

Solvation sheath reorganization enables fast ion transfer kinetics in lithium-ion battery

Corresponding Author: Professor Xiulin Fan

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

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

In this manuscript, Li et al. propose an elegant and practical strategy for electrolyte design based on reorganizing Li^+ solvation structures via the introduction of an optimized moderator molecule. The introduction of the D parameter as a screening tool is both original and conceptually valuable. The demonstrated performance of FA-DCM electrolyte, particularly at ultra-low temperatures in pouch cells, is highly promising. The study is well designed and supported by extensive experimental and computational analyses. Nevertheless, several key issues must be addressed prior to publication:

1. The solvation structures and Li^+ hopping mechanisms were analyzed using MD simulations at equilibrium. In practical cell operation, however, strong electric fields and concentration gradients are present. Have the authors considered how the solvation dynamics and ion transport pathways might change under non-equilibrium, high-current cycling conditions?

we believe that additional insight or simulations in this regime would greatly enhance the mechanistic understanding.

2. The manuscript emphasizes discrete Li^+ hopping facilitated by compact solvation clusters. However, recent studies (e.g., ion-hopping decoupling from anion drift) suggest that Li^+ -anion correlated motions can significantly affect macroscopic ionic conductivity. Could the authors analyze and comment on the extent of Li^+ -anion correlated motion in their FA-DCM electrolyte compared to conventional systems?

3. Under high-rate, transient clustering or "dynamic association" of Li^+ with multiple anions or solvents can occur due to forced ion migration. Has the possibility of such transient cluster formation been examined in the FA-DCM system? This could impact fast-charging stability and uniformity of Li^+ transport at practical device scales.

4. The proposed discrete Li^+ hopping mechanism is shown to be effective in model electrodes. However, in practical electrodes with higher porosity and tortuosity, ion transport limitations are often exacerbated. Could the authors comment on how the observed gains in Li^+ mobility with FA-DCM electrolyte scale with increasing electrode complexity, and whether additional strategies might be required to optimize performance in thick electrodes?

5. The manuscript highlights an increased population of mobile Li^+ due to CIP formation. However, a quantitative analysis of the absolute concentration of free (solvent-separated) Li^+ vs. CIP vs. AGG species is not fully presented. Could the authors provide such a quantitative breakdown from their MD simulations or experimental data to better support their transport enhancement claims?

6. The presence of a large fraction of CIP species is proposed to enhance transport. However, CIP species may have different electrochemical stability compared to free solvated Li^+ . Could the authors analyze or comment on whether CIP species are more or less prone to side reactions at high voltages or under fast cycling?

7. The authors should include electrolyte stability and performance data at ≥ 60 °C to provide a complete view of the operational window.

8. The discrete hopping mechanism enables fast bulk Li^+ transport, but may also lead to increased kinetic heterogeneity at the electrode interface (due to asynchronous arrival of Li^+ and counter-ions). Have the authors considered whether the enhanced bulk mobility introduces new challenges for interfacial reaction uniformity, SEI homogeneity, or lithium plating/stripping dynamics?

Reviewer #2

(Remarks to the Author)
see attach

Reviewer #3

(Remarks to the Author)

The manuscript titled "Solvation sheath reorganization enables fast ion transfer kinetics" presents a comprehensive study on a novel electrolyte design approach for lithium-ion batteries, employing a low-dipole, small-sized moderator (dichloromethane, DCM) to reorganize the solvation sheath. The authors introduce a descriptor-based framework for selecting such moderators and validate the concept through molecular simulations, electrochemical characterizations, and practical pouch cell demonstrations. Of all the moderators examined, DCM exhibits the smallest molecular volume and lowest dipole. The FA-DCM electrolyte demonstrates outstanding performance in high-rate and low-temperature operations, outperforming state-of-the-art commercial electrolytes. The graphite-NMC full cell electrochemical measurements were carried out at room temperature and a low temperature of -40/-50 °C. The study suggests an alternative to commonly used carbonate-based electrolytes, such as 1 M LiPF₆ in EC: DMC for low-temperature applications because of its high freezing point and elevated activation energy. The authors claim that FA-DCM demonstrates superior compatibility with high-voltage cathodes. The work addresses critical challenges in battery performance under extreme temperatures, a significant bottleneck in LIB deployment for EVs and aerospace. Theoretical study and experimental analysis, such as NMR, XPS, and full/pouch cell testing, strengthen the findings. Demonstration of low-temperature operation down to -75 °C with practical 1.0 Ah pouch cells is impressive.

We suggest a minor revision for the manuscript before it can be published. The following queries should be addressed in the revised version.

1. DCM is a halogenated solvent with known toxicity and volatility. The manuscript does not sufficiently address the environmental and safety implications.
2. The economic and industrial feasibility of large-scale FA-DCM electrolyte production is not discussed.
3. Page 14, the incompatibility between acetonitrile, AN, and graphite should be elaborated.
4. Supplementary Information page 28, Figure 17: Please show the fitted line along with the experimental EIS data. Include insets highlighting the region till 10 ohms (Z_{real}) for 17b and 15 ohms (Z_{real}) for 17c.
5. Page 21, The authors report that the FA-DCM electrolyte forms a thinner SEI layer on the graphite anode compared to the base electrolyte, with a higher LiF concentration. Since LiF is known to contribute to the formation of a stable, compact, and ionically conductive SEI, a more in-depth discussion is required on how the increased LiF content correlates with improved interfacial stability and electrochemical performance.
6. Advanced Li-ion batteries use Si-based anodes. It would be interesting to discuss applicability of solvation sheath reorganization using DCM moderator to Si-based anodes.

