine acts as an electron donor, whereas oxygen functions as an electron acceptor. The author should consider the distinct electronic roles of oxygen and fluorine in the FSI $^-$ anion. Particularly since LiFSI accounts for approximately 75% of the coordination environment.
3. In Figure 3a-d, the TFBM has significantly more AGGs/CIPs compared to TFPM. Why does it not yield better Echem performance?
4. 99.3% overall Coulombic efficiency (CE) in a Li/Cu cell is not unprecedented for LiFSI-based systems. For example, values of 99.4% have been reported in 1 M LiFSI in BTFE/DME (Energy Environ. Sci., 2022, 15, 1647–1658), and up to 99.7% in 1.2 M LiFSI/F5DEE (Nat. Energy, 2022, 7, 94–106). At a minimum, the authors should provide a fair comparison with the current state-of-the-art.
5. If dissolution is indeed an issue in the TFBM system, can the difference in SEI composition be identified via XPS? Based on the current data (Figure 5a and S14), the SEI appears similar in both the TFBM and TFPM systems. How, then, can the authors substantiate their claim that dissolution leads to the growth of redundant SEI?
6. The high-voltage stability of fluorinated solvents is not surprising and has also been reported in mentioned Nature Energy paper. Fluorination lowers the HOMO energy level of the molecules, thereby enhancing their oxidative stability. However, how does solvent modification help prevent Al corrosion typically induced by LiFSI?
7. What is the extent of gas evolution in TFBM and TFPM cells during cycling at 4.4 V?

Reviewer #3

(Remarks to the Author)

Electrolyte solvent engineering could tune both the SEI structure and chemistry, which has been considered as a critical and pragmatic approach to enable high performance Li-metal batteries. Unfortunately, the lack of solvent screening principle has hindered their efficient development. In this work, the authors innovatively proposed a solvent screening principle based on unique RESPO- μ dual-descriptors to enable high-energy LMBs at ultra-low temperatures. Furthermore, the authors design and synthesize a new class of weakly solvating fluorinated ethers to validate the effectiveness of this RESPO- μ screening principle. The work provides valuable insights into electrolyte design to enhance electrochemical kinetics and reversibility simultaneously, achieving an unprecedented high energy density of 345.3 Wh kg^{-1} at -40°C . Therefore, from my perspective, this manuscript is very interesting and should be very helpful to the field that is rapidly evolving recently. I would enthusiastically recommend publication of this work after the following minor issues are properly addressed.

1. In the research of solvent descriptors, researchers have proposed numbers of parameters as criteria for solvent screening, among which electrostatic potential is also a very important screening parameter. What are the advantages of the RESPO parameter proposed by the authors compared to electrostatic potential?
2. The designed TFPM electrolyte presented good capacity retention and cycling stability at both room temperature and low

temperature. Has the author explored the rate performance at low temperatures with TFPm electrolyte?

3. Among the series of fluorinated ether molecules designed, the formation of a hexagonal coordination structure can significantly improve the performance of batteries, especially at ultra-low temperature. What influence does this configuration have on the lithium deposition and kinetics at low temperatures?

4. The solvation of TFPm and TFBM is very similar, and the composition of SEI is almost the same at room temperature. However, there is a significant difference in impedance between these two at low temperatures (-40 and -60°C), and there is also a significant difference in battery performance. What is the main affecting factor?

Reviewer #4

(Remarks to the Author)

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

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

accept revised manuscript

Reviewer #3

(Remarks to the Author)

The authors have appropriately addressed the my concerns and requests by providing additional data and clarification. I recommend accepting the revised manuscript for publication.

Reviewer #4

(Remarks to the Author)

The revised manuscript clearly explains the impact of moderate dipole moments on interphase stability through a self-cleaning mechanism. It is thorough, well organized, and I recommend its publication in Nature Communications.

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Dear editor and reviewers,

We have carefully considered all the comments and have fully addressed them point-by-point in “response to reviewer’s comments” below. To facilitate reading of this letter, we have, (i) *systematically reported the editor and reviewer comments in italics and in blue* followed by **our responses in red**, and (ii) handled each reviewer separately. The corresponding changes made to both “Manuscript” and “Supplementary Information” were **highlighted in yellow**.

We once again thank the editor and reviewers for their constructive comments that help in improving and strengthening our paper. Having done our best to satisfactorily answer the editor and reviewers’ comments as well as their requests for extra data, we hope that this revised version could meet the high standards of *Nature Communications*.

REVIEWER COMMENTS

Reviewer #1 (Remarks to the Author):

In this paper, the authors evaluate the electrochemical properties, solvation environment, and performance of asymmetric fluorinated solvents for lithium-ion batteries. The primary focus is to improve the low temperature operation of liquid electrolytes for lithium metal batteries through fluorinated solvents. They also performed theoretical calculations to offer possible explanations for the observed electrochemical trends and behavior. They identified 3,3,3-trifluoropropyl-1-methyl ether (TFPM) as the top performing solvent for low temperature operation with a 2 M LiFSI salt.

*My primary concern with this paper is the lack of novelty for their research approach. There are countless papers and reviews describing the enhanced low temperature performance of fluorinated and/or asymmetric solvents for lithium-ion batteries in this and similar journals. These reports use a similar approach to this work by understanding how to control the solvation/coordination of lithium with fluorinated solvents to impact factors such as ionic conductivity, kinetics, oxidation stability, and stable SEI formation. This also includes prior work by the authors from 2023 (Angew. Chem. Int. Ed. **2023**, 62, e202218151) in which they look at a structurally similar 1,1,2,2-tetrafluoro-3-methoxypropane (TFMP) solvent. They use a 7:1 mix of TFMP with DME with 1 m LiFSI. They showed cycling at $-40\text{ }^{\circ}\text{C}$ with NMC811 for 100 cycles with the electrolyte in coin cell format. This work and general conclusions are very similar to this current study.*

In the current work, the authors also present a thorough characterization of the system across multiple time and length scales with a variety of analytical techniques as they previously did for TFMP from 2023. They show improvement in coin cell cycling at $-40\text{ }^{\circ}\text{C}$ with NMC811 for 200 cycles with minimal loss in capacity for the TFPM solvent compared to the TFMP solvent. They also expand the practical use of the TFPM solvent by demonstration of 6.0 Ah pouch cells that can operate at low temperature ($-40\text{ }^{\circ}\text{C}$) with good capacity retention and coulombic efficiency. They also demonstrate $-60\text{ }^{\circ}\text{C}$ operation in a coin cell with good performance for 150 cycles. The use of lean electrolyte conditions and low N/P ratio in these cells and comparison of its ambient and low temperature performance with current literature highlights the potential utility of the electrolyte solvent. However, is this enough to overcome the lack of novelty in

their approach compared to prior work from their group and others which should be addressed? If addressed, it could be accepted. Aside from this issue, the following points should also be considered:

Authors' Response: We would like to thank the reviewer for his/her useful comments and suggestions to further improve our manuscript. But we dissent from the reviewer that a work lacks novelty if something related to it has been studied, regardless of what it achieves and how important it is. However, please be aware that, for the LiCO₂ cathode material alone (discovered in 1980), there are many papers published on the Nature, Science and Nature sister journals in the past 10 years. Similarly, fluoroethylene carbonate (FEC) was first identified as solvent for graphite anode at 1999, they are many works investigated its effect on other types of anodes, such as silicon and lithium metal anodes, many of which have been published on Nature sister journals, Angew. Chem., JACS and PANS. **Therefore, we certainly can't conclude that a work lacks novelty if something related to it has been studied, as a matter of fact, we should look into what it achieves and how important it is.**

For reviewer's concern on the novelty of our work, we would like to emphasize the novelty in the following several aspects:

First, as pointed out by the Reviewer, there are indeed many papers describing the enhanced low temperature performance of fluorinated and/or asymmetric solvents for lithium-ion batteries, which was realized by controlling the solvation/coordination of Li⁺ with fluorinated solvents to promote ionic conductivity, kinetics, oxidation stability, and stable SEI formation, including our previous study (*Angew. Chem. Int. Ed.*, **2023**, 62, e202218151). However, most of these studies were realized by employing multiple salts/solvents to compensate their individual drawbacks. **Achieving fast kinetics, superior interphase stability, and uniform Li deposition simultaneously in a single-salt single-solvent system is extremely challenging, with only very few reports up to now.** To be specific, there is one very recent paper reported the operation of Li-metal pouch-cell at low temperature of -20 °C using single-salt single-solvent electrolyte (*Joule*, **2025**, 9, 101823). While in our study, a Li-metal pouch-cell was demonstrated to deliver an unprecedentedly high energy density of 345.3 Wh kg⁻¹ over 40 cycles at -40 °C. **Based on the dramatically different electrolyte system, namely multiple-solvent vs. single-solvent, one should NOT conclude that our work lacks novelty.**

Second, recent electrolyte solvent design based on weakening the solvation ability has shown great potential, however, the lack of solvent screening principle has hindered their efficient development. In this study, we innovatively proposed a guideline for rational electrolyte solvent screening, where the restrained electrostatic potential of the coordinated O (RESP_O) was proposed as one descriptor to quantify the solvation effect, followed by introducing the dipole moment (μ) as correction descriptor to optimize solvents' sensitivity to the electric fields and interphase stability. Under the guidance of this RESP_O- μ screening principle, a new class of asymmetric fluorinated ethers was rationally designed, of which the 3,3,3-trifluoropropyl-1-methyl ether (TFPM) with moderate RESP_O and μ was identified to mediate a stable six-membered chelating structure with Li⁺, significantly promoting Li kinetics and reversibility from 30 to -60 °C. This study provides a highly efficient principle for rational electrolyte solvent screening, opens up new frontiers in electrolyte design towards practical high-energy LMBs under extreme temperatures, demonstrating that our study has both scientific novelty and importance.

Third, as commented by the Reviewer, the screened TFPM electrolyte exhibits much superior performance compared to previous literatures. Specifically, **(1)** For the Li||Cu cell, TFPM electrolyte demonstrates ultra-stable cycling for over 850 cycles with a high average CE of 99.3%, representing the pioneering work for “single salt single solvent” electrolytes reported thus far at relatively high current densities of 1.0 mA cm⁻² (Supplementary Table 2); **(2)** for Li-metal coin-cells with high areal capacity and low N/P ratio, the cycling life advantage for TFPM electrolyte is very obvious at low-temperature (≤ -20 °C) in comparison with other reported electrolytes (Supplementary Table 4); **(3)** for the Li-metal pouch-cells, the cell using TFPM electrolyte delivers an unprecedentedly high energy density of 345.3 Wh kg⁻¹ over 40 cycles at -40 °C, which stands out in terms of the highest energy density and longest cycles in comparison with the reported studies at low temperatures (≤ -20 °C) (Supplementary Table 7), validating the superiority of our study.

