

Solvent polarizability governs Li⁺ transport kinetics for high energy lithium metal batteries

Corresponding Author: Professor Xiulin Fan

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

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The submitted work, 'Polarizability-Governed Li⁺ Kinetics for High-Energy Li-Metal Batteries', proposes a novel viewpoint: the desolvation capability of Li⁺ is correlated with the polarizability of the electrolyte components. The topic is timely and potentially impactful for the rational design of electrolytes in high-energy Li-metal systems. I would be supportive of publication once the authors have clarified a few minor issues.

Comment 1: For accurate molecular polarizability calculations, a balanced basis set with both polarization and diffuse functions is essential. Although M05-2X/6-311+G(d,p) has been widely used, the Pople-type basis set may not provide the most systematic description of electron response properties. Since polarizability is the key descriptor underpinning the proposed relationship, it would be helpful if the authors could use another proper basis set or provide evidence to confirm that the reported trends are not sensitive to the basis set.

Comment 2: The RDF mentioned in the Methods section is not mentioned in the manuscript or supplementary information. If RDF analysis was performed, the corresponding results should be shown and discussed to clarify how they support the structural interpretation of Li⁺ solvation. Otherwise, the description in the Methods section should be revised for consistency.

Comment 3: The selection of the cutoff radius for the defined cluster in Figure 3 needs to be based on certain criteria. Since cluster statistics can be sensitive to this parameter, the authors should clarify whether the cutoff was determined from the first peak of the RDF or another structural feature, and briefly comment on the reason for the chosen value.

Comment 4: The process of calculating MSD in Figure 3l needs to be presented in detail in Methods section or Supplementary Information. In particular, the authors should explicitly state the formula used for MSD calculation. Providing the exact mathematical expression and fitting procedure would improve methodological transparency and reproducibility.

Comment 5: The specific distribution of the clusters shown in Figure 3k needs to be listed in a table in Supplementary Information. Providing the exact number of each cluster type would improve clarity and allow readers to better evaluate the statistical significance of the observed trends.

Comment 6: It is unclear whether charge scaling was applied to the Li⁺/FSI⁻ ions in the MD simulations. In many previous studies, the ionic charges are scaled to better describe ion-ion and ion-dipole interactions. The authors should clarify whether such treatment was adopted in this work, and if so, specify the scaling factor.

Comment 7: The statement that energy minimization at 0K was performed to obtain the 'ground-state structure' may not be strictly appropriate in the context of MD simulations. Energy minimization typically serves to remove unfavorable atomic contacts and relax the initial configuration, rather than to identify a true thermodynamic ground state. The authors may consider revising this description for clarity.

Comment 8: There are some grammatical and spelling errors. For example, in page 5, line 97 "under an interfacial electric", which misses the word "field". The authors should check the manuscript carefully and make revisions.

Reviewer #2

(Remarks to the Author)

The manuscript titled "Polarizability-govern Li⁺ kinetics for high-energy Li-metal batteries" deciphered a quantitative structure kinetics relationship by demonstrating that polarizability dictates Li⁺ desolvation and transport, which is interesting and meaningful for the deployment of high-energy Li-metal batteries. I recommend publication after minor revisions and the questions are listed below:

1. In this work, the authors propose a quantitative relationship between molecular polarizability and electrolyte dynamics. The underlying molecular-level mechanism of this strong linear correlation requires further explanation, such as which factors influence polarizability, whether there is a qualitative relationship with molecular functional groups, and whether it is related to molecular volume.
2. The authors discovered a relationship between polarizability and the Li ion desolvation energy. Do other common physical parameters, such as dielectric constant and DN value, also have a quantitative relationship with the desolvation energy? Please explain it.
3. Figure 1c illustrates the evolution of Li⁺ solvate distributions with inert solvents of different polarizabilities under an applied electric field. However, the corresponding description in the text lacks clarity and requires a more detailed exposition.
4. Please elaborate on how Figure 2d demonstrates that polarizabilities obtained from experiments and theoretical calculations show close agreement.
5. The *in situ* Raman spectra demonstrate the structural integrity of Li⁺ clusters under an electric field through the Li-FSI (~750 cm⁻¹) complex. However, the role of the Li-DME (~880 cm⁻¹) complex in supporting this conclusion remains unclear. Please provide a detailed explanation.
6. To completely assess the compatibility of the electrolyte with Li metal, it is essential to perform the cycling performance in Li||Cu half cells at a low temperature. Besides, to confirm the superior Li⁺ kinetics in the electrolyte, the cycling of Li||NCM811 cells at a higher rate at -35 °C should be performed.

Reviewer #3

(Remarks to the Author)

The manuscript presents a systematic and well executed study on polarizability-governed Li⁺ kinetics for high-energy Li metal batteries. The comprehensive multi-scale analysis, combined with the practical demonstration of a 7.5 Ah pouch cell and exceptional low temperature stability, provides valuable insights for rational electrolyte design. To further enhance the manuscript prior to publication, I recommend addressing the following points.