Minor comments:

1. Page 4, put a space before cm^{-1} and references 28, 29.
2. Page 9, start a new paragraph when NMR is discussed.

Reviewer #4

(Remarks to the Author)

Although the work proposes a descriptor-based screening strategy and reports promising low-temperature battery performance, several fundamental and scientific concerns undermine the strength of the central claims and limit the impact and generalizability of the study.

The comments and suggestions for improving this work are as follows:

- 1) The manuscript frequently claims improved "fast ion transfer kinetics." However, the improvements are primarily in liquid-

phase transport and interfacial desolvation, not in solid-state diffusion, which is typically the rate-limiting step in battery operation. The terminology should be clarified and limited to the electrolyte domain.

2) The authors do not measure or analyze Li^+ diffusion within the solid electrodes (e.g., graphite, NMC811), where kinetic bottlenecks often lie. Techniques such as GITT-based diffusion coefficient extraction or operando XRD would help separate bulk limitations from interfacial ones.

3) The central mechanistic claim—enhanced ion mobility due to solvation shell disruption—should be supported by ^7Li DOSY NMR to quantify Li^+ diffusion. ^1H and ^{19}F DOSY could further confirm the dynamic solvation exchange involving DCM and FSI^- . This experimental validation is currently missing and would greatly strengthen the work.

4) While improved SEI/CEI composition is discussed (LiF – LiCl -rich), the quantitative interfacial impedance analysis (e.g., R_{SEI} vs R_{ct} from EIS fitting) is limited. More robust correlation between interphase composition and electrochemical impedance would help establish cause–effect relationships.

5) Dichloromethane (DCM) has low boiling point and is environmentally concerning. The paper lacks discussion on volatility, flammability, and toxicity, which may limit practical applicability despite performance advantages.

6) The proposed $D = 1/(\mu \cdot V)$ descriptor is interesting but lacks theoretical foundation. Why should this specific functional form (inverse product) correlate with solvation disruption? Comparative performance against known Gutmann donor number, dielectric constant, or Lewis basicity is not shown.

7) Although ionic conductivity is reported at $-70\text{ }^\circ\text{C}$ to $25\text{ }^\circ\text{C}$, activation energy (E_a) for ion transport is not extracted. Arrhenius or VTF plots would provide a clearer understanding of temperature-dependent kinetics.

8) Is the effect of DCM reversible or stable over time and cycling? The paper does not show long-term aging or electrolyte stability under extended cycling or storage.

9) The comparison is mainly between FA-TTE and FA-DCM. A control using FA alone or other small molecule moderators would clarify whether DCM is uniquely effective or if the result is generalizable.

10) TEM images show SEI thickness but do not report spatial uniformity or standard deviation. More statistical analysis across particles would improve reliability of conclusions.

11) Operando Raman or FTIR spectroscopy could provide real-time insights into DCM – FSI^- – Li^+ interactions and validate the simulated solvation structures experimentally.

12) The full-cell performance at low temperature is excellent, but long-term cycling at room temperature is not included. This data would be important for assessing general electrolyte viability.

13) While full cells are tested, a $\text{Li}||\text{Li}$ symmetric cell cycling test would help evaluate long-term interfacial stability and dendrite suppression behavior.

14) Important physical parameters such as density and viscosity of the FA-DCM electrolyte are not reported, yet they directly affect Li^+ ion mobility and solvation dynamics.

15) The link between electrolyte composition and SEI chemistry (e.g., Cl -containing species) is hypothesized but not strongly confirmed. More targeted XPS or TOF-SIMS depth profiles could help.

16) At elevated temperatures, DCM may evaporate or leak. Mass loss over time or pressure buildup should be tested and reported.

17) Although DCM affects SEI, its influence on oxidative stability at high voltage (e.g., with NMC811 at $>4.3\text{ V}$) is not evaluated.

18) The claim of interface stabilization would be stronger if demonstrated in anode-free or Li -metal full cells, where Coulombic efficiency is highly sensitive to SEI quality.

19) The GITT data shows reduced overpotentials, but the actual diffusion coefficients are not calculated or compared across systems.

20) The effects of LiFSI salt and DCM moderator are entangled. A control with DCM but no LiFSI , or other salts, would help isolate the role of the moderator.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This manuscript presents an innovative electrolyte design strategy for Li -ion batteries under extreme conditions. The D -value descriptor and DCM-based electrolyte demonstrate excellent performance in practical pouch cells. I find the manuscript suitable for publication. However, the following minor issues need to be addressed.

Q1. The D -value ($D = C \cdot 1/\mu \cdot 1/V$) is a key contribution but its derivation is only in Supplementary Note 4. Please add a brief explanation (3–4 sentences) in the main text on page 6 about: (a) the physical meaning of this relationship, and (b) whether this descriptor can be applied to other solvent systems beyond AN-based electrolytes.

Q2. The SEI/CEI thickness measurements from TEM (Fig. 6c–d) and XPS depth profiling (Fig. 6e–f) are crucial but lack statistical information. Please specify: (a) how many particles/locations were analyzed for the TEM thickness measurements, (b) the sputtering rate and total depth for XPS profiling, and (c) add a table summarizing the atomic percentages of key elements (F , N , S , Cl for FA-DCM; F , P , C , O for BE) at different depths to quantitatively support the claimed "dual-layer SEI architecture."