In summary, our study overcomes the long-standing challenges of Li compatibility and electrochemical kinetics, and provides a highly efficient principle for rational electrolyte solvent screening. This leads to an unprecedentedly high energy density of 345.3 Wh kg⁻¹ over 40 cycles at -40 °C for Li-metal pouch-cell, which is unattainable for previous electrolyte design and can be expanded to other metal batteries. Therefore,

our work has both scientific novelty and importance, and will be of significant interest to the broad readership of *Nat. Commun.* in both scientific and industrial arena. The significant progress, as well as the importance of high-energy and low-temperature batteries in our society, warrants the publication of our manuscript in *Nat. Commun.*

Comment #1: Figure 2 only shows the coordination environment for a single lithium cation and solvent molecule. While this highlights the point the authors are trying to make regarding the differences in energies and bond distances for Li-O and F-O, it does not provide a real picture of the solvation environment. How do the bond distances and coordination environment change as the number of solvent molecules is increased? Additionally, where is the anion in the solvation structure? This can be extracted from the MD simulations and further optimized via DFT to show the “true” Li⁺ coordination in the solvent. This will provide a much more accurate representation of the bonding energies and distances in the electrolyte system.

Authors’ Response: We thank the reviewer for this insightful comment. We agree with the Reviewer that the solvation structure extracted from the MD simulation can more accurately reflect the binding energies and distances in the electrolyte system. Thus, per your suggestion, the most probable solvation structures (3 anions and 1 solvent) of four electrolytes were extracted and further optimized via DFT. As shown in the following **Figure R1**, the TFPM electrolyte exhibits the largest Li-O distance of 2.056 Å, indicating the weakest coordination ability of O atom in TFPM, which is consistent with the “single Li⁺ and single solvent molecule” calculated results shown in Figure 2a-d in Manuscript. Furthermore, the binding energies (i.e., negative value of de-solvation energy) were also calculated according to the solvation structure and their distributions extracted from MD simulation. As shown in the following **Figure R2**, the 2 M LiFSI/TFPM electrolyte exhibits the lowest Avg. ΔE_{dsv} of 2.14 eV, outperforming that of 2 M LiFSI/PM (2.25 eV), 2 M LiFSI/TFBM (2.29 eV), and 2 M LiFSI/BM (2.62 eV), which is beneficial for facile de-solvation and homogeneous Li deposition. The relevant discussion was added to the Revised Manuscript and Supplementary Information.

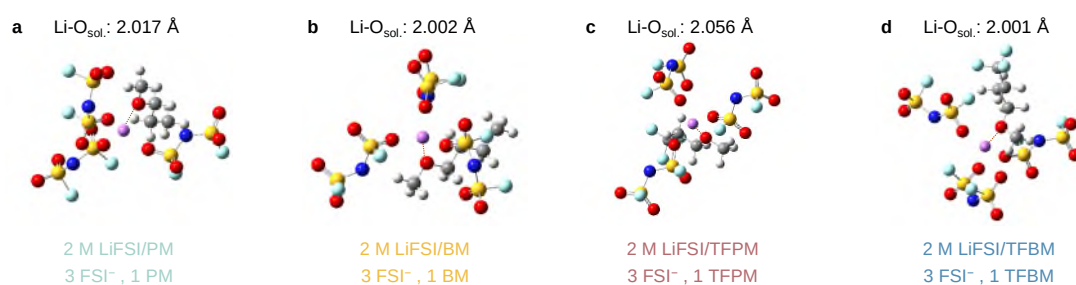


Figure R1. The most probable solvation structures of (a) 2 M LiFSI/PM, (b) 2 M LiFSI/BM, (c) 2 M LiFSI/TFPM, and (d) 2 M LiFSI/TFBM electrolytes extracted from MD simulations.

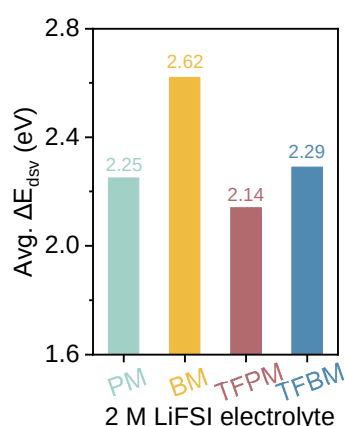


Figure R2. Average de-solvation energy (Avg. ΔE_{dsv}) of different electrolytes calculated according to the solvation structure and their distributions extracted from MD simulation.

Authors' modification to the Manuscript and Supplementary Information:

(Page 5 in Manuscript):

According to the statistic results from MD, all electrolytes including 2 M LiFSI/PM, 2 M LiFSI/BM, 2 M LiFSI/TFPM, and 2 M LiFSI/TFBM possess anion-rich solvation structure, of which more than 95% first solvation sheath was dominated by two or more FSI⁻ anions (Figure 3a-d), with the most probable solvation structure being 3 anions and 1 solvent molecule coordinated with Li⁺ (Supplementary Figure 8).

(Page 8 in Supplementary Information):

The most probable solvation structures of four electrolytes were added to the Supplementary Information as newly added Supplementary Figure 8.

Comment #2: Why was LiFSI chosen rather than other electrolyte salts (i.e. LiTFSI,

LiClO₄, LiPF₆)? Comment on if you would expect similar or different behavior for other common Li salts with these solvents.

Authors' Response: Thanks for your insightful comment. Li salt not only dominates the ion transport behavior in the bulk electrolyte, but also largely affects the solid electrolyte interphase (SEI) components on the anode, which may result in vastly different electrochemical performance of LMBs. LiFSI exhibits superior hydrolysis resistant, high conductivity, and good solubility in ether solvents. While combined with weakly solvating ether solvents, the reduced Li⁺-solvent coordination will not only promote the de-solvation process but also intensify the Li⁺-FSI⁻ pairing to facilitate the formation of anion-derived inorganic-rich SEI at a regular concentration, which enhances the electrochemical kinetics and reversibility simultaneously, especially for LMBs. Therefore, the combination of LiFSI-ether electrolytes has been widely adopted and studied for high-energy density LMBs.^[1-5]

As for the other Li salts mentioned by the Reviewer, (1) LiTFSI has a similar structure and elemental compositions to the LiFSI, which possesses even better thermal and moisture stability than LiFSI. Nevertheless, the larger volume of TFSI⁻ anion and lower conductivity of LiTFSI limits its kinetics at high-rate conditions or ultra-low temperatures; (2) LiClO₄ does NOT contain F element and fails to contribute inorganic LiF, of which the LiF has been recognized as an excellent SEI component to promotes reversible Li plating/stripping. Furthermore, the high oxidation state of Cl (+7) raises serious safety concerns; (3) LiPF₆ is the most widely used and mature Li salt in commercial Li-ion batteries. However, it suffers from poor thermal and moisture stability as well as limited solubility in ether solvents.

To comprehensively address the Reviewer's comments, we extended our study to assess the properties of TFPM with different Li salts. **First**, as shown in the following **Figure R3**, LiFSI presents a higher max solubility (i.e., 5.9 M) than that of LiTFSI (i.e., 5.1 M), LiClO₄ (i.e., 3.8 M), and LiPF₆ (i.e., 1.6 M) in TFPM solvent, which contributes to the sufficient ionization of LiFSI at the applied concentration (2 M) and avoid salt precipitation at ultra-low temperatures. **Second**, the physical properties of TFPM solvent with different Li salts at 2 M (expect 1.5 M for LiPF₆) were also measured (**Figure R4**). Among these four TFPM electrolytes, 2 M LiFSI/TFPM electrolyte emerges as the optimal candidate for practical application due to its highest ionic conductivity, relatively lower density and viscosity. **Third**, to show the universality of

TFPM solvent with different salts in improving the electrochemical performance, 50 $\mu\text{m Li}||4.0\text{ mAh cm}^{-2}$ NMC811 cell using 2 M LiTFSI/TFPM electrolyte was also evaluated (**Figure R5**), which exhibits similarly good performance as that using 2 M LiFSI/TFPM electrolyte. However, the 2 M LiTFSI/TFPM electrolyte delivers inferior rate capability and low-temperature performance.

Therefore, the LiFSI salt remains the best choice in this study.

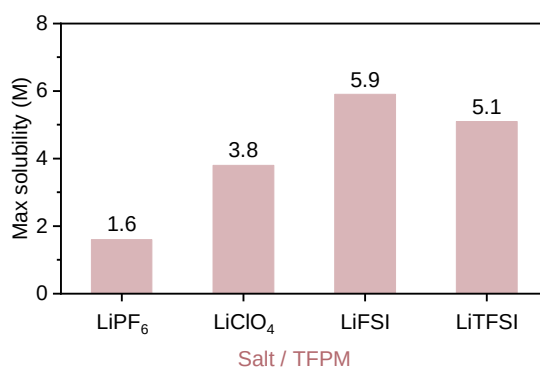


Figure R3. Max solubility of different Li salts in TFPM.

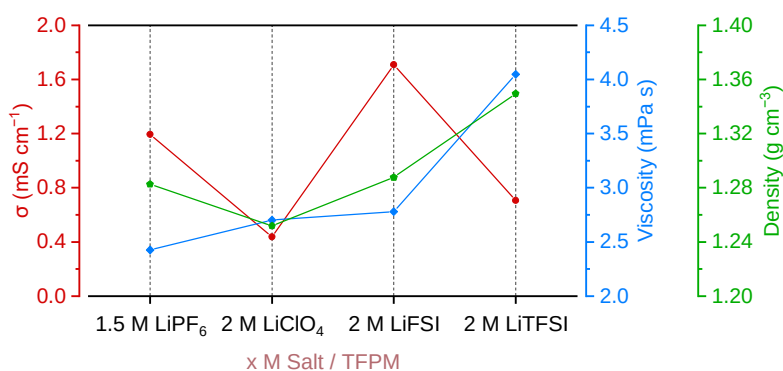


Figure R4. Physical properties of TFPM with different Li salts.