1. In several key electrochemical performance figures (e.g., Figure 5a, 5f, and Supplementary Figures 27-29), the authors present the cycling performance using only absolute capacity or areal capacity. While areal capacity is an important metric, the absence of specific capacity makes it difficult to assess the actual utilization rate of the high loading NCM811 cathode. The authors are advised to provide the specific capacity alongside the absolute/areal capacity by using a secondary Y-axis, or at least clearly specify the active material mass loading in the corresponding figure captions. In addition, please clearly specify the exact evaluation conditions for the various electrochemical performances including anode-free cell and low temperature testing.
2. The authors highlight the 160 mAh/g capacity at 4C, demonstrating that the low-polarizability inert solvent (TFME) remarkably improves the rate capability by reducing the interfacial desolvation energy. However, the heavy use of inert diluents in LHCE inherently diminishes bulk ionic conductivity. It is recommended to discuss how the sluggish bulk ionic transport affects the rate capability from the perspective of mass transfer within the pores of the thick and densely-packed cathode architecture.
3. The authors attribute the excellent stability at -35°C to the preserved anion-rich solvation structure and fast Li⁺ kinetics. However, it remains unclear whether this mechanism holds at elevated temperatures (e.g., 45°C or 60°C), where intense thermal agitation and macroscopic solvent density changes could disrupt the interfacial solvates. It is recommended to provide cycling stability of Li||NCM811 and Cu||NCM523 cell at the high-temperature and discuss the structural stability of the solvates in the environment. Furthermore, a brief discussion on other potential factors contributing to the low-temperature performance, such as the enhanced mechanical robustness or reduced solubility of the inorganic-rich SEI at low temperature, would strengthen the manuscript.
4. For the 7.5 Ah Li metal pouch cell evaluation, the externally applied pressure condition is missing. Because Li-metal cell performance is highly sensitive to applied pressure, the authors must state the exact pressure used during the evaluation to ensure reproducibility and validate the practical relevance of the 541.6 Wh/kg energy density.
5. Please correct the following typos prior to publication: In the Chemical reagents section, change "lihtium" to "lithium"; in the Figure 4 caption, change "volatge" to "voltage"; in the first paragraph of the Results section, change "interfacial electric" to "interfacial electric field". In the text referring to the pouch cells, change "Fig. 6a" to "Fig. 5a".

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

All concerns have been well addressed, this manuscript can be accepted now.

Reviewer #2

(Remarks to the Author)

I am fully satisfied with the revisions. All concerns raised in the initial review have been thoroughly and convincingly addressed. The results are noteworthy, the methods are sound, and the work meets the expectations for the journal. I have no further comments or requests for revision. I am pleased to recommend acceptance as is.

Reviewer #3

(Remarks to the Author)

The authors have satisfactorily addressed all of my concerns and comments in the revised version of the manuscript. I am pleased to recommend this work for publication in Nature Communications.

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Detailed responses to the reviewers' comments

Manuscript Number: NCOMMS-26-012089

Title: Polarizability-govern Li^+ kinetics for high-energy Li-metal batteries

Authors: Chuangchao Sun, Linxiang Chen, Junyi Hua, Shengpeng Zhang, Yong Li, Liyi Zhao, Hao Cheng, Daixin Ye, Haikuo Zhang, Lianbang Wang, Xiulin Fan

Comments from the reviewers:

Reviewer #1: The submitted work, 'Polarizability-Governed Li^+ Kinetics for High-Energy Li-Metal Batteries', proposes a novel viewpoint: the desolvation capability of Li^+ is correlated with the polarizability of the electrolyte components. The topic is timely and potentially impactful for the rational design of electrolytes in high-energy Li-metal systems. I would be supportive of publication once the authors have clarified a few minor issues.

Reply: We sincerely thank Reviewer #1 for the thorough and insightful evaluation of our manuscript. The constructive comments and suggestions have greatly helped to improve the quality of this work. We responded to each point in detail below and revised the manuscript accordingly. We hope our response and modifications have clarified all the concerns and thereby meet the reviewer's expectations.

Comment 1: For accurate molecular polarizability calculations, a balanced basis set with both polarization and diffuse functions is essential. Although M05-2X/6-311+G(d,p) has been widely used, the Pople-type basis set may not provide the most systematic description of electron response properties. Since polarizability is the key

descriptor underpinning the proposed relationship, it would be helpful if the authors could use another proper basis set or provide evidence to confirm that the reported trends are not sensitive to the basis set.

Reply: Thanks for the reviewer's constructive comments. We have optimized the method and the calculations were performed using the M05-2X functional in conjunction with the Def2-TZVP basis set and GD3 dispersion correction, which is more proper for calculations related to molecular polarizability. The theoretical polarizability values in Supplementary Table 1 have been updated. Consequently, Fig. 2e and Fig. 2f, which involve the updated data, have been replotted. The corresponding sections in the manuscript have also been revised accordingly.

In the revised manuscript, we made revisions and added the following sentences (Page 25, Line 458):

Then the polarizability (α) was analyzed with M05-2X functional in conjunction with the Def2-TZVP basis set and GD3 dispersion model.

Comment 2: The RDF mentioned in the Methods section is not mentioned in the manuscript or supplementary information. If RDF analysis was performed, the corresponding results should be shown and discussed to clarify how they support the structural interpretation of Li⁺ solvation. Otherwise, the description in the Methods section should be revised for consistency.

Reply: We sincerely appreciate the reviewer's careful comments. We apologize for the oversight that the radial distribution function (RDF) analysis, although mentioned in the Methods section, was not included in the main text of Supplementary Materials in the original submission. In the Supplementary Materials, we have now included the RDF results. The Methods section has also been carefully checked and revised to ensure full consistency with the presented results.

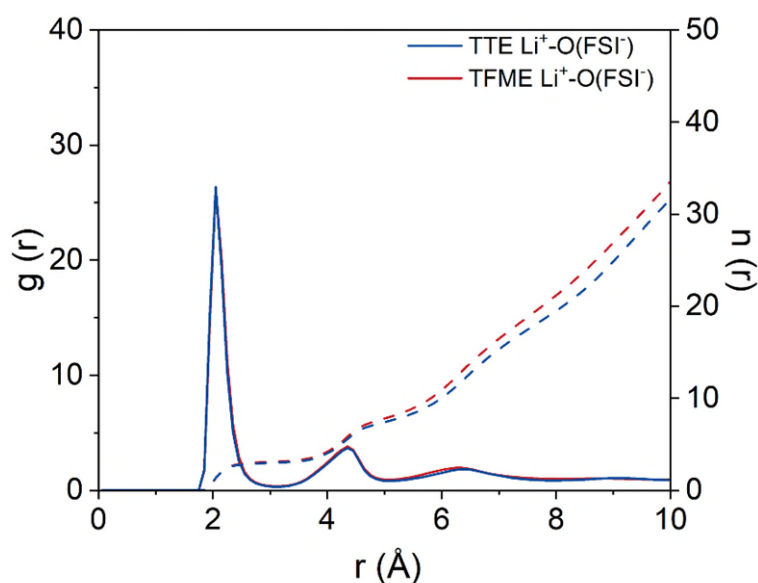


Fig. R1 | Radical distribution functions (RDF) calculated from MD simulations of the TTE and TFME electrolytes.