Q3. The acknowledgment of DCM toxicity and volatility on page 24 is brief. Please expand this discussion to: (a) explicitly describe the stability results from Supplementary Figs. 59–61 in the main text (specific conditions, duration, and capacity retention values), (b) compare DCM's safety profile with the already-tested DCE moderator, which also shows high D -value

and good performance (Fig. 5d), and (c) discuss whether the D-value framework could guide identification of safer alternatives. This would strengthen the practical relevance without requiring new experiments.

Q4. MD simulation results at various temperatures are scattered across multiple supplementary figures (33-38). Please add a supplementary table summarizing Li^+ diffusion coefficients and residence times at 25°C, 0°C, -20°C, and -40°C for FA-DCM and FA-TTE electrolytes to facilitate comparison.

Reviewer #2

(Remarks to the Author)

This is a well-executed and highly original study.

The authors provide both a new theoretical descriptor and compelling low-temperature pouch-cell data, which together meet the novelty and mechanistic standards of Nature Communications.

The manuscript is scientifically sound, well supported by data, and written clearly.

Reviewer #3

(Remarks to the Author)

The manuscript titled "Solvation Sheath Reorganization Enables Fast Ion Transfer Kinetics" presents a study on a novel electrolyte design approach for lithium-ion batteries (LIBs), employing dichloromethane (DCM) to reorganize the solvation sheath. The FA-DCM electrolyte demonstrates excellent electrochemical performance in 4.5 V graphite||NMC811 full cells, delivering a remarkable capacity of 179.8 mAh g⁻¹ at 6 C. At an ultra-low temperature of -50 °C, the pouch cell exhibits stable cycling, achieving a high capacity of 0.51 Ah. This study establishes an effective strategy for developing electrolytes tailored for fast-charging and low-temperature LIBs, providing an alternative to conventional carbonate-based electrolytes with improved compatibility for high-voltage cathodes.

The queries raised during the previous review have been adequately addressed by the authors, and I recommend accepting the manuscript as such.

1. The toxicity of DCM has been addressed, and the authors mention excellent sealing of their pouch cells.
2. The cost comparison of different electrolytes has been added in Table R6.
3. The incompatibility issues between acetonitrile and graphite have been explained in the manuscript using graphite||LFP full cells as an example.
4. Revised EIS data have been provided.
5. X-ray photoelectron spectroscopy (XPS) depth profiling, together with time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis, has been included to understand the SEI chemistry.
6. SiC||NMC full cells were tested to demonstrate compatibility with silicon-based anodes.

Reviewer #4

(Remarks to the Author)

The authors have provided a comprehensive and thoughtful revision of the manuscript "Solvation Sheath Reorganization Enables Fast Ion Transfer Kinetics."

I appreciate the careful and data-driven responses to the earlier review. The revisions have substantially improved the scientific rigor, mechanistic clarity, and overall impact of the work.

Reviewer #5

(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 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The authors have submitted a comprehensive and well-considered revision of the manuscript. I appreciate the detailed, data-driven responses to the previous comments. These modifications have significantly enhanced the scientific rigor, mechanistic clarity, and overall impact of the work

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Detailed responses to the reviewers' comments

Manuscript ID: **NCOMMS-25-35862-T**

Title: **Solvation sheath reorganization enables fast ion transfer kinetics**

Authors: Menglu Li, Di Lu, Jinze Wang, Shuoqing Zhang, Ling Lv, Baochen Ma, Haotian Zhu, Long Li, Sheng Yang, Zirui Li, Yuefei Wu, Jiacheng Qi, Liwu Fan, Ruhong Li, Lixin Chen, Tao Deng, Xiulin Fan

Reviewer #1 (Remarks to the Author):

In this manuscript, Li et al. propose an elegant and practical strategy for electrolyte design based on reorganizing Li^+ solvation structures via the introduction of an optimized moderator molecule. The introduction of the D parameter as a screening tool is both original and conceptually valuable. The demonstrated performance of FA-DCM electrolyte, particularly at ultra-low temperatures in pouch cells, is highly promising. The study is well designed and supported by extensive experimental and computational analyses. Nevertheless, several key issues must be addressed prior to publication:

Reply: We express our sincere gratitude to Reviewer #1 for conducting a thorough review of our manuscript. The valuable and constructive comments made by the reviewer are of great benefit to improving our manuscript. The specific questions have been addressed point-by-point as below. We hope our response and modifications have clarified all the concerns and thereby meet the reviewer's expectations.

1. The solvation structures and Li^+ hopping mechanisms were analyzed using MD simulations at equilibrium. In practical cell operation, however, strong electric fields and concentration gradients are present. Have the authors considered how the solvation dynamics and ion transport pathways might change under non-equilibrium, high-current cycling conditions?

We believe that additional insight or simulations in this regime would greatly enhance the mechanistic understanding.

Reply: We thank the reviewer for this valuable suggestion. To address this concern, we have extended our molecular dynamics (MD) simulations to explicitly include an applied electric field, thereby mimicking the non-equilibrium conditions. The analysis shows that the solvation patterns presented at equilibrium persist during non-equilibrium conditions (Fig. R1), while the residence times of Li^+ near solvent and anion species are shortened, indicating accelerated exchange dynamics under electric field (Fig. R2 and R3). Notably, the FA-DCM electrolyte maintains a more labile and

homogeneous solvation environment under electric field perturbation, which is consistent with the experimentally observed improvements in ion transport at high rates. These additional simulations provide further confidence that the proposed Li^+ hopping mechanism is robust even under non-equilibrium operating conditions.