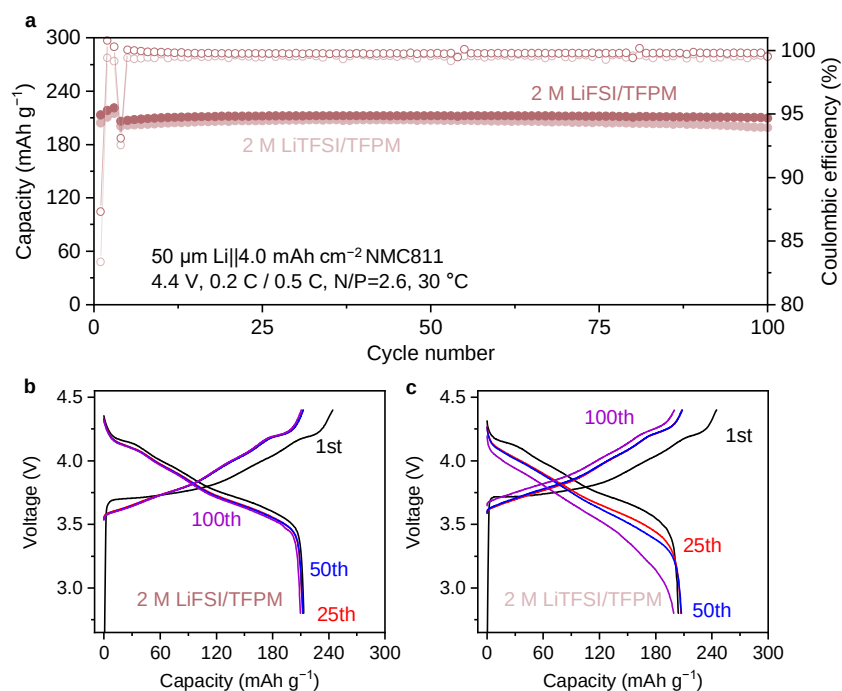


Figure R5. (a) Cycling performance of the 50 μm Li||4.0 mAh cm^{-2} NMC811 cells. The corresponding charge-discharge profiles of the cell with (b) 2 M LiFSI/TFPM and (c) 2 M LiTFSI/TFPM electrolytes at 30 $^{\circ}\text{C}$.

Comment #3: Was the impact of LiFSI concentration on any of the electrochemical properties evaluated since it appears that only 2 M solution was evaluated?

Authors' Response: Thanks for your comment. Prior to conducting the comprehensive study, we actually conduct preliminary evaluations of the electrolytes with different concentrations. For the conventional Li-ion batteries, the concentration of the electrolyte was normally controlled at ~ 1 M to achieve a balance between ionic conductivity, viscosity, and interfacial stability. Increasing the electrolyte salt concentration could effectively reduce the solvent molecules while extensively recruit anions within the Li^+ inner solvation sheath, leading to a high anodic stability as well as an anion-derived inorganic-rich SEI with better Li cyclability, but at a cost of high viscosity and cost.

Therefore, we first evaluated the Li||Cu cells using four electrolytes at a conventional LiFSI concentration of 1 M. As shown in the following **Figure R6**, the cell using four electrolytes all demonstrate high CEs of $\geq 98.5\%$ with the 1 M LiFSI/TFPM electrolyte being the highest of 99.5%. Next, to optimize the electrolyte performance, we further

studied the ionic conductivity of TFPM system at different LiFSI concentration (**Figure R7**). The ionic conductivity of LiFSI/TFPM electrolyte demonstrated a linear correlation with concentration at low concentrations, followed by a saturation turning point upon exceeding 2 M. Furthermore, the 2 M LiFSI/TFPM electrolyte also demonstrates better low temperature Li||Cu CE (**Figure R8**) and Li-metal cycling performance (**Figure R9**) than 1 M LiFSI/TFPM electrolyte.

Therefore, the concentration of the electrolyte was optimized at 2 M in this study with a balance of ionic conductivity, viscosity, de-solvation kinetics, interfacial stability, and battery performance.

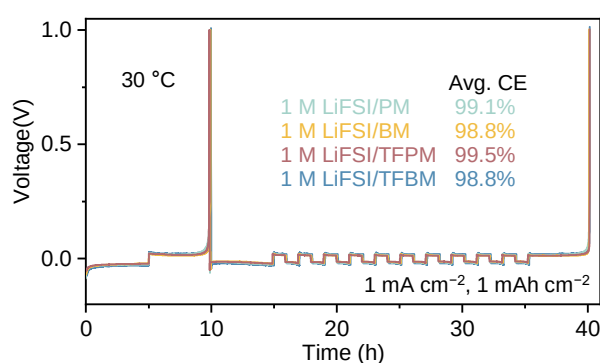


Figure R6. Modified Aurbach measurement of Li||Cu cells using electrolytes with 1 M LiFSI at a current density of 1.0 mA cm^{-2} for 1.0 mAh cm^{-2} at 30°C .

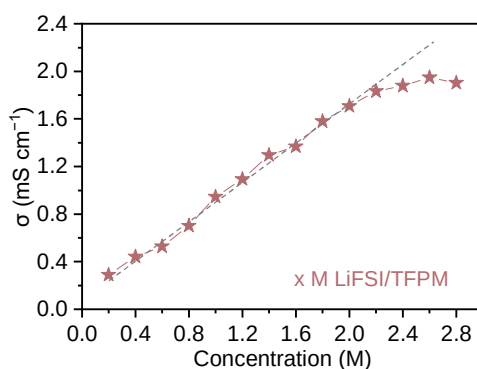


Figure R7. Concentration dependent ionic conductivity of LiFSI/TFPM electrolyte.

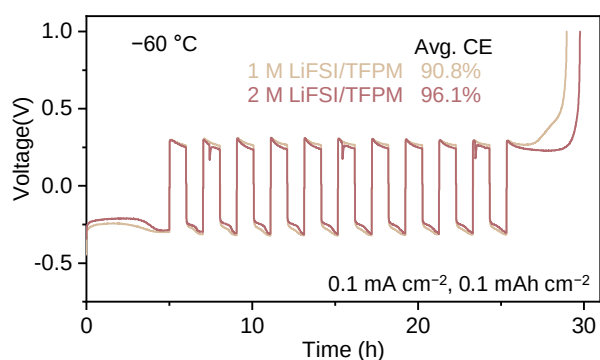


Figure R8. Modified Aurbach measurement of Li||Cu cells using 1 M and 2M LiFSI/TFPM electrolytes at $-60\text{ }^{\circ}\text{C}$ with a current density of 0.1 mA cm^{-2} for 0.1 mAh cm^{-2} .

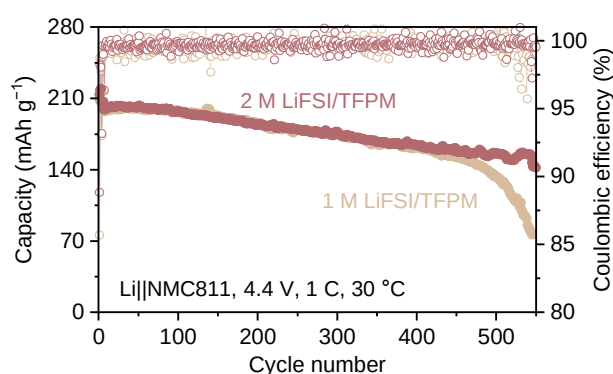


Figure R9. Cycling performance of the Li||NMC811 cells using 1 M and 2 M LiFSI/TFPM electrolytes at 1.0 C and 30 °C.

Comment #4: While the radar chart is a visually nice figure (7f), it does not appear that there was a true qualitative methodology for assessing the designed electrolytes since 4 out of the 5 aspects show the electrolyte has the ideal properties. This makes it appear to readers as if these aspects have been solved, which I do not think that is the case since it is only a qualitative assessment. This could be deceiving to readers and should have some qualitative figures of merit for the rankings. If not, it should be removed from the main text.

Authors' Response: Thank you for this valuable suggestion. We agree with the Reviewer that the original radar chart may be misleading since it is a qualitative assessment. To better reflect the real case, following the methodology described in *Nat. Energy*, **2022**, 7, 94. (Yu *et al.*) and *Nat. Energy*, **2025**, 10, 365. (Choi *et al.*), we carefully listed all relevant data respects to anodic stability, Li-metal compatibility, desolvation, ionic conduction, and interphase stability in the following **Table R1**. Based on these quantitative data, we reassigned the ratings to these aspects and modified the radar plot carefully (**Figure R10**). The relevant data and discussion have been updated in Manuscript and Supplementary Information.

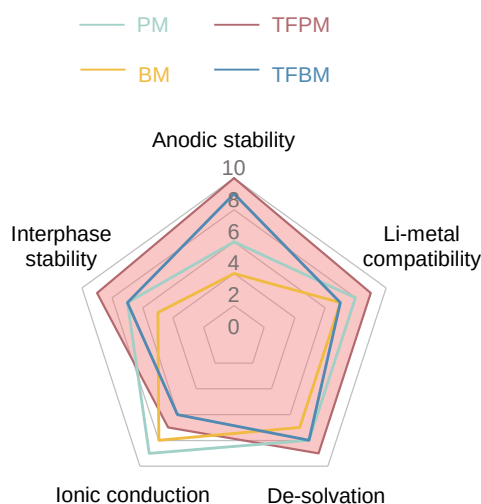


Figure R10. Radar plot with five aspects to evaluate the designed electrolytes. Ratings of 0 to 10 are given to each electrolyte (10 stands for ideal properties).

Table R1. Rationale for radar plot.

Aspect	Reference data & ratings	2 M LiFSI/solvent			
		PM	BM	TFPM	TFBM
Anodic stability	Leakage current in CA test of Li Al cells after 24 h ($\mu\text{A cm}^{-2}$)	1.48	2.22	0.19	0.34
	Ratings	6	4	10	9
Li-metal compatibility	Avg. CE (%) and cycle number of Li Cu cells	99.2@400	99.1@260	99.3@850	99.0@380
	Ratings	8	7	9	7
De-solvation	Avg. ΔE_{dsv} (eV)	2.25	2.62	2.14	2.29
	Ratings	8	7	9	8
Ionic conduction	Ionic conductivity at 30 °C (mS cm^{-1})	4.12	2.69	1.71	1.26
	Ratings	9	8	7	6
Interphase stability	The S and F ratios (%) in XPS after 120 s of Ar^+ sputtering, indicative of robust inorganic components in the SEI.	4.84	2.51	11.44	8.38
		9.48	6.05	12.60	8.85
	Ratings	7	5	9	7

Authors' modification to the Manuscript and Supplementary Information:

(Page 10 in Manuscript):

Under the guidance of $\text{RESP}_{\text{O}-\mu}$ dual descriptors, despite possessing slightly lower

ionic conductivity, the TFPM electrolyte stands out in the aspects of interphase stability, de-solvation, Li-metal compatibility, and anodic stability (Figure 7f and Supplementary Table 8), which enables the stable operation of high-energy LMBs at ultra-low temperatures.

(Page 18 in Manuscript):

The original Figure 7f was updated based on the quantitative data in the Manuscript.