In the revised Supplementary Materials, we added Fig. R1 as Supplementary Fig. 13 and renumbered the subsequent Figures.

Comment 3: The selection of the cutoff radius for the defined cluster in Figure 3 needs to be based on certain criteria. Since cluster statistics can be sensitive to this parameter, the authors should clarify whether the cutoff was determined from the first peak of the RDF or another structural feature, and briefly comment on the reason for the chosen value.

Reply: Thanks for the reviewer’s insightful comments. The cutoff radius used for cluster definition in Figure 3 was determined based on the RDF analysis. Specifically, the first peak of the $\text{Li}^+\text{-FSI}^-$ is located at approximately 2.1 Å, which represents the most favorable coordination distance within the first solvation shell. Therefore, we selected 2.1 Å as the cutoff radius to carry out cluster statistics.

In the revised manuscript, we added the following sentences (Page 11, Line 205):

Based on the RDF results (Supplementary Fig. 13), we performed cluster statistics using a cutoff radius of 2.1 Å.

Comment 4: The process of calculating MSD in Figure 3l needs to be presented in detail in Methods section or Supplementary Information. In particular, the authors should explicitly state the formula used for MSD calculation. Providing the exact mathematical expression and fitting procedure would improve methodological transparency and reproducibility.

Reply: Thanks for the reviewer's constructive comments. MSD was analyzed using VMD by tracking the trajectories of Li⁺ ions during the MD simulations. Afterwards, the diffusion coefficient was calculated based on the equation, $D = \lim_{t \rightarrow +\infty} [\frac{1}{6t} \langle [\mathbf{r}(t)]^2 \rangle]$, where t represents simulation time, $\langle [\mathbf{r}(t)]^2 \rangle$ stands for MSD. By fitting the linear region of the MSD vs. time curves, D of Li⁺ can be accurately extracted, providing insight into their transport kinetics in different electrolyte systems.

In the revised manuscript, we added the following sentences (Page 25, Line 452):

D can be calculated based on the equation, $D = \lim_{t \rightarrow +\infty} [\frac{1}{6t} \langle [\mathbf{r}(t)]^2 \rangle]$, where t represents simulation time, $\langle [\mathbf{r}(t)]^2 \rangle$ stands for MSD.

Comment 5: The specific distribution of the clusters shown in Figure 3k needs to be listed in a table in Supplementary Information. Providing the exact number of each

cluster type would improve clarity and allow readers to better evaluate the statistical significance of the observed trends.

Reply: Thanks for the reviewer's constructive suggestion. The specific distribution of the clusters shown in Figure 3k has been listed in Supplementary Table 2 in the revised Supplementary Materials.

Comment 6: It is unclear whether charge scaling was applied to the Li^+/FSI^- ions in the MD simulations. In many previous studies, the ionic charges are scaled to better describe ion-ion and ion-dipole interactions. The authors should clarify whether such treatment was adopted in this work, and if so, specify the scaling factor.

Reply: Thanks for the reviewer's helpful suggestion. In this work, the charges of Li^+ and FSI^- were scaled by 0.8 to better describe ion-ion and ion-dipole interactions, in accordance with previous literature reports. The Methods section has also been expanded with additional details and supported by relevant references.

In the revised manuscript, we added the following sentences (Page 25, Line 443):

The charges of Li^+ and FSI^- were scaled by 0.8 to better describe ion-ion and ion-dipole interactions, in accordance with previous literature reports^{1,2}.

Comment 7: The statement that energy minimization at 0K was performed to obtain the 'ground-state structure' may not be strictly appropriate in the context of MD simulations. Energy minimization typically serves to remove unfavorable atomic contacts and relax the initial configuration, rather than to identify a true thermodynamic ground state. The authors may consider revising this description for clarity.

Reply: Thanks for the reviewer's insightful comments. It is true that the description of the energy minimization step as 'ground-state structure' is not strictly appropriate in the context of MD simulations. We have revised the corresponding description in the revised manuscript to improve clarity and ensure more accurate terminology.

In the revised manuscript, we made revisions and added the following sentences (Page 25, Line 443):

An initial energy minimization at 0 K was performed to remove unfavorable atomic contacts and relax the initial configuration in each system, followed by the equilibrium under the constant pressure (10^5 Pa) at 350 K and 300 K in the NPT ensemble for 1 ns and 3 ns, respectively.

Comment 8: There are some grammatical and spelling errors. For example, in page 5, line 97 "under an interfacial electric", which misses the word "field". The authors should check the manuscript carefully and make revisions.

Reply: We appreciate the reviewer's careful reading and helpful suggestion. We have carefully checked the manuscript for any grammatical and spelling errors and made the necessary corrections.

Reviewer #2: The manuscript titled "Polarizability-govern Li^+ kinetics for high-energy Li-metal batteries" deciphered a quantitative structure kinetics relationship by demonstrating that polarizability dictates Li^+ desolvation and transport, which is interesting and meaningful for the deployment of high-energy Li-metal batteries. I recommend publication after minor revisions and the questions are listed below.

Reply: We sincerely thank Reviewer #2 for the thorough and insightful evaluation of our manuscript. The constructive comments and suggestions have greatly helped to improve the quality of this work. We responded to each point in detail below and revised the manuscript accordingly. We hope our response and modifications have clarified all the concerns and thereby meet the reviewer's expectations.