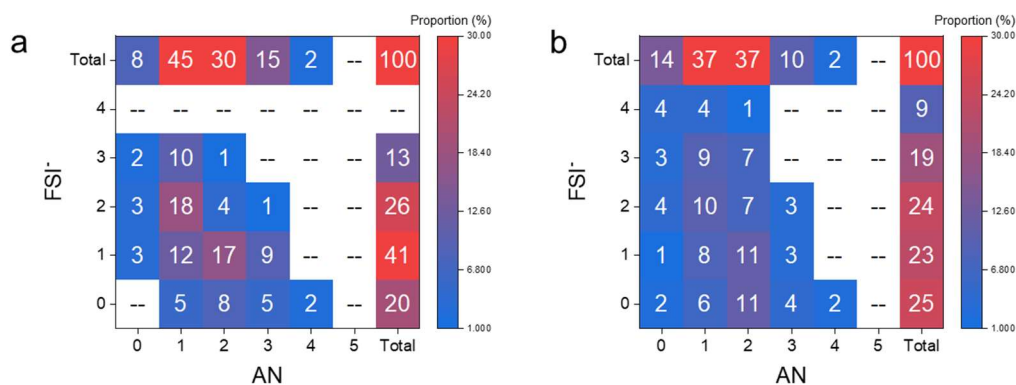


Fig. R1 | Heatmaps of Li^+ solvation sheath in FA-DCM (a) and FA-TTE electrolyte (b) at 298 K, $E=0.1 \text{ V } \text{\AA}^{-1}$.

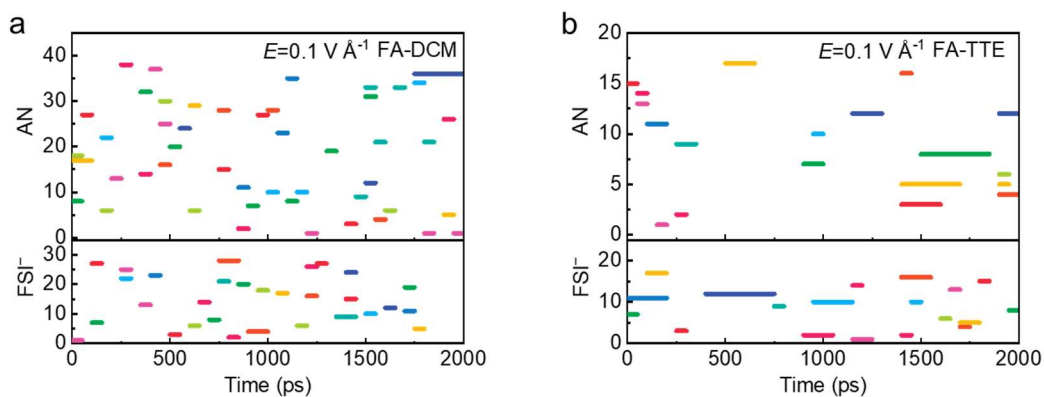


Fig. R2 | Evolution of Li^+ solvation environment in FA-DCM (a) and FA-TTE electrolyte (b) from MD simulations at 298 K, $E=0.1 \text{ V } \text{\AA}^{-1}$. The vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li^+ in the simulation time of 2,000 ps.

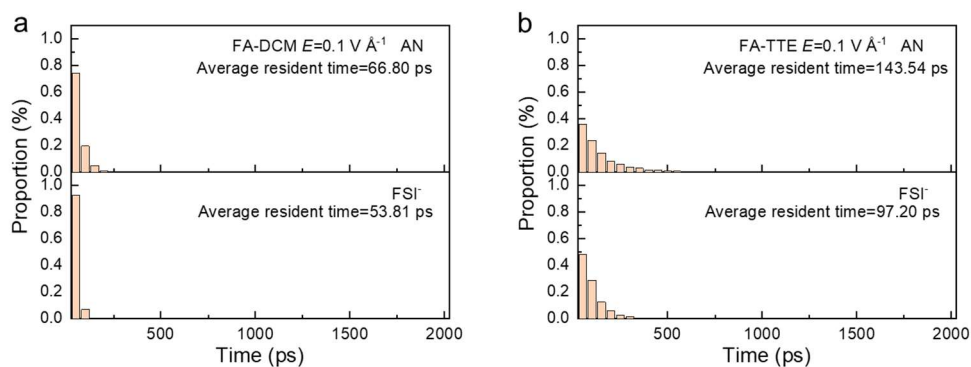


Fig. R3 | Residence time distribution of AN and FSI⁻ in FA-DCM (a) and FA-TTE electrolyte (b) at 298 K, $E=0.1 \text{ V } \text{\AA}^{-1}$.