(Page 44 in Supplementary Information):

Table R1 was added to Supplementary Information as newly added Supplementary Table 8.

Comment #5: I think there is a typo in line 275, should it be “PM, TFPM, and TFBM” rather than “BM, TFPM, and TFBM” since the BM shows Al corrosion in Figure S21b while the PM, TFPM, and TFBM electrolytes do not.

Authors’ Response: Thank you for catching this error. We have carefully checked and modified the description in the manuscript.

Authors’ modification to the Manuscript:

(Page 8 in Manuscript):

In contrast, the PM, TFPM, and TFBM electrolytes show no Al corrosion and negligible leakage current with the TFPM electrolyte being the lowest.

Comment #6: There are also multiple typos and grammar errors in the paper with the following words misused: line 40 “demanding”; line 46 “wakening”; line 88 “enhances”; line 111 “facial”; lines 117-118 sentence is very difficult to understand; and line 349 “slighter”.

Authors’ Response: Thank you for catching these errors. We have proof-read and polished the English carefully in the revised manuscript.

Authors’ modification to the Manuscript and Supplementary Information:

(Page 2 in Manuscript):

To fulfill the demand for high-energy and ultra-low temperature LMBs, the following

critical requirements for electrolytes should be met simultaneously, ...

(Page 2 in Manuscript):

Among the various electrolyte design strategies, **weakening** the solvation ability of the solvent through steric hindrance, changing chelation sites or structures, and incorporating fluorination represents the most promising approach.

(Page 4 in Manuscript):

The solvent with weak solvation ability could **enhance** Li⁺-anion coordination to promotes anion-derived inorganic-rich SEIs, while it often compromises the solubility and ionic conductivity.

(Page 4 in Manuscript):

Therefore, it is necessary to highlight molecules with moderate μ (1.5~3.5 Debye) holding great potential for **facile** de-solvation and interphase regulation.

(Page 4 in Manuscript):

RESP is a modified ESP method that incorporates physical constraints (e.g., atomic electronegativity equilibration and bond symmetry constraints) to optimize charge distributions, ensuring further improvement of the rationality of the charge model, which leads to more efficient and accurate to distinguish the ethers with different solvation ability.

(Page 10 in Manuscript):

Under the guidance of RESP_O- μ dual descriptors, despite possessing **slightly** lower ionic conductivity, the TFPM electrolyte stands out in the aspects of interphase stability, de-solvation, Li-metal compatibility, and anodic stability (Figure 7f and **Supplementary Table 8**), which enables the stable operation of high-energy LMBs at ultra-low temperatures.

Reviewer #2 (Remarks to the Author):

Zehang et al. introduced a promising approach for screening electrolyte solvents for lithium-metal batteries operating under ultra-low temperatures and high voltages using the $RESP_{O-\mu}$ principle. As a result, the fluorinated ethers TFPM and TFBM demonstrate superior electrochemical performance compared to their non-fluorinated counterparts, PM and BM. However, it should be noted that a conceptually similar strategy involving rational solvent tuning was previously proposed in a diethyl ether (DEE)-based system by Zhiao et al. (Nat. Energy 2022, 7, 94–106), where improvements in oxidation stability and low-temperature performance were achieved by manipulating the solvation structure. While the present manuscript is thorough, methodically executed, and well-organized, the central concept remains insufficiently substantiated. How solvents with moderate dipole moment (μ) contribute to interphase stability? This mechanism warrants further clarification through either direct or indirect experimental validation. Given the high standards of Nature Communications, the authors are encouraged to address the following concerns before the manuscript can be considered for publication.

Authors' Response: We would like to thank the reviewer for his/her comments and insightful suggestions on our manuscript. We have addressed all comments below and revised the manuscript accordingly.

Dipole moment (μ) reflects the unevenness of molecular charge distribution and is an important parameter for studying the behavior of molecule under the electric field. Li et al. compared a series of solvents with different μ and found that solvents with higher μ tend to preferentially adsorb on the surface of Li-metal anode, thereby affecting the electrochemical performance of the SEI.^[6] Liu et al. reported an asymmetric Li salt, lithium 1,1,1-trifluoro-N-[2-[2-(2-methoxyethoxy)ethoxy]ethyl] methanesulfonamide (LiFEA) that possesses a pseudo-crown ether-like anion, with a large molecular dipole, which allows for self-cleaning of unfavorable organic components in the SEI during cycling (Nat. Energy, 2023, 8, 934).^[7] However, excessively high molecular dipole could also dissolve out the desired inorganic components, thus reducing the stability of SEI. Later on, they carefully designed and synthesized another Li salt, lithium 2-[2-(2-methoxy ethoxy)ethoxy]ethanesulfonyl(trifluoromethanesulfonyl) imide (LiETFSI) with suitable molecular dipole, which rationalized this self-cleaning behavior and further improved its compatibility towards Li-metal anode.^[8] Therefore, the μ of solvent

must be regulated carefully to balance its ability to absorb and stabilize the interphase as well as its solubility to the SEI.

To further clarify the vital impact of μ on the interphase stability, we first combined quartz crystal microbalance analysis with electrochemical methods (EQCM) to measure the in-situ gravimetric variation of SEI during initial Li plating and subsequent resting processes (**Figure R11**).^[9-11] After 300 seconds of discharge, a high mass of 13170 ng cm^{-2} , corresponding to plated Li with SEI layer, was generated in the BM electrolyte (**Figure R11a**). During the subsequent resting process, the SEI formed by BM electrolyte slowly dissolved at a rate of $6.6 \text{ ng s}^{-1} \text{ cm}^{-2}$ due to the low dissolution ability of BM solvent (low μ). The initial plated Li with SEI layers formed by TFPM and TFBM electrolytes showed similar mass (**Figure R11b-c**). However, the SEI dissolved rapidly in the TFBM electrolyte at a high rate of $20.9 \text{ ng s}^{-1} \text{ cm}^{-2}$ due to the high μ of TFBM, whereas a moderate dissolution rate of $9.3 \text{ ng s}^{-1} \text{ cm}^{-2}$ was found for the TFPM electrolyte. This balanced dissolution process facilitated the formation of a robust inorganic-rich SEI.

Next, the sensitivity of different solvents to the electric field was evaluated through Tafel plots (**Figure R12-13**).^[12] Due to the higher μ , TFPM (i.e. 2.41 mA cm^{-2}) and TFBM (i.e. 1.26 mA cm^{-2}) electrolytes showed higher exchange current density (j_0) than PM (i.e. 0.98 mA cm^{-2}) and BM (i.e. 0.93 mA cm^{-2}) electrolytes at 30°C . However, TFBM electrolyte provided a lower j_0 than TFPM electrolyte, which may be attributed to the high viscosity of TFBM electrolyte. Among these four electrolytes, TFPM electrolyte exhibited the highest j_0 at both 30°C and -40°C , which enables fast charge transfer and rapid de-solvation, thereby achieving excellent rate and low-temperature performance.

Based on the above thorough discussions, we can draw the conclusion that the solvent with moderate μ could achieve a good balance between interphase stability and sensitivity to the electric fields. The relevant data and discussions were added to the Manuscript and Supplementary Information.

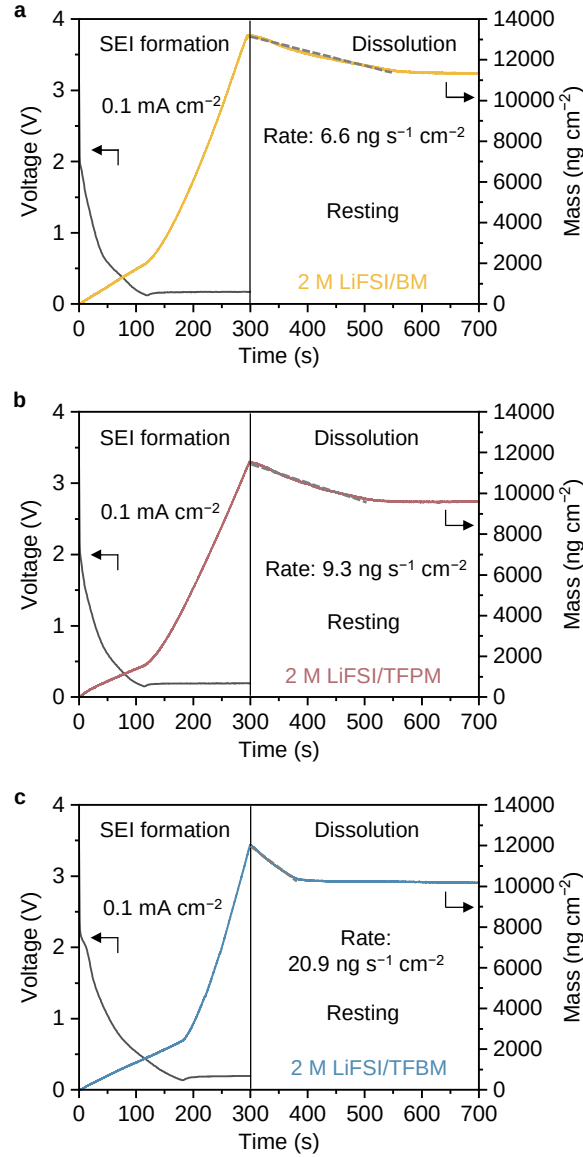


Figure R11. In-situ EQCM results of mass change in (a) 2 M LiFSI/BM (low μ), (b) 2 M LiFSI/TFPM (moderate μ), and (c) 2 M LiFSI/TFBM (high μ) electrolytes during initial Li plating at a current density of 0.1 mA cm⁻² and subsequent resting process.

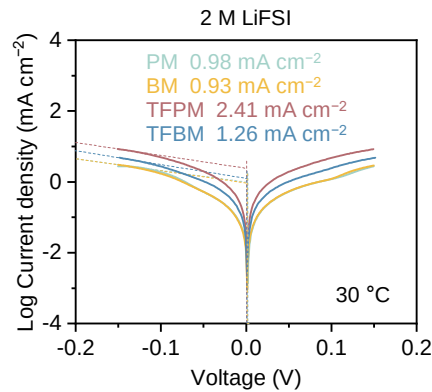


Figure R12. Tafel plots of Li plating/stripping in four electrolytes at 30 °C.

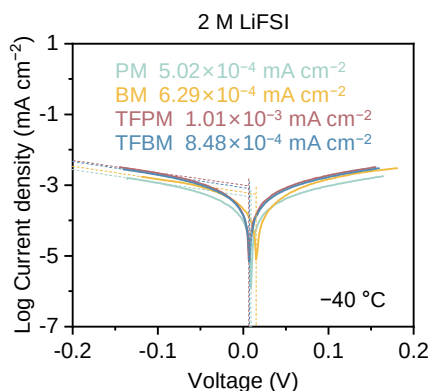


Figure R13. Tafel plots of Li plating/stripping in four electrolytes at -40 °C.