Comment 1: In this work, the authors propose a quantitative relationship between molecular polarizability and electrolyte dynamics. The underlying molecular-level mechanism of this strong linear correlation requires further explanation, such as which factors influence polarizability, whether there is a qualitative relationship with molecular functional groups, and whether it is related to molecular volume.

Reply: Thanks for the reviewer's constructive suggestion. To verify whether other potential factors may influence polarizability, the impacts of molecular functional groups and molecular volume were analyzed (Fig. R2). With similar molecular volume, perfluorination, monofluorination and chlorination all lead to an increase in polarizability, whereas the introduction of ether linkages into the molecular chain results in a decrease (Fig. R2a). For compounds within the same class, polarizability increases with molecular volume (Fig. R2b). These observations provide only a qualitative understanding of the effects of these two factors on polarizability and the precise quantitative relationships require derivation from Clausius–Mossotti relation (Supplementary Note 2).

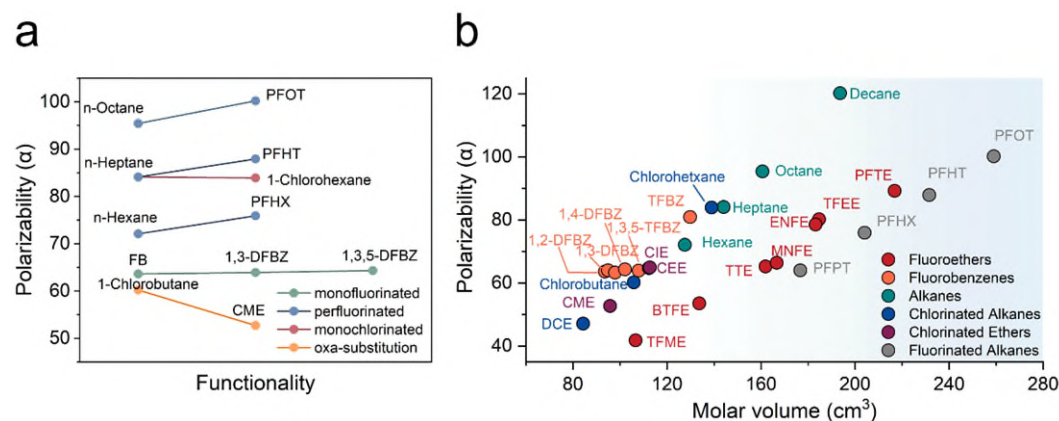


Fig. R2 | Influences of (a) functional groups and (b) molecular volume on polarizability.

In the revised Supplementary Materials, we added Fig. R2 as Supplementary Fig. 3 and renumbered the subsequent Figures.

In the revised manuscript, we made revisions and added the following sentences (Page 7, Line 128):

To verify whether other potential factors may influence polarizability, the impacts of molecular functional groups and molecular volume were analyzed (Supplementary Fig. 3). With similar molecular volume, perfluorination, monofluorination and chlorination all lead to an increase in polarizability, whereas the introduction of ether linkages into the molecular chain results in a decrease (Supplementary Fig. 3a). For compounds within the same class, polarizability increases with molecular volume (Supplementary Fig. 3b). These observations provide only a qualitative understanding of the effects of these two factors on polarizability and the precise quantitative relationships require derivation from Clausius–Mossotti relation (Supplementary Note 2).

Comment 2: The authors discovered a relationship between polarizability and the Li ion desolvation energy. Do other common physical parameters, such as dielectric constant and DN value, also have a quantitative relationship with the desolvation energy? Please explain it.

Reply: We really appreciate the reviewer's comments, which improved the quality of our paper. Other common physical parameters including dielectric constants and donor numbers (DN) were determined using the parallel-plate capacitor model (Fig. 2a) and ^{23}Na NMR technique (Fig. R3a), respectively. The respective influences of these two

physical parameters on the desolvation energy were further investigated, and the results indicate that no clear quantitative relationship exists (Figs. R3b,c).

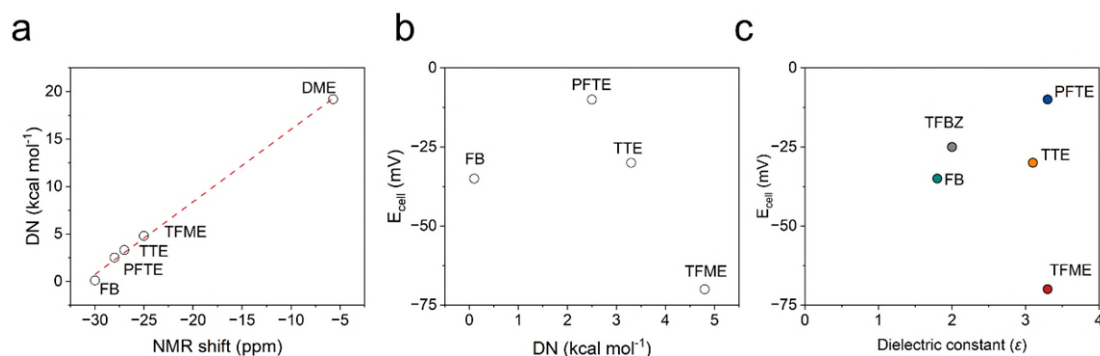


Fig. R3 | **a** Plot of the ^{23}Na shift of NaTFSI dissolved in various inert solvents versus their DN. Influences of **(b)** DN and **(c)** dielectric constant on the desolvation energy.

In the revised Supplementary Materials, we added Fig. R3 as Supplementary Fig. 7 and renumbered the subsequent Figures.

In the revised manuscript, we added the following sentences (Page 9, Line 159):

The influences of other common physical parameters including dielectric constants and donor numbers (DN) on the desolvation energy were also investigated (Supplementary Fig. 7) and the results indicate that no clear quantitative relationship exists.