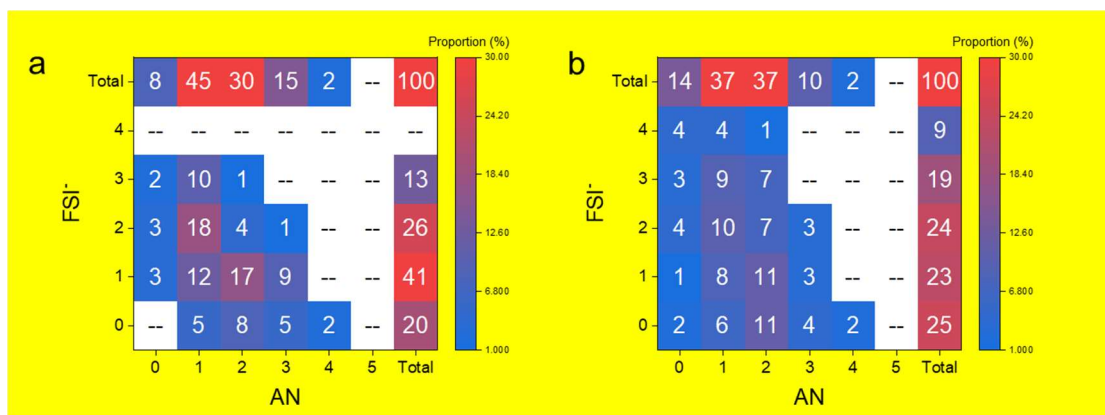
In the revised manuscript (Pages 13 and 14), we added the following text and highlighted it:

Moreover, to approximate practical conditions, we applied an electric field ($E=0.1 \text{ V } \text{\AA}^{-1}$) in the simulations to further clarify the solvation dynamics of the electrolyte under non-equilibrium states. Notably, the interfacial environment remains relatively stable instead of exhibiting increasing kinetic heterogeneity in FA-DCM electrolyte (Supplementary Fig. 17), thus maintaining a more homogeneous solvation environment and markedly accelerated Li^+ hopping. In contrast, the Li^+ hopping frequency in FA-TTE is lower than that in the FA-DCM electrolyte (Supplementary Fig.18-20).

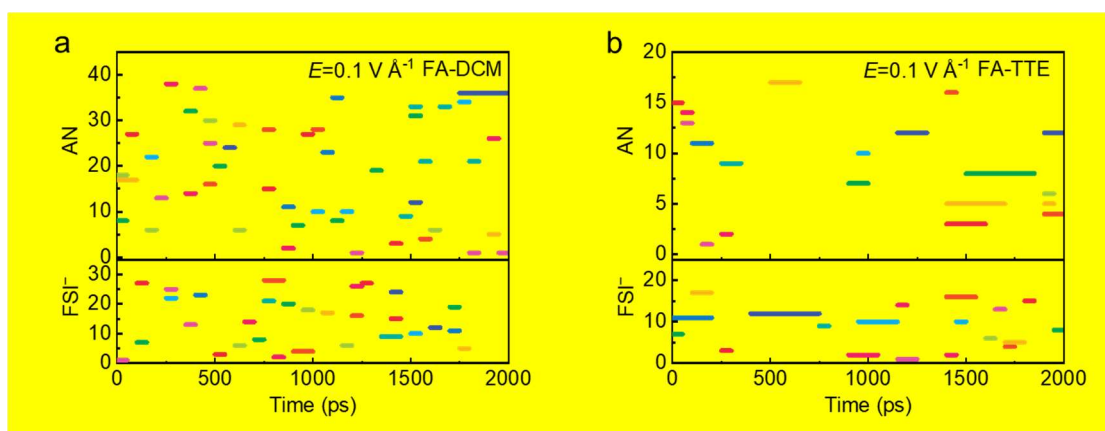
In the revised computational method, we added the following text and highlighted it in yellow (Page 35):

To investigate the effects of electric field and temperature, simulations were conducted under various electric field strengths and temperatures, while all other simulation parameters remained consistent with the procedures described above.

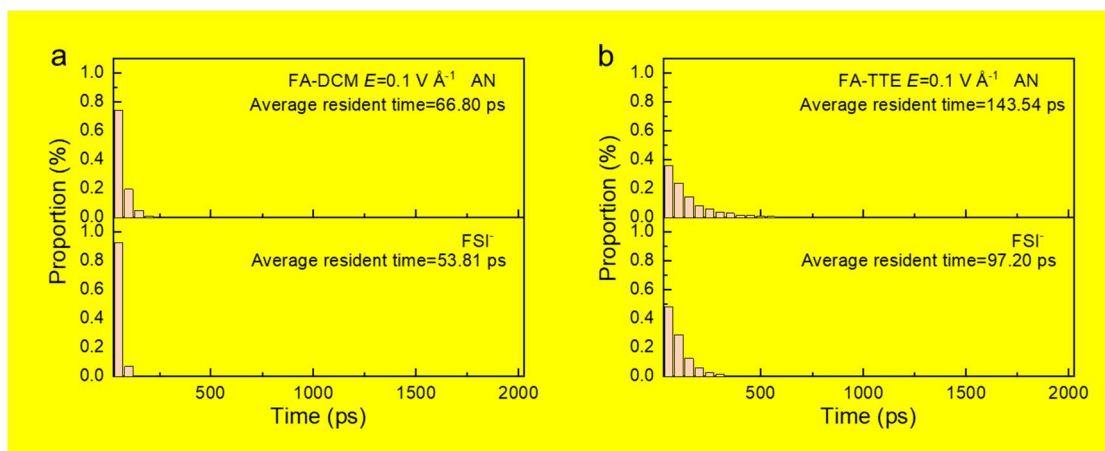
In the revised supporting information (Pages 38-40), we added Fig. R1-3 as Supplementary Fig. 18-20, respectively:



Supplementary Fig. 18 | Heatmaps of Li^+ solvation sheath in FA-DCM (a) and FA-TTE electrolyte (b) at 298 K, $E=0.1 \text{ V } \text{\AA}^{-1}$.