Authors' modification to the Manuscript and Supplementary Information:

(Page 7 in Manuscript):

To clarify the vital impact of μ on the interphase stability, the electrochemical quartz crystal microbalance (EQCM) was employed to monitor the gravimetric variation of SEI in-situ. As shown in the Supplementary Figure 19, after 300 seconds of discharge, a high mass of 13170 ng cm^{-2} , corresponding to the plated Li with SEI layer, is generated in the BM electrolyte. During the subsequent resting process, the SEI formed by BM electrolyte slowly dissolves at a rate of $6.6 \text{ ng s}^{-1} \text{ cm}^{-2}$ due to the low dissolution ability of BM solvent (low μ). The initial plated Li with SEI layers formed by TFPM and TFBM electrolytes show similar mass. However, the SEI dissolves rapidly in the TFBM electrolyte at a high rate of $20.9 \text{ ng s}^{-1} \text{ cm}^{-2}$ due to the high μ of TFBM, whereas a moderate dissolution rate of $9.3 \text{ ng s}^{-1} \text{ cm}^{-2}$ was found for the TFPM electrolyte, facilitating the formation of a robust inorganic-rich SEI. Moreover, the TFPM electrolyte also shows substantially higher exchange current density compared to the other three electrolytes at both 30 °C and -40 °C (Supplementary Figure 20-21), demonstrating its superior sensitivity to the electric field that promotes Li plating/stripping kinetics. This validates that the TFPM solvent with moderate μ could achieve a good balance between sensitivity to the electric fields within EDL and interphase stability.

(Page 19 in Supplementary Information):

In-situ EQCM results was added to the Supplementary Information as newly added

Supplementary Figure 19.

(Page 20 in Supplementary Information):

Tafel plots at 30 °C was added to the Supplementary Information as newly added Supplementary Figure 20.

(Page 21 in Supplementary Information):

Tafel plots at −40 °C was added to the Supplementary Information as newly added Supplementary Figure 21.

Comment #1: In the ^7Li NMR spectra, the observed downfield shift (de-shielding) of Li^+ in LiFSI/BM and LiFSI/PM suggests weaker solvation compared to LiFSI/TFPM and LiFSI/TFBM. However, molecular dynamics (MD) simulations indicate that TFPM and TFBM electrolytes exhibit highly similar solvation structures, as stated in the manuscript: $\text{Li}^+(\text{FSI}^-)_{3.03}(\text{TFPM})_{0.99}$, and $\text{Li}^+(\text{FSI}^-)_{2.93}(\text{TFBM})_{1.08}$. How can the significantly lower de-solvation energy observed for LiFSI/TFPM be rationalized relative to the other systems?

Authors' Response: Thanks for your insightful comment. We agree with the reviewer that the downfield shift of Li^+ in the ^7Li NMR suggests weaker solvation of LiFSI/BM and LiFSI/PM electrolytes compared to LiFSI/TFPM and LiFSI/TFBM electrolytes. However, in TFPM and TFBM electrolytes, the shielding effect of Li nuclei is significantly enhanced because of the coordination of F with Li^+ , resulting in high chemical shifts. To further clarify the coordination ability of different atoms, ^{17}O and ^{19}F NMR spectra were also collected in the original Manuscript (Figure 2f-g), which reveals weakest coordination ability of O and strongest coordination ability of F for the TFPM solvent. The Li-F and Li-O bidentate coordination in TFPM electrolyte leads to the lowest coordination number of solvent (i.e., 0.99) in the Li^+ primary solvation sheath, according to the MD simulations.

Indeed, as commented by the Reviewer, TFPM and TFBM electrolytes exhibit similar solvation structures, namely $\text{Li}^+(\text{FSI}^-)_{3.03}(\text{TFPM})_{0.99}$ and $\text{Li}^+(\text{FSI}^-)_{2.93}(\text{TFBM})_{1.08}$. The de-solvation energies of four electrolytes were then carefully calculated according to the solvation structures and their distributions extracted from MD simulation. As shown in the following **Figure R14**, the 2 M LiFSI/TFPM electrolyte exhibits the lowest Avg.

ΔE_{dsv} of 2.14 eV, outperforming that of 2 M LiFSI/PM (2.25 eV), 2 M LiFSI/TFBM (2.29 eV), and 2 M LiFSI/BM (2.62 eV), which is beneficial for facile de-solvation and homogeneous Li deposition. We are fully aware that de-solvation energy for TFPM electrolyte is only slightly lower than the other three (rather than being significantly lower than). We sincerely appreciate the reviewer for identifying the inaccuracies in our Manuscript. Based on your valuable comment, we have carefully revised the relevant description to improve the accuracy of our statements.

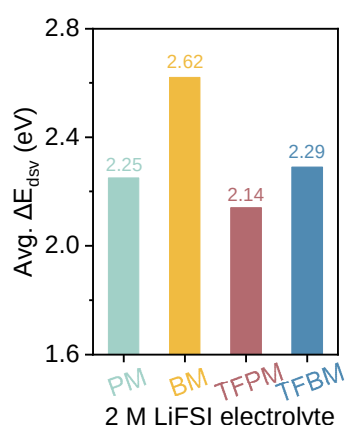


Figure R14. Average de-solvation energy (Avg. ΔE_{dsv}) of different electrolytes calculated according to the solvation structures and their distributions extracted from MD simulation.

Authors' modification to the Manuscript and Supplementary Information:

(Page 8 in Manuscript):

(1) due to the weakened coordination ability of O and F-mediated coordination effect, TFPM solvent induces a stable six-membered chelating solvation structure with highly rich in anion, resulting in very low de-solvation energy while maintaining sufficient salt dissociation;

Comment #2: In both ^{17}O and ^{19}F NMR spectra, the addition of Li salt results in an upfield shift for oxygen and a downfield shift for fluorine. This suggests that fluorine acts as an electron donor, whereas oxygen functions as an electron acceptor. The author should consider the distinct electronic roles of oxygen and fluorine in the FSI⁻ anion. Particularly since LiFSI accounts for approximately 75% of the coordination environment.

Authors' Response: Thanks for your insightful comment. The difference in chemical shifts for O and F observed in NMR spectra predominantly arises from different coordination effects. Generally, regardless of solvent or anion, the O atom possesses a much more negative electrostatic potential (ESP) than F atom. As a result, the Li–O_{sol.} coordination results in the O nucleus being shielded by the Li nucleus due to the strong electrostatic interactions, rendering the O atom electron-accepting. In contrast, Li–F_{sol.} coordination is significantly weaker than Li–O_{sol.} coordination, leading to electron localization at the F nucleus (de-shielding effect) and rendering F atoms electron-donating.

As mentioned by the Reviewer, all electrolytes possess anion-rich solvation structure according to the statistic results from MD simulations. However, FSI[−] anion always coordinates with Li⁺ through O atom rather than F atom, which has been widely observed in previous publications.^[4,12-14] To better address the Reviewer's concern, the most probable solvation structures (3 anions and 1 solvent) of four electrolytes were extracted from MD and further optimized via DFT. As shown in the following **Figure R15**, the FSI[−] anions only coordinate with Li⁺ through O atom in all four solvates.

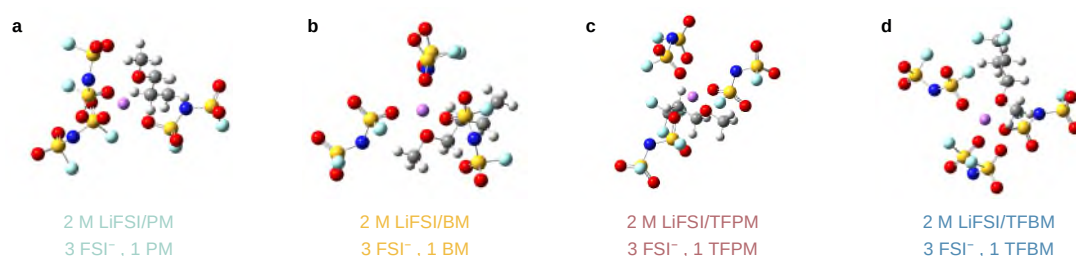


Figure R15. The most probable solvation structures of (a) 2 M LiFSI/PM, (b) 2 M LiFSI/BM, (c) 2 M LiFSI/TFPM, and (d) 2 M LiFSI/TFBM electrolytes extracted from MD simulations.

Comment #3: In Figure 3a-d, the TFBM has significantly more AGGs/CIPs compared to TFPM. Why does it not yield better Echem performance?

Authors' Response: We thank the reviewer for this insightful comment, which enables us to better clarify the differences between TFPM and TFBM. Actually, all solvents reported in this study are weakly solvating ethers, which bestows all four electrolytes

rich in CIPs and AGGs according to MD simulations and Raman spectra (Figure 3). This yields very decent Li||Cu CEs in all four electrolytes. However, according to the EQCM results shown in Figure R11, the TFBM solvent with high μ exhibits a high SEI dissolution rate of $20.9 \text{ ng s}^{-1} \text{ cm}^{-2}$, resulting in highly unstable SEI. Furthermore, as shown in Supplementary Figure 10-11, TFBM electrolyte exhibits the lowest conductivity and highest viscosity among these four electrolytes, hindering efficient ion transport under high-rate and low-temperature conditions, which leads to inferior battery performance, especially under ultra-low temperature (Figure 6f).

***Comment #4:** 99.3% overall Coulombic efficiency (CE) in a Li/Cu cell is not unprecedented for LiFSI-based systems. For example, values of 99.4% have been reported in 1 M LiFSI in BTFE/DME (Energy Environ. Sci., 2022, 15, 1647–1658), and up to 99.7% in 1.2 M LiFSI/F5DEE (Nat. Energy, 2022, 7, 94–106). At a minimum, the authors should provide a fair comparison with the current state-of-the-art.*

Authors' Response: Thanks for your comment. As commented by the Reviewer, there are indeed some previous studies reports higher Li||Cu CEs than ours. However, most of which are multi salt or multi solvent systems, and it would be overly complex to include them all for comparison. Moreover, multi salt and/or multi solvent systems can achieve synergistic effects to promote electrochemical performance by selecting salts/solvents with desired characteristics, whereas achieving high CE and long cycle life remains a great challenge in a “single-salt single-solvent” system. In addition, the Li||Cu CEs highly depend on the testing conditions, such as current density. Generally, testing at low current densities would lead to high CEs, therefore, it is not reasonable to compare the CEs under different current densities. Based on the above considerations, we have explicitly specified in the **title** of Supplementary Table 2 that we only compare **the state-of-the-art reported single-salt single-solvent electrolytes at a current density of 1.0 mA cm^{-2}** .