Comment 3: Figure 1c illustrates the evolution of Li^+ solvate distributions with inert solvents of different polarizabilities under an applied electric field. However, the corresponding description in the text lacks clarity and requires a more detailed exposition.

Reply: We really appreciate the reviewer's comments, which improved the quality of our paper. The solvation clusters exhibit a certain distribution within the electrolyte. Under an applied electric field, inert solvents with high α cause significant disruption to anion-rich solvation clusters, resulting in a smaller fraction of retained anion-rich species (left shaded area, Fig. 1c). Conversely, those with low α exert a far weaker influence under the same conditions, allowing a larger fraction of the anion-rich solvation clusters to be preserved (right shaded area, Fig. 1c).

In the revised manuscript, we made revisions and added the following sentences (Page 6, Line 106):

The solvation clusters exhibit a certain distribution within the electrolyte. Under an applied electric field, inert solvents with high α cause significant disruption to anion-rich solvation clusters, resulting in a smaller fraction of retained anion-rich species (left shaded area, Fig. 1c). Conversely, those with low α exert a far weaker influence under the same conditions, allowing a larger fraction of the anion-rich solvation clusters to be preserved (right shaded area, Fig. 1c).

Comment 4: Please elaborate on how Figure 2d demonstrates that polarizabilities obtained from experiments and theoretical calculations show close agreement.

Reply: We really appreciate the reviewer's comments, which improved the quality of our paper. For nearly all the data points, the deviation between the experimentally measured and computationally calculated polarizabilities is within 5% of the calculated values (blue region in Fig. 2d). Furthermore, the experimental and calculated values also exhibit a strong linear correlation ($y = 1.02x + 0.70$, $R^2 = 0.99$) (the inset in Fig. 2d).

In the revised manuscript, we added the following sentences (Page 8, Line 143):

For nearly all the data points, the deviation between the experimentally measured and computationally calculated polarizabilities is within 5% of the calculated values (blue region in Fig. 2d). Furthermore, the experimental and calculated values also exhibit a strong linear correlation ($y = 1.02x + 0.70$, $R^2 = 0.99$) (inset in Fig. 2d).

Comment 5: The *in situ* Raman spectra demonstrate the structural integrity of Li^+ clusters under an electric field through the Li-FSI ($\sim 750\text{ cm}^{-1}$) complex. However, the role of the Li-DME ($\sim 880\text{ cm}^{-1}$) complex in supporting this conclusion remains unclear. Please provide a detailed explanation.

Reply: Thanks for the reviewer's insightful comments. In anion-rich solvation structure, Li^+ is coordinated simultaneously with both anions and solvent molecules. Therefore, the integrity of Li^+ solvates should be reflected by both $\text{Li}^+\text{-FSI}^-$ ($\sim 750\text{ cm}^{-1}$) and $\text{Li}^+\text{-DME}$ ($\sim 880\text{ cm}^{-1}$) complexes, which exhibit markedly different response behaviors during Li plating/stripping in TTE and TFME electrolytes (Fig. 3b,c).

In the revised manuscript, we made revisions and added the following sentences (Page 11, Line 190):

In anion-rich solvation structure, Li^+ is coordinated simultaneously with both anions and solvent molecules. Therefore, the integrity of Li^+ solvates should be reflected by both $\text{Li}^+\text{-FSI}^-$ ($\sim 750\text{ cm}^{-1}$) and $\text{Li}^+\text{-DME}$ ($\sim 880\text{ cm}^{-1}$) complexes, which exhibit markedly different response behaviors during Li plating/stripping in TTE and TFME electrolytes (Fig. 3b,c).

Comment 6: To completely assess the compatibility of the electrolyte with Li metal, it is essential to perform the cycling performance in $\text{Li}||\text{Cu}$ half cells at a low temperature.

Besides, to confirm the superior Li^+ kinetics in the electrolyte, the cycling of Li||NCM811 cells at a higher rate at -35°C should be performed.

Reply: Thanks for the reviewer's constructive suggestion. To completely verify the compatibility of the electrolyte with Li metal and the superior Li^+ kinetics in the TFME electrolyte, the cycle performance of Li||Cu half cell at -35°C and Li||NCM811 cell at a higher rate at -35°C were also performed (Fig. R4).

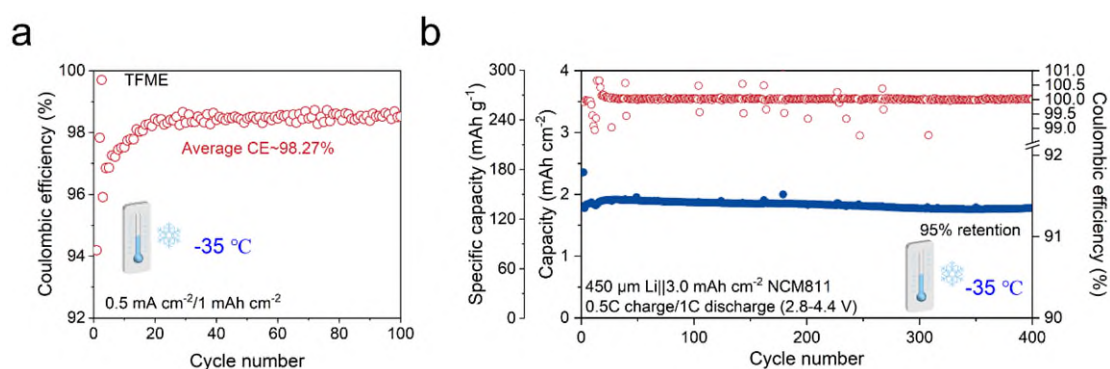


Fig. R4 | Cycle performance of (a) Li||Cu half cell at -35°C and (b) Li||NCM811 cell at a charge rate of 0.5C and a discharge rate of 1C at -35°C .