Supplementary Fig. 19 | Evolution of Li^+ solvation environment in FA-DCM (a) and FA-TTE electrolyte (b) from MD simulations at 298 K, $E=0.1 \text{ V } \text{\AA}^{-1}$. The vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li^+ in the simulation time of 2,000 ps.



Supplementary Fig. 20 | Residence time distribution of AN and FSI^- in FA-DCM (a) and FA-TTE electrolyte (b) at 298 K, $E=0.1 \text{ V } \text{\AA}^{-1}$.

2. The manuscript emphasizes discrete Li^+ hopping facilitated by compact solvation clusters. However, recent studies (e.g., ion-hopping decoupling from anion drift) suggest that Li^+ -anion correlated motions can significantly affect macroscopic ionic conductivity. Could the authors analyze and comment on the extent of Li^+ -anion correlated motion in their FA-DCM electrolyte compared to conventional systems?

Reply: We thank the reviewer for raising this insightful point. To specifically address the role of Li^+ -anion correlated motions, we carried out MD simulations to quantify the average interaction distance between Li^+ and each coordinating anion. In the FA-DCM electrolyte, the mean Li^+ -anion interaction distance was calculated to be 49.0 Å (Fig. R4a), which is notably shorter than that observed in the FA-TTE electrolyte (71.0 Å, Fig. R4b). This shorter interaction distance reflects more frequent but transient Li^+ -anion encounters, which facilitate efficient hopping rather than long-lived ion-pair drag. Importantly, as shown in Fig. R5, this trend persists at lower temperature (0 °C), indicating that FA-DCM system (45.86 Å) preserves favorable solvation dynamics even under kinetically demanding conditions, while the interaction between Li^+ -anions in the FA-TTE electrolyte become more heavily (226.13 Å), impeding the transfer of Li^+ . These findings suggest that while correlated Li^+ -anion motions do exist, they are less constraining in FA-DCM electrolyte than in conventional highly concentrated systems, thereby contributing to the shorter residence time observed (0 °C, FA-DCM: 7.17 mS cm^{-1} ; FA-TTE: 1.79 mS cm^{-1} ; Fig. 3f) and shorter residence time (FA-DCM: 193.81 ps for AN, 144.28 ps for FSI; FA-TTE: 348.18 ps for AN, 249.01 ps for FSI; Fig. R6, 7).

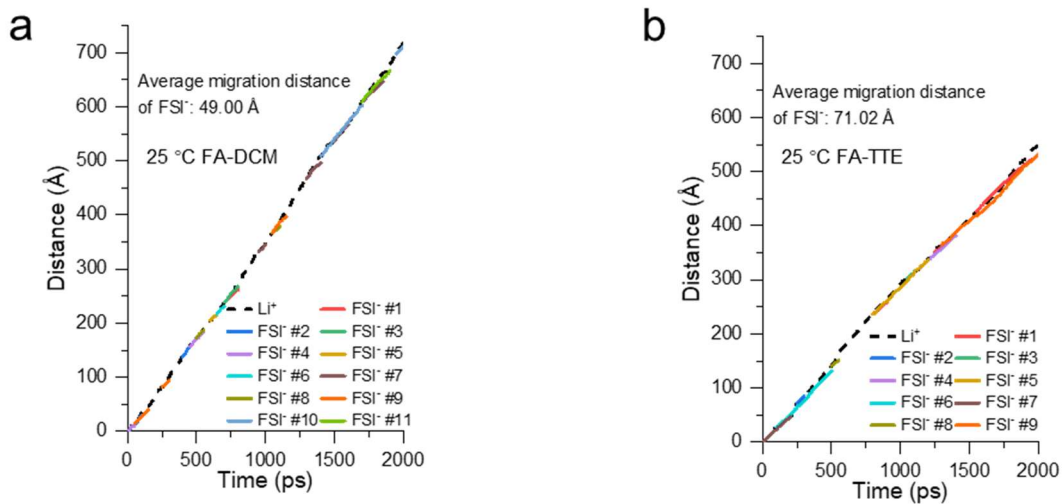


Fig. R4 | Li^+ -anion correlated motion in FA-DCM electrolyte (a) and FA-TTE electrolyte (b) at 25°C.

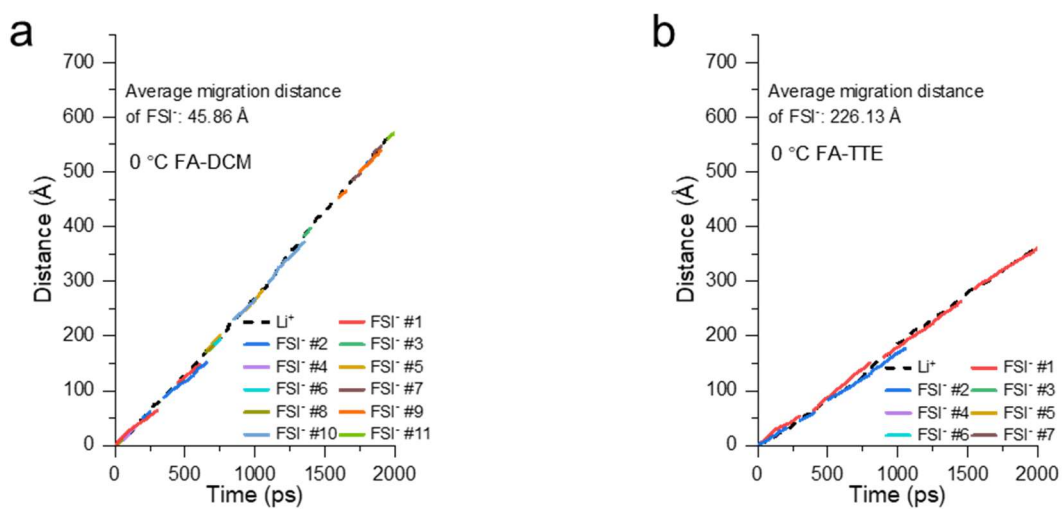


Fig. R5 | Li^+ -anion correlated motion in FA-DCM electrolyte (a) and FA-TTE electrolyte (b) at 0°C.