The first study mentioned by the Reviewer (*Energy Environment. Sci.*, 2022, 15, 1647–1658) reported a CE value of 99.4% with the modified Aurbach method at a current density of 0.5 mA cm^{-2} using dual solvent of BTFE/DME (our work: 99.5% at 1.0 mA cm^{-2} with a single-salt single-solvent formulation); The second paper (*Nat. Energy*, 2022, 7, 94–106) reported long cycling CE values of up to 99.7%, however, the testing

current density was also 0.5 mA cm^{-2} , thus these work were excluded from our comparisons. As discussed in our Manuscript (page 6): “TFPM electrolyte demonstrates ultra-stable cycling for over 850 cycles with a high average CE of 99.3%, representing the pioneering work for “single salt single solvent” electrolytes reported thus far at a relatively high current density of 1.0 mA cm^{-2} (Supplementary Table 2),” demonstrating the superiority of our TFPM electrolyte.

Comment #5: If dissolution is indeed an issue in the TFBM system, can the difference in SEI composition be identified via XPS? Based on the current data (Figure 5a and S14), the SEI appears similar in both the TFBM and TFPM systems. How, then, can the authors substantiate their claim that dissolution leads to the growth of redundant SEI?

Authors’ Response: Thanks for your insightful comment. At first glance, the SEI components appear to be similar in TFPM and TFBM electrolytes. Take a closer look, it is found that the LiF peak intensity, reflecting the absolute F content, is much higher for TFPM than TFBM electrolyte (Figure 5b). Besides, more LiN_xO_y and Li_2S_x , the thoroughly decomposition products of FSI^- anion, were detected for TFPM electrolyte. This indicates that the SEI formed in the TFBM electrolyte maybe dissolved out by the TFBM solvent with high μ value. To verify this hypothesis, the electrochemical quartz crystal microbalance (EQCM) was newly employed to monitor the gravimetric variation of SEI in-situ. As shown in the **Figure R11**, the SEI dissolves rapidly in the TFBM electrolyte at a high rate of $20.9 \text{ ng s}^{-1} \text{ cm}^{-2}$ due to the high μ of TFBM, whereas a moderate dissolution rate of $9.3 \text{ ng s}^{-1} \text{ cm}^{-2}$ was found for the TFPM electrolyte.

As originally summarized in our Manuscript (page 8): “the TFPM electrolyte is superior to the TFBM electrolyte in the following aspects: (1) due to the weakened coordination ability of O and F-mediated coordination effect, TFPM solvent induces a stable six-membered chelating solvation structure with highly rich in anion, resulting in low desolvation energy while maintaining sufficient salt dissociation; (2) the TFBM electrolyte exhibits lower ionic conductivity and higher viscosity compared to the TFPM electrolyte, hindering efficient ion transport, especially under high-rate and low-temperature conditions; (3) the TFBM solvent with high μ tends to absorb on the surface of Li-metal strongly, leading to the aggressive dissolution of interphase components, while the TFPM solvent with moderate μ could achieve a balance between sensitivity to the electric fields within EDL and interphase protection; (4) because of the strong

dissolution ability of TFBM solvent, FSI⁻ anions do not have enough time to decompose before being dissolved out, resulting in insufficient anion reduction; (5) since the “interphase dissolution–electrolyte decomposition” process is constantly going on in the TFBM electrolyte, the interphase is in a highly dynamic evolution, which yields highly unstable SEI with large resistance. While the TFPM with moderate μ enables sufficient reduction of FSI⁻ anions, leading to the formation of highly robust inorganic-rich SEI with low resistance. These merits significantly enhance the electrochemical kinetics and interfacial stability for Li-metal anodes, which is extremely beneficial for enabling high-energy and low-temperature LMBs.”

Authors’ modification to the Manuscript and Supplementary Information:

(Page 7 in Manuscript):

To clarify the vital impact of μ on the interphase stability, the electrochemical quartz crystal microbalance (EQCM) was employed to monitor the gravimetric variation of SEI in-situ. As shown in the Supplementary Figure 19, after 300 seconds of discharge, a high mass of 13170 ng cm⁻², corresponding to the plated Li with SEI layer, is generated in the BM electrolyte. During the subsequent resting process, the SEI formed by BM electrolyte slowly dissolves at a rate of 6.6 ng s⁻¹ cm⁻² due to the low dissolution ability of BM solvent (low μ). The initial plated Li with SEI layers formed by TFPM and TFBM electrolytes show similar mass. However, the SEI dissolves rapidly in the TFBM electrolyte at a high rate of 20.9 ng s⁻¹ cm⁻² due to the high μ of TFBM, whereas a moderate dissolution rate of 9.3 ng s⁻¹ cm⁻² was found for the TFPM electrolyte, facilitating the formation of a robust inorganic-rich SEI. Moreover, the TFPM electrolyte also shows substantially higher exchange current density compared to the other three electrolytes at both 30 °C and -40 °C (Supplementary Figure 20-21), demonstrating its superior sensitivity to the electric field that promotes Li plating/stripping kinetics. This validates that the TFPM solvent with moderate μ could achieve a good balance between sensitivity to the electric fields within EDL and interphase stability.

(Page 19 in Supplementary Information):

In-situ EQCM results was added to the Supplementary Information as newly added Supplementary Figure 19.

(Page 20 in Supplementary Information):

Tafel plots at 30 °C was added to the Supplementary Information as newly added **Supplementary Figure 20**.

(Page 21 in Supplementary Information):

Tafel plots at −40 °C was added to the Supplementary Information as newly added **Supplementary Figure 21**.

***Comment #6:** The high-voltage stability of fluorinated solvents is not surprising and has also been reported in mentioned Nature Energy paper. Fluorination lowers the HOMO energy level of the molecules, thereby enhancing their oxidative stability. However, how does solvent modification help prevent Al corrosion typically induced by LiFSI?*

Authors' Response: Thanks for your insightful comment. Indeed, the Al corrosion is a critical issue associated with imide salt (e.g., LiFSI)-based electrolyte. There are many previous studies have demonstrated that by modifying the solvent structure to weaken its solvation ability, the resulting weakly solvating solvent can barely solvate the Al^{3+} , thereby accumulating a passivation layer of $\text{Al}(\text{FSI})_x$ complexes on Al surface to suppress the Al corrosion kinetically.^[15,16] Furthermore, the weakly solvating electrolytes could also promote the decomposition of FSI^- anion, which facilitates the formation of a LiF-rich passivation layer.^[2,16] To confirm this point, XPS analysis was applied to study the components on Al surface after CA test. As shown in the following **Figure R16**, a high content of LiF was detected on the Al electrode in TFPM and TFBM electrolytes, which aids in the prevention of Al corrosion.

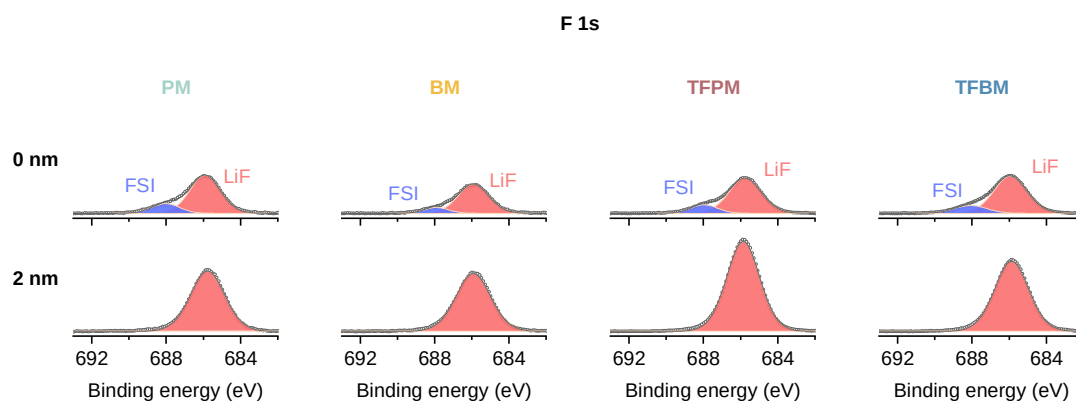


Figure R16. F 1s XPS spectra of Al electrode after CA test before and after Ar^+ sputtering.

Comment #7: What is the extent of gas evolution in TFBM and TFPM cells during cycling at 4.4 V?

Authors' Response: Thanks for your comment. Per your suggestion, differential electrochemical mass spectroscopy (DEMS) was carried out to evaluate the gas evolution during the initial charging-discharging of Li||NMC9055 cells (**Figure R17**). There is almost no gas generated for both TFPM and TFBM electrolytes during the charging process, demonstrating the excellent stability of TFPM and TFBM electrolytes even at high cut-off voltage of 4.4 V. When discharging to below 3.9 V, a small amount of CO₂, C₃H₆, and H₂ (ppm level) was detected. Specifically, more gases were released in the TFBM than that in the TFPM electrolyte, which can be attributed to the highly robust interphases derived from TFPM electrolyte, minimizing the parasitic reaction. Besides, no obvious cell swelling was observed for the pouch cell after cycling (**Figure 7**), indicating that the gas evolution is very mild in TFPM electrolyte.