In the revised Supplementary Materials, we added Fig. R4 as Supplementary Fig. 38 and renumbered the subsequent Figures.

In the revised manuscript, we added the following sentences (Page 18, Line 317):

To completely verify the compatibility of the electrolyte with Li metal and the superior Li^+ kinetics in the TFME electrolyte, the cycle performance of Li||Cu half cell at -35°C and Li||NCM811 cell at a higher rate at -35°C were also performed (Supplementary Fig. 38).

Reviewer #3: The manuscript presents a systematic and well executed study on polarizability-governed Li^+ kinetics for high-energy Li metal batteries. The comprehensive multi-scale analysis, combined with the practical demonstration of a 7.5 Ah pouch cell and exceptional low temperature stability, provides valuable insights for rational electrolyte design. To further enhance the manuscript prior to publication, I recommend addressing the following points.

Reply: We sincerely thank Reviewer #3 for the thorough and insightful evaluation of our manuscript. The constructive comments and suggestions have greatly helped to improve the quality of this work. We responded to each point in detail below and revised the manuscript accordingly. We hope our response and modifications have clarified all the concerns and thereby meet the reviewer's expectations.

Comment 1: In several key electrochemical performance figures (e.g., Figure 5a, 5f, and Supplementary Figures 27-29), the authors present the cycling performance using only absolute capacity or areal capacity. While areal capacity is an important metric, the absence of specific capacity makes it difficult to assess the actual utilization rate of the high loading NCM811 cathode. The authors are advised to provide the specific capacity alongside the absolute/areal capacity by using a secondary Y-axis, or at least clearly specify the active material mass loading in the corresponding figure captions. In addition, please clearly specify the exact evaluation conditions for the various electrochemical performances including anode-free cell and low temperature testing.

Reply: We really appreciate the reviewer's suggestion, which improved the quality of our paper. The specific capacity has been provided alongside the absolute/areal capacity by using a secondary Y-axis in Fig. 5a and Supplementary Figs. 27-29 and the exact evaluation conditions for the various electrochemical performances have been supplemented in the corresponding figures including anode-free cell and low temperature testing. Since Fig. 5f already contains two left Y-axes, we replotted the data using specific capacity as the ordinate and present it as Figure R5.

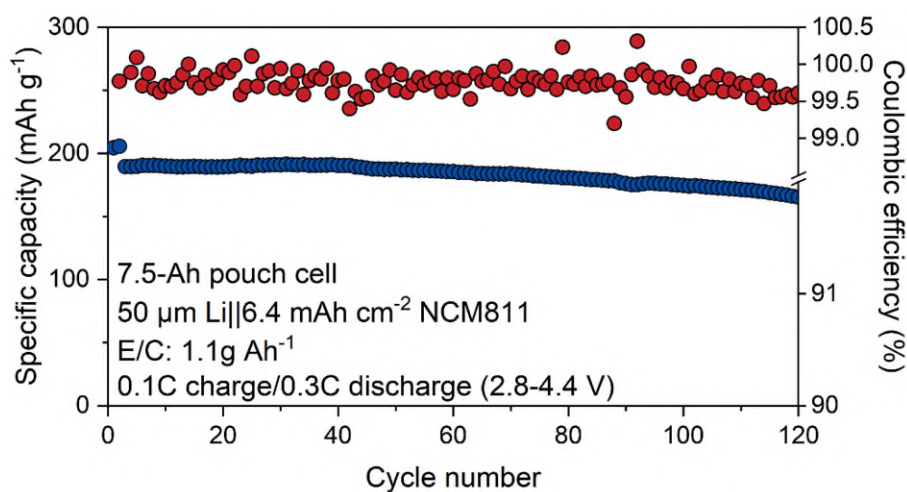


Fig. R5. | Cycle performance of 7.5-Ah Li||NCM811 pouch cell using specific capacity as the left Y-axis.

In the revised Supplementary Materials, we added Fig. R5 as Supplementary Fig. 42.

In the revised manuscript, we added the following sentences (Page 19, Line 329):

To assess the actual utilization rate of the high loading NCM811 cathode in 7.5-Ah Li||NCM811 pouch cell, the cycling data were replotted with specific capacity as the left Y-axis (Supplementary Fig. 42) and the results confirm that the cathode capacity is indeed fully exploited (Initial discharging specific capacity at 0.1C charge/0.3C discharge: 190 mAh g^{-1}).

Comment 2: The authors highlight the 160 mAh/g capacity at 4C, demonstrating that the low-polarizability inert solvent (TFME) remarkably improves the rate capability by reducing the interfacial desolvation energy. However, the heavy use of inert diluents in LHCE inherently diminishes bulk ionic conductivity. It is recommended to discuss how

the sluggish bulk ionic transport affects the rate capability from the perspective of mass transfer within the pores of the thick and densely-packed cathode architecture.

Reply: Thanks for the reviewer's constructive suggestion. To discuss how the sluggish bulk ionic transport affects the rate capability from the perspective of mass transfer within the pores of the thick and densely-packed cathode architecture, we measured the ionic conductivities of two electrolytes and perform the rate capability of Li||NCM811 cells featuring a thick cathode with a high areal capacity of 4.9 mAh cm^{-2} using two electrolytes (Fig. R6). Despite the heavy use of inert diluents, the TFME electrolyte incorporating inert solvent with low polarizability achieved a conductivity of 5.43 mS cm^{-1} , which is significantly higher than that of 3.73 mS cm^{-1} observed for the TTE electrolyte (Fig. R6a). Compared to the results in Fig. 5c, further rate capability of Li|| 4.9 mAh cm^{-2} NCM811 cells (Fig. R6b) demonstrate that the mass transfer within the pores of the thick and densely-packed cathode architecture is obviously hindered due to the sluggish bulk ionic transport. Even so, our TFME electrolyte still enables the Li|| 4.9 mAh cm^{-2} NCM811 cell to achieve a 125 mAh g^{-1} capacity at 1C, which indicates the superior Li^+ transport kinetics.