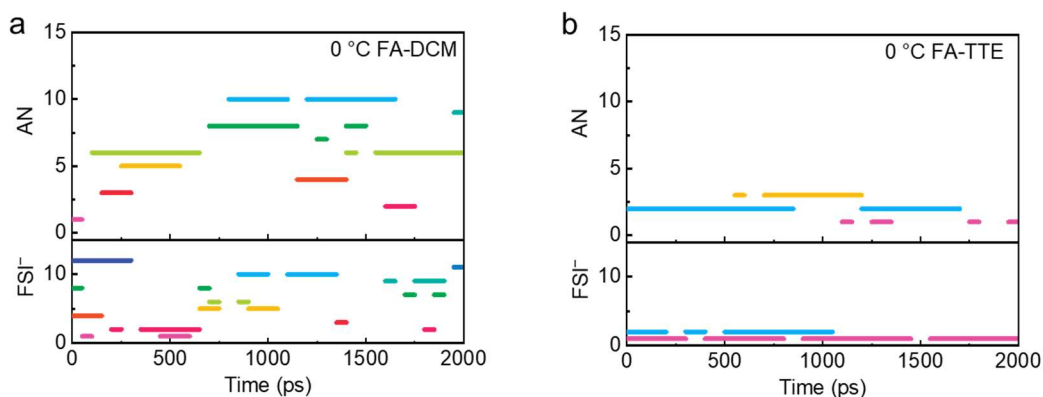


Fig. R6 | Evolution of Li^+ solvation environment in FA-DCM electrolyte (a) and FA-TTE electrolyte (b) from MD simulations at 273K. The vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li^+ in the simulation time of 2,000 ps.

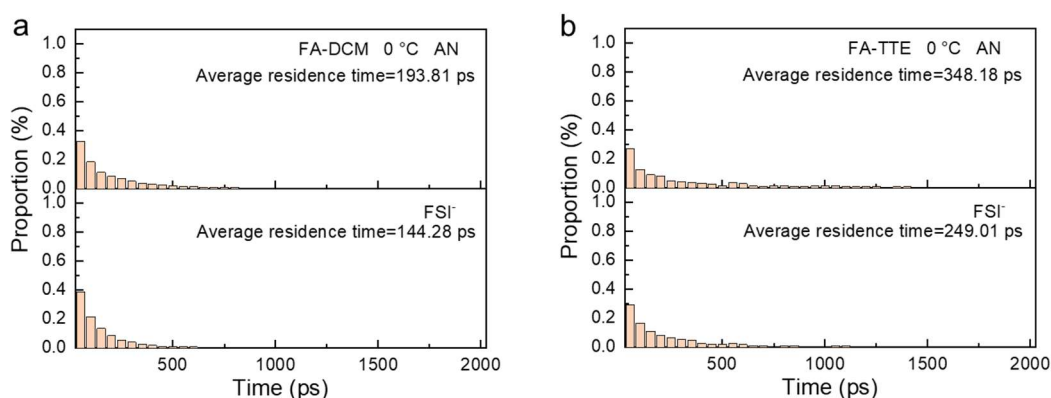
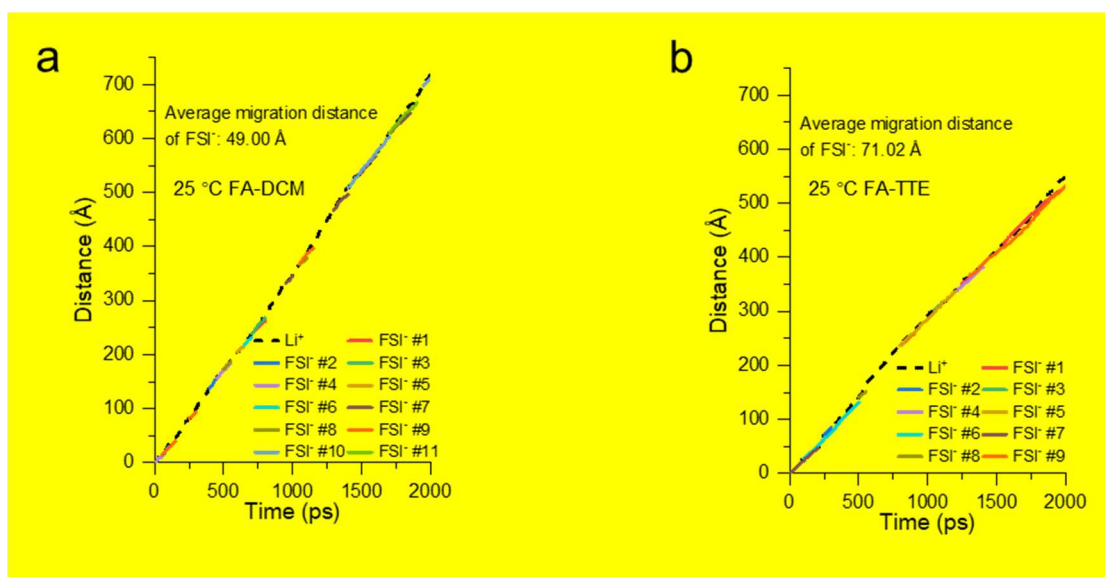


Fig. R7 | Residence time distribution of AN and FSI^- in FA-DCM electrolyte (a) and FA-TTE electrolyte (b) at 273K.