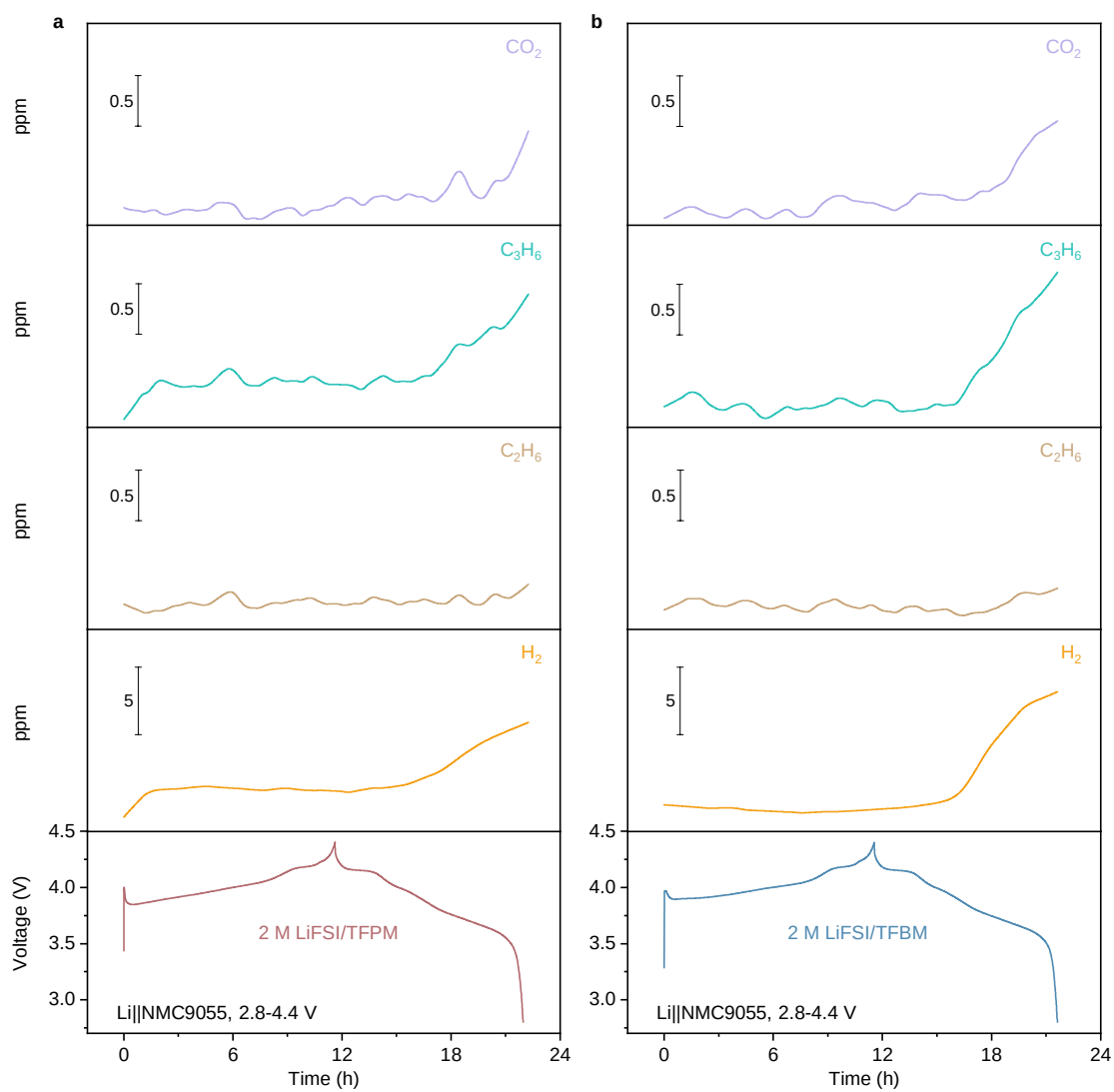


Figure R17. In-suit DEMS analysis of gas evolution for the Li||NMC9055 cells using (a) 2 M LiFSI/TFPM and (b) 2 M LiFSI/TFBM electrolytes during the first cycle.

The comments from Reviewer #3

Electrolyte solvent engineering could tune both the SEI structure and chemistry, which has been considered as a critical and pragmatic approach to enable high performance Li-metal batteries. Unfortunately, the lack of solvent screening principle has hindered their efficient development. In this work, the authors innovatively proposed a solvent screening principle based on unique $RESP_{O-\mu}$ dual-descriptors to enable high-energy LMBs at ultra-low temperatures. Furthermore, the authors design and synthesize a new class of weakly solvating fluorinated ethers to validate the effectiveness of this $RESP_{O-\mu}$ screening principle. The work provides valuable insights into electrolyte design to enhances electrochemical kinetics and reversibility simultaneously, achieving an unprecedented high energy density of 345.3 Wh kg^{-1} at -40°C . Therefore, from my perspective, this manuscript is very interesting and should be very helpful to the field that is rapidly evolving recently. I would enthusiastically recommend publication of this work after the following minor issues are properly addressed.

Authors' Response: We would like to thank the reviewer for his/her useful comments and suggestions to further improve our manuscript. We have revised our manuscript carefully based on the reviewer's comments.

Comment #1: *In the research of solvent descriptors, researchers have proposed numbers of parameters as criteria for solvent screening, among which electrostatic potential is also a very important screening parameter. What are the advantages of the $RESP_O$ parameter proposed by the authors compared to electrostatic potential?*

Authors' Response: Thanks for your insightful comment, which allows us to better clarify the advantages of the $RESP_O$ parameter. The electrostatic potential (ESP) reflects the charge distribution on the surface of solvent molecules rather than the intrinsic electronegativity of solvent atoms. When a strongly electronegative F atom is close to O atom, the ESP of O atom will be significantly reduced, resulting in an ESP value that does not match the solvent's solubility and solvation ability, which reduces the accuracy of ESP as a screening parameter. The restrained electrostatic potential (RESP) is a method for calculating atomic charges and also a modified ESP method that incorporates physical constraints (e.g., atomic electronegativity equilibration and bond symmetry constraints) to optimize charge distributions, ensuring further

improvement of the rationality of the charge distribution model. RESP₀ method can eliminate the interference of F atoms and accurately describe the charge distribution of O atoms, leading to more efficient and accurate to distinguish the fluorinated ethers with different coordination ability of O atoms. The relevant discussion has been added to the Manuscript.

Authors' modification to the Manuscript:

(Page 4 in Manuscript):

RESP is a modified ESP method that incorporates physical constraints (e.g., atomic electronegativity equilibration and bond symmetry constraints) to optimize charge distributions, ensuring further improvement of the rationality of the charge model, which leads to more efficient and accurate to distinguish the ethers with different solvation ability.

Comment #2: The designed TFPM electrolyte presented good capacity retention and cycling stability at both room temperature and low temperature. Has the author explored the rate performance at low temperatures with TFPM electrolyte?

Authors' Response: Per your suggestion, the rate performance of Li||NMC811 cells with different electrolytes at $-40\text{ }^{\circ}\text{C}$ was also tested. As shown in the following **Figure R18**, the Li||NMC811 cell with 2 M LiFSI/TFPM electrolyte exhibits very decent rate performance from 0.1 C to 0.5 C even at $-40\text{ }^{\circ}\text{C}$, which still delivers a high capacity of 109.5 mAh g^{-1} at 0.5 C.

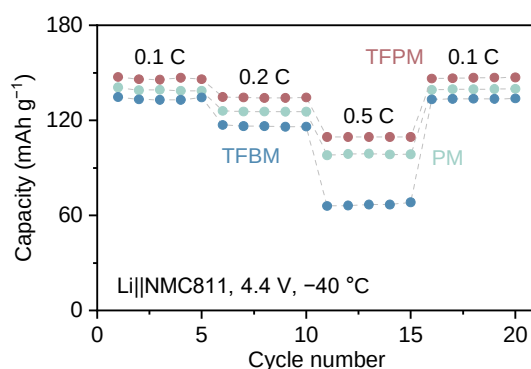


Figure R18. Rate performance of the Li||NMC811 cells at $-40\text{ }^{\circ}\text{C}$.

Authors' modification to the Manuscript and Supplementary Information:

(Page 9 in Manuscript):

Besides, the cell using TFPM electrolyte also demonstrates good rate performance even at $-40\text{ }^{\circ}\text{C}$ (Supplementary Figure 32).

(Page 32 in Supplementary Information):

Rate performance of the Li||NMC811 cells at $-40\text{ }^{\circ}\text{C}$ was added to the Supplementary Information as newly added Supplementary Figure 32.

Comment #3: Among the series of fluorinated ether molecules designed, the formation of a hexagonal coordination structure can significantly improve the performance of batteries, especially at ultra-low temperature. What influence does this configuration have on the lithium deposition and kinetics at low temperatures?

Authors' Response: We thank the reviewer for this insightful comment, which allows us to better elucidate the correlation between the six-membered chelating solvation structure and its excellent Li compatibility at ultra-low temperatures. First, as shown in Figure 2a-d, the six-membered ring formed by Li-TFPM complexes exhibit the most negative binding energy, indicating a more stable structure. The synergistic O and F chelation is anticipated to enhance the Li salt dissociation while mitigating the ionic conductivity reduction typically associated with fluorination, thereby preventing salt precipitation and enabling fast ion transport at ultra-low temperatures. Second, at low temperatures, the de-solvation step becomes the rate-determining step. The stable six-membered chelating structure with pronounced spatial effects will inhibit further coordination of free solvents and promote anion coordination, leading to anion-rich coordination structure of $\text{Li}^+(\text{FSI}^-)_{3.03}(\text{TFPM})_{0.99}$ with an extremely high $\text{FSI}^-/\text{solvent}$ ratio of 3.06. This consequently bestows the lowest de-solvation energy of 2.14 eV for TFPM electrolyte, enabling uniform Li deposition with fast kinetics at low temperatures.

Comment #4: The solvation of TFPM and TFBM is very similar, and the composition of SEI is almost the same at room temperature. However, there is a significant difference in impedance between these two at low temperatures (-40 and $-60\text{ }^{\circ}\text{C}$), and there is also a significant difference in battery performance. What is the main affecting factor?

Authors' Response: Thanks for your insightful comment. Indeed, as commented by the Reviewer, the solvation structure of TFPM and TFBM electrolyte is very similar.

At first glance, the SEI components appear to be similar in TFPM and TFBM electrolytes. Take a closer look, it is found that the LiF peak intensity, reflecting the absolute F content, is much higher for TFPM than TFBM electrolyte (Figure 5b). Besides, more LiN_xO_y and Li_2S_x , the thoroughly decomposition products of FSI^- anion, were detected for TFPM electrolyte. This indicates that the SEI formed in the TFBM electrolyte maybe dissolved out by the TFBM solvent with high μ value. To verify this hypothesis, the electrochemical quartz crystal microbalance (EQCM) was newly employed to monitor the gravimetric variation of SEI in-situ. As shown in the **Figure R19**, the SEI dissolves rapidly in the TFBM electrolyte at a high rate of $20.9 \text{ ng s}^{-1} \text{ cm}^{-2}$ due to the high μ of TFBM, whereas a moderate dissolution rate of $9.3 \text{ ng s}^{-1} \text{ cm}^{-2}$ was found for the TFPM electrolyte. Moreover, the TFPM electrolyte also shows substantially higher exchange current density compared to the TFBM electrolyte at both 30°C and -40°C (**Figure R20-21**), demonstrating its superior sensitivity to the electric field that promotes Li plating/stripping kinetics.