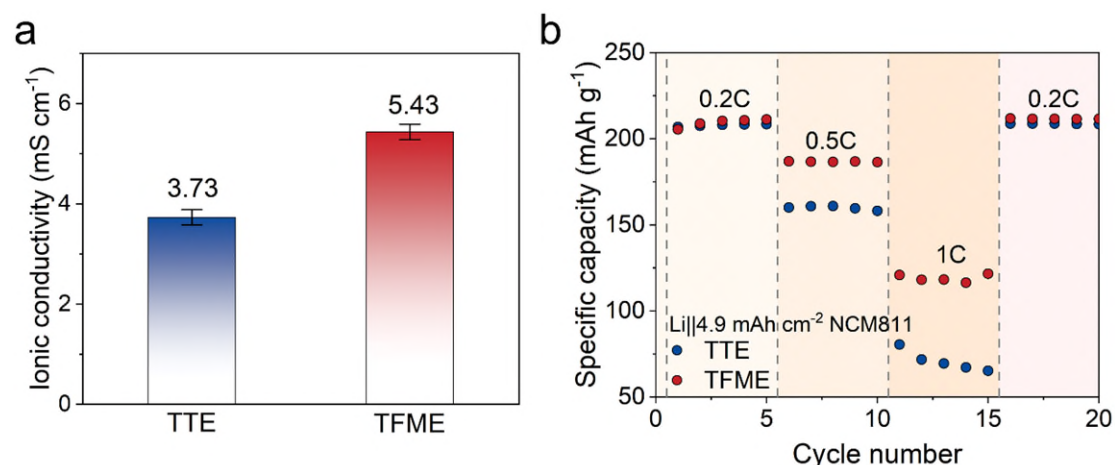


Fig. R6. | **a** Ionic conductivities of TTE and TFME electrolytes. Each sample was measured three times and the average value was taken. **b** Rate capability of Li|| 4.9 mAh cm^{-2} NCM811 cells with TTE and TFME electrolytes.

In the revised Supplementary Materials, we added Fig. R6 as Supplementary Fig. 36 and renumbered the subsequent Figures.

In the revised manuscript, we added the following sentences (Page 18, Line 311):

Despite the heavy use of inert diluents, the TFME electrolyte incorporating inert solvent with low polarizability achieved a conductivity of 5.43 mS cm^{-1} , which is significantly higher than that of 3.73 mS cm^{-1} observed for the TTE electrolyte (Supplementary Fig. 36a). Compared to the results in Fig. 5c, further rate capability of $\text{Li}||4.9 \text{ mAh cm}^{-2}$ NCM811 cells (Supplementary Fig. 36b) demonstrate that the mass transfer within the pores of the thick and densely-packed cathode architecture is obviously hindered due to the sluggish bulk ionic transport. Even so, TFME electrolyte still enables the $\text{Li}||4.9 \text{ mAh cm}^{-2}$ NCM811 cell to achieve a 125 mAh g^{-1} capacity at 1C, which indicates the superior Li^+ transport kinetics.

Comment 3: The authors attribute the excellent stability at -35°C to the preserved anion-rich solvation structure and fast Li^+ kinetics. However, it remains unclear whether this mechanism holds at elevated temperatures (e.g., 45°C or 60°C), where intense thermal agitation and macroscopic solvent density changes could disrupt the interfacial solvates. It is recommended to provide cycling stability of $\text{Li}||\text{NCM811}$ and $\text{Cu}||\text{NCM523}$ cell at the high-temperature and discuss the structural stability of the solvates in the environment. Furthermore, a brief discussion on other potential factors contributing to the low-temperature performance, such as the enhanced mechanical robustness or reduced solubility of the inorganic-rich SEI at low temperature, would strengthen the manuscript.

Reply: Thanks for the reviewer's constructive suggestion. The cycle performances of Li||NCM811 and Cu||NCM523 cells at 45 °C were shown in Figs. R7 and R8. Although elevated temperature intensifies the perturbation of interfacial solvation structures and triggers more side reactions, the TFME electrolyte with the well-preserved anion-rich solvation structure enables Li||NCM811 cell to achieve a cycling with 90% capacity retention after 200 cycles (Fig. R7) and Cu||NCM523 cell to achieve a cycling with 80% capacity retention after 80 cycles (Fig. R8) at 45 °C, far superior to the TTE electrolyte. Besides the compatibility of the electrolyte with Li metal and the superior Li⁺ kinetics in TFME electrolyte, the enhanced mechanical robustness of SEI (Fig. R9) and reduced solubility of the inorganic-rich SEI at low temperature also contribute to the excellent low-temperature performance.

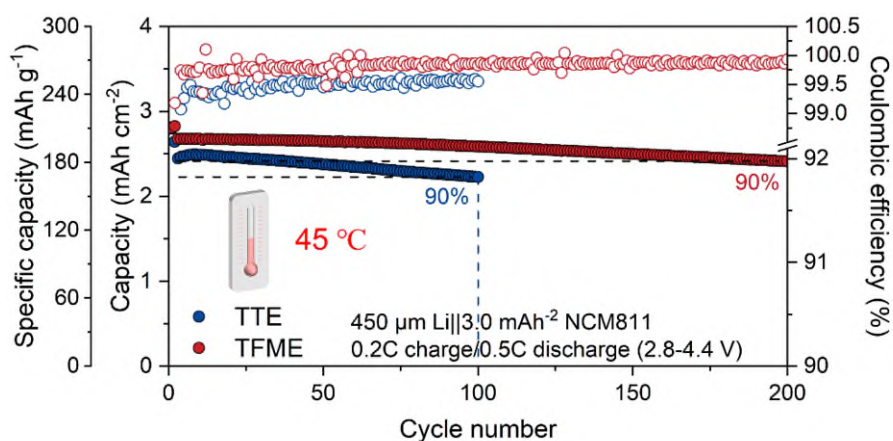


Fig. R7. | Cycle performance of Li||NCM811 cells at 45 °C (0.2C charge/0.5C discharge).