Therefore, as summarized in our Manuscript (page 8): “the TFPM electrolyte is superior to the TFBM electrolyte in the following aspects: (1) due to the weakened coordination ability of O and F-mediated coordination effect, TFPM solvent induces a stable six-membered chelating solvation structure with highly rich in anion, resulting in low desolvation energy while maintaining sufficient salt dissociation; (2) the TFBM electrolyte exhibits lower ionic conductivity and higher viscosity compared to the TFPM electrolyte, hindering efficient ion transport, especially under high-rate and low-temperature conditions; (3) the TFBM solvent with high μ tends to absorb on the surface of Li-metal strongly, leading to the aggressive dissolution of interphase components, while the TFPM solvent with moderate μ could achieve a balance between sensitivity to the electric fields within EDL and interphase protection; (4) because of the strong dissolution ability of TFBM solvent, FSI^- anions do not have enough time to decompose before being dissolved out, resulting in insufficient anion reduction; (5) since the “interphase dissolution–electrolyte decomposition” process is constantly going on in the TFBM electrolyte, the interphase is in a highly dynamic evolution, which yields highly unstable SEI with large resistance. While the TFPM with moderate μ enables sufficient reduction of FSI^- anions, leading to the formation of highly robust inorganic-rich SEI with low resistance. These merits significantly enhance the electrochemical kinetics and interfacial stability for Li-metal anodes, which is

extremely beneficial for enabling high-energy and low-temperature LMBs.”

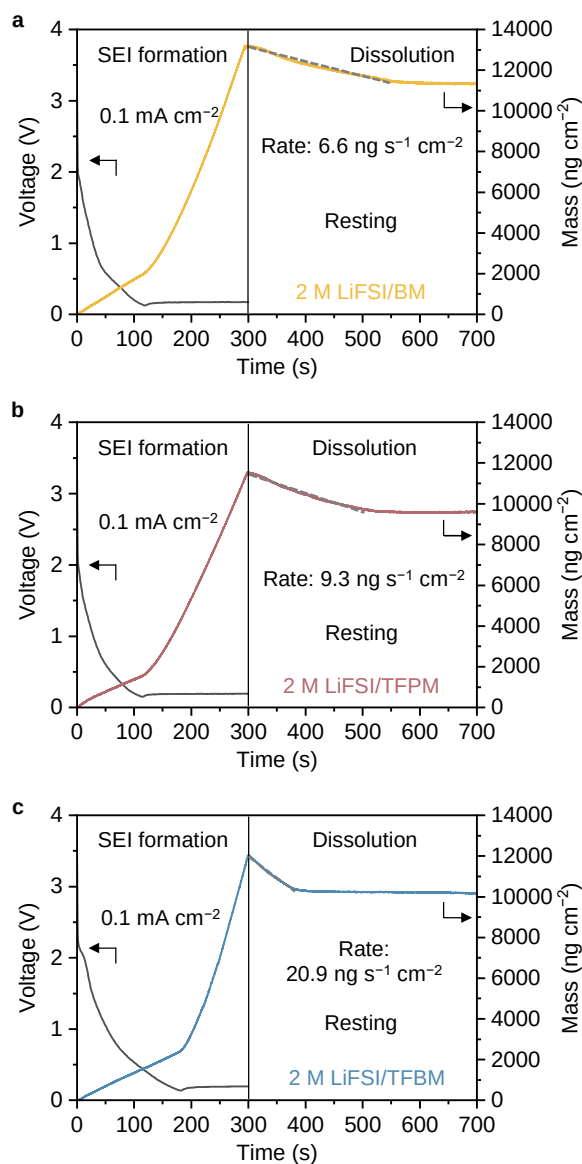


Figure R19. In-situ EQCM results of mass change in (a) 2 M LiFSI/BM (low μ), (b) 2 M LiFSI/TFPM (moderate μ), and (c) 2 M LiFSI/TFBM (high μ) electrolytes during initial Li plating at a current density of 0.1 mA cm⁻² and subsequent resting process.

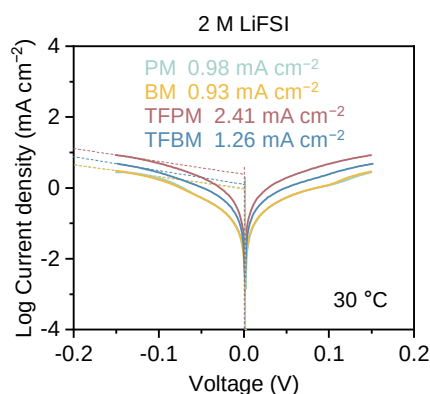


Figure R20. Tafel plots of Li plating/stripping in four electrolytes at 30 °C.

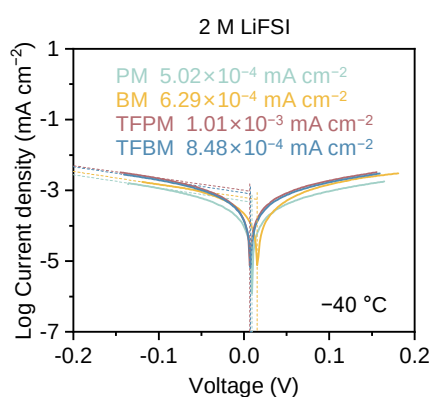


Figure R21. Tafel plots of Li plating/stripping in four electrolytes at -40 °C.

Authors' modification to the Manuscript and Supplementary Information:

(Page 7 in Manuscript):

To clarify the vital impact of μ on the interphase stability, the electrochemical quartz crystal microbalance (EQCM) was employed to monitor the gravimetric variation of SEI in-situ. As shown in the Supplementary Figure 19, after 300 seconds of discharge, a high mass of 13170 ng cm^{-2} , corresponding to the plated Li with SEI layer, is generated in the BM electrolyte. During the subsequent resting process, the SEI formed by BM electrolyte slowly dissolves at a rate of $6.6 \text{ ng s}^{-1} \text{ cm}^{-2}$ due to the low dissolution ability of BM solvent (low μ). The initial plated Li with SEI layers formed by TFPM and TFBM electrolytes show similar mass. However, the SEI dissolves rapidly in the TFBM electrolyte at a high rate of $20.9 \text{ ng s}^{-1} \text{ cm}^{-2}$ due to the high μ of TFBM, whereas a moderate dissolution rate of $9.3 \text{ ng s}^{-1} \text{ cm}^{-2}$ was found for the TFPM electrolyte, facilitating the formation of a robust inorganic-rich SEI. Moreover, the TFPM electrolyte also shows substantially higher exchange current density compared to the

other three electrolytes at both 30 °C and −40 °C (Supplementary Figure 20-21), demonstrating its superior sensitivity to the electric field that promotes Li plating/stripping kinetics. This validates that the TFPM solvent with moderate μ could achieve a good balance between sensitivity to the electric fields within EDL and interphase stability.

(Page 19 in Supplementary Information):

In-situ EQCM results was added to the Supplementary Information as newly added Supplementary Figure 19.

(Page 20 in Supplementary Information):

Tafel plots at 30 °C was added to the Supplementary Information as newly added Supplementary Figure 20.

(Page 21 in Supplementary Information):

Tafel plots at −40 °C was added to the Supplementary Information as newly added Supplementary Figure 21.

The comments from Reviewer #4

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

Authors' Response: We sincerely appreciate the reviewer for his/her useful comments and suggestions to further improve our manuscript.

References

- 1 Yu, Z. *et al.* Molecular design for electrolyte solvents enabling energy-dense and long-cycling lithium metal batteries. *Nature Energy* **5**, 526, doi:10.1038/s41560-020-0634-5 (2020).
- 2 Zhang, G. *et al.* Amonofluoride ether-based electrolyte solution for fast-charging and lowtemperature non-aqueous lithium metal batteries. *Nature Communications* **14**, 1081, doi:10.1038/s41467-023-36793-6 (2023).
- 3 Piao, N. *et al.* Designing temperature-insensitive solvated electrolytes for low-temperature lithium metal batteries. *Journal of the American Chemical Society* **146**, 18281, doi:10.1021/jacs.4c01735 (2024).
- 4 Wu, L. Q. *et al.* Unveiling the role of fluorination in hexacyclic coordinated ether electrolytes for high-voltage lithium metal batteries. *Journal of the American Chemical Society* **146**, 5964, doi:10.1021/jacs.3c11798 (2024).
- 5 Li, A. M. *et al.* Methylation enables the use of fluorine-free ether electrolytes in high-voltage lithium metal batteries. *Nature Chemistry* **16**, 922, doi:10.1038/s41557-024-01497-x (2024).
- 6 Li, P. C. *et al.* Dipole moment influences the reversibility and corrosion of lithium metal anodes. *Advanced Materials* **36**, e2406359, doi:10.1002/adma.202406359 (2024).
- 7 Xia, Y. *et al.* Designing an asymmetric ether-like lithium salt to enable fast-cycling high-energy lithium metal batteries. *Nature Energy* **8**, 934, doi:10.1038/s41560-023-01282-z (2023).
- 8 Zhou, P. *et al.* Rational lithium salt molecule tuning for fast charging/discharging lithium metal battery. *Angewandte Chemie International Edition* **63**, e202316717, doi:10.1002/anie.202316717 (2024).
- 9 Ji, Y. *et al.* In situ probing the origin of interfacial instability of Na metal anode. *Chem* **9**, 2943, doi:10.1016/j.chempr.2023.06.002 (2023).
- 10 Tułodziecki, M., Tarascon, J. M., Taberna, P. L. & Guéry, C. Catalytic reduction of TFSI-containing ionic liquid in the presence of lithium cations. *Electrochemistry Communications* **77**, 128, doi:10.1016/j.elecom.2017.02.014 (2017).
- 11 Liu, T. *et al.* In situ quantification of interphasial chemistry in Li-ion battery. *Nat Nanotechnol* **14**, 50, doi:10.1038/s41565-018-0284-y (2019).
- 12 Choi, I. R. *et al.* Asymmetric ether solvents for high-rate lithium metal batteries. *Nature Energy* **10**, 365, doi:10.1038/s41560-025-01716-w (2025).
- 13 Yu, Z. *et al.* Rational solvent molecule tuning for high-performance lithium metal battery electrolytes. *Nature Energy* **7**, 94, doi:10.1038/s41560-021-00962-y (2022).
- 14 Zhang, E. *et al.* Monofluorinated acetal electrolyte for high-performance lithium metal batteries. *Proceedings of the National Academy of Sciences of the United States of America* **122**, e2418623122, doi:10.1073/pnas.2418623122 (2025).
- 15 Chen, Y. *et al.* Steric effect tuned ion solvation enabling stable cycling of high-voltage lithium metal battery. *Journal of the American Chemical Society* **143**, 18703, doi:10.1021/jacs.1c09006 (2021).
- 16 Ding, K. *et al.* Tuning the solvent alkyl chain to tailor electrolyte solvation for stable Li-metal batteries. *ACS Applied Materials & Interfaces* **14**, 44470, doi:10.1021/acsami.2c13517 (2022).