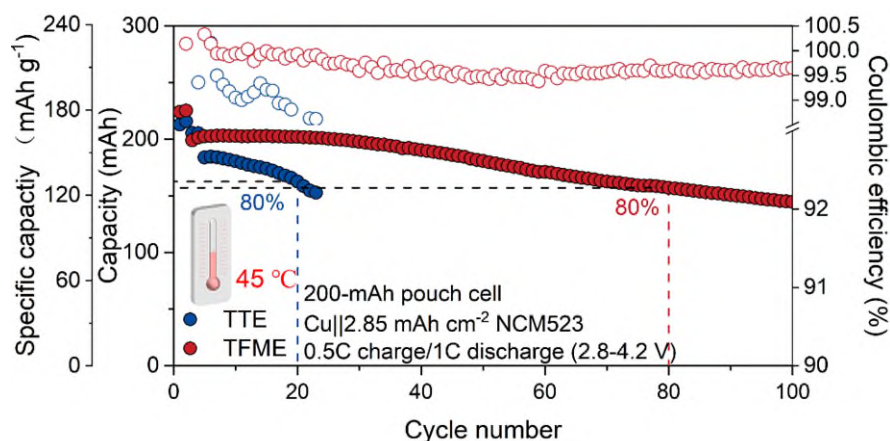


Fig. R8. | Cycle performance of 200-mAh Cu||NCM523 pouch cells at 45 °C.

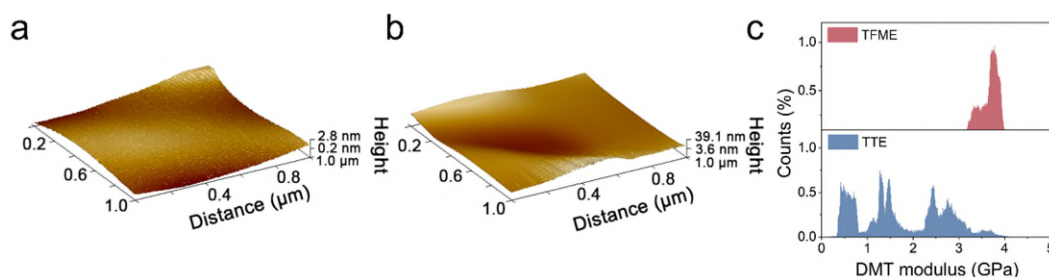


Fig. R9. | The height image of the SEI formed in (a) TFME and (b) TTE electrolytes. c DMT

modulus distribution of the SEI formed in two electrolytes.

In the revised Supplementary Materials, we added Fig. R7 as Supplementary Fig. 33, Fig. R8 as Supplementary Fig. 34 and Fig. R9 as Supplementary Fig. 39 and renumbered the subsequent Figures.

In the revised manuscript, we added the following sentences (Page 17, Line 305):

The cycle performances of Li||NCM811 and Cu||NCM523 cells at 45 °C were shown in Supplementary Figs. 33 and 34. Although elevated temperature intensifies the perturbation of interfacial solvation structures and triggers more side reactions, the

TFME electrolyte with the well-preserved anion-rich solvation structure enables Li||NCM811 cell to achieve a cycling with 90% capacity retention after 200 cycles (Supplementary Fig. 33) and Cu||NCM523 cell to achieve a cycling with 80% capacity retention after 80 cycles (Supplementary Fig. 34) at 45 °C, far superior to the TTE electrolyte.

In the revised manuscript, we added the following sentences (Page 18, Line 317):

Besides the compatibility of the electrolyte with Li metal and the superior Li⁺ kinetics in TFME electrolyte, the enhanced mechanical robustness of SEI (Supplementary Fig. 39) and reduced solubility of the inorganic-rich SEI at low temperature also contribute to the excellent low-temperature performance^{3,4}.

Comment 4: For the 7.5 Ah Li metal pouch cell evaluation, the externally applied pressure condition is missing. Because Li-metal cell performance is highly sensitive to applied pressure, the authors must state the exact pressure used during the evaluation to ensure reproducibility and validate the practical relevance of the 541.6 Wh/kg energy density.

Reply: We really appreciate the reviewer's suggestion, which improved the quality of our paper. The stacking pressure is 0.729 Mpa for the 7.5-Ah Li-metal pouch cell evaluation and the detailed parameters of the 7.5-Ah Li-metal pouch cell have been listed in Supplementary Table 3 in the revised Supplementary Materials.

In the revised manuscript, we made revisions and added the following sentences (Page 18, Line 319):

Targeting a Li-metal pouch cell with energy density beyond 500 Wh kg⁻¹, we performed systematic optimization of all component parameters (Supplementary Table 3).

Comment 5: Please correct the following typos prior to publication: In the Chemical reagents section, change "lihtium" to "lithium"; in the Figure 4 caption, change "volatge" to "voltage"; in the first paragraph of the Results section, change "interfacial electric" to "interfacial electric field". In the text referring to the pouch cells, change "Fig. 6a" to "Fig. 5a".

Reply: Thanks for the reviewer's careful reading and helpful comments. We have carefully checked the manuscript and made the necessary corrections.

References

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3. Yue, L. et al., Wide temperature electrolytes for lithium batteries: solvation chemistry and interfacial reactions. *Small Methods* **8**, 2400183 (2024).
4. Sayavong, P. et al., Dissolution of the solid electrolyte interphase and its effects on lithium metal anode cyclability. *J. Am. Chem. Soc.* **145**, 12342-12350 (2023).