In the revised manuscript (Page 18), we added the following text, and highlighted it in yellow:

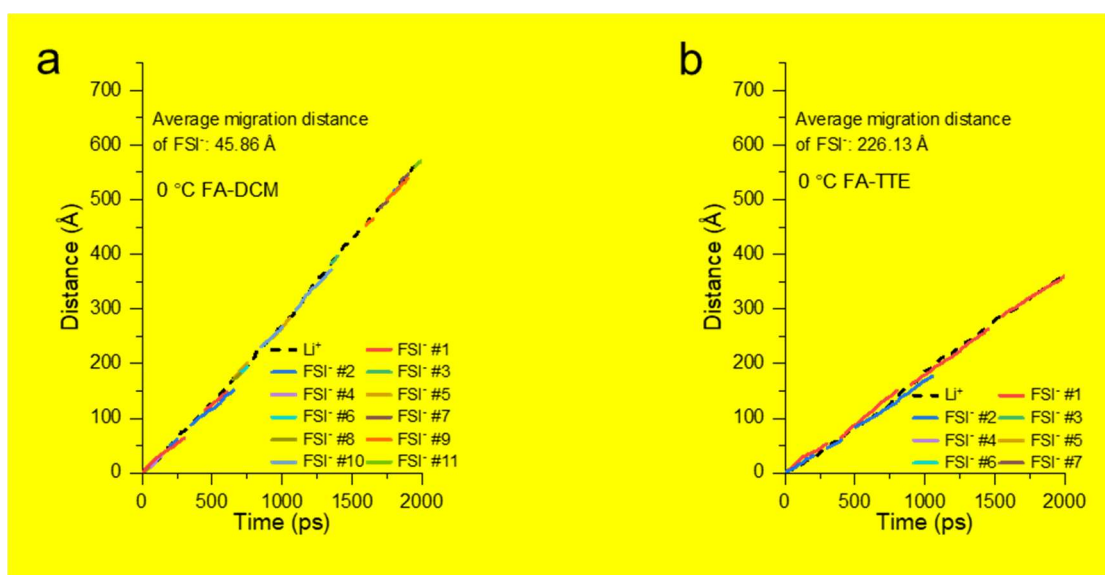
MD simulations suggest that while correlated Li^+ -anion motions exist, they are less constraining in FA-DCM electrolyte than in FA-TTE electrolyte regardless of temperatures, leading to reduced residence times for FA-DCM electrolyte at 0 °C (193.8 ps for AN, 144.3 ps for FSI^-) (Supplementary Fig. 33-36).

In the revised supporting information (Pages 54-57), we added Fig. R4-7 as Supplementary Fig. 33-36, respectively:



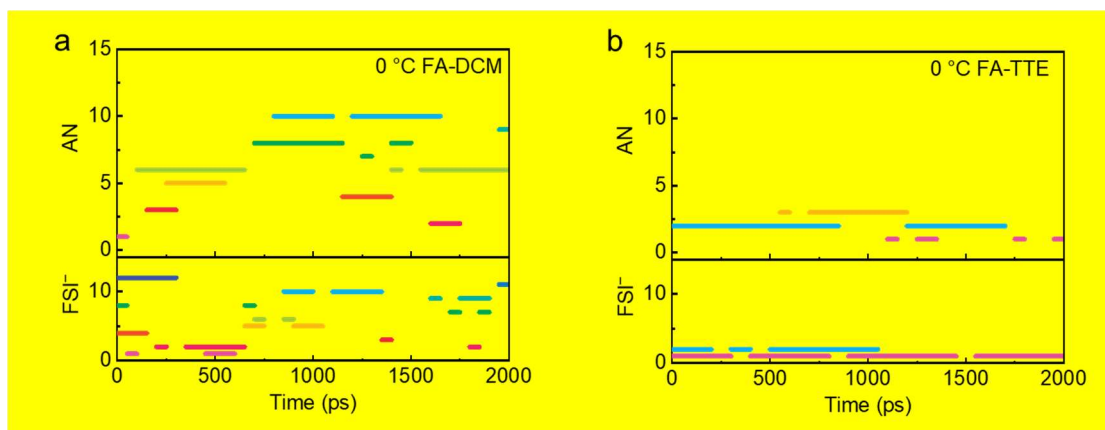
Supplementary Fig. 33 | Li⁺-anion correlated motion in FA-DCM electrolyte (a) and FA-TTE electrolyte (b) at 25 °C.

To specifically address the role of Li⁺-anion correlated motions, we carried out MD simulations to quantify the average interaction distance between Li⁺ and each coordinating anion. In the FA-DCM electrolyte, the mean Li⁺-anion interaction distance was calculated to be 49.0 Å, which is notably shorter than that observed in the FA-TTE electrolyte (71.0 Å). This closer spacing reflects more frequent but transient Li⁺-anion encounters, which facilitate efficient hopping rather than long-lived ion-pair drag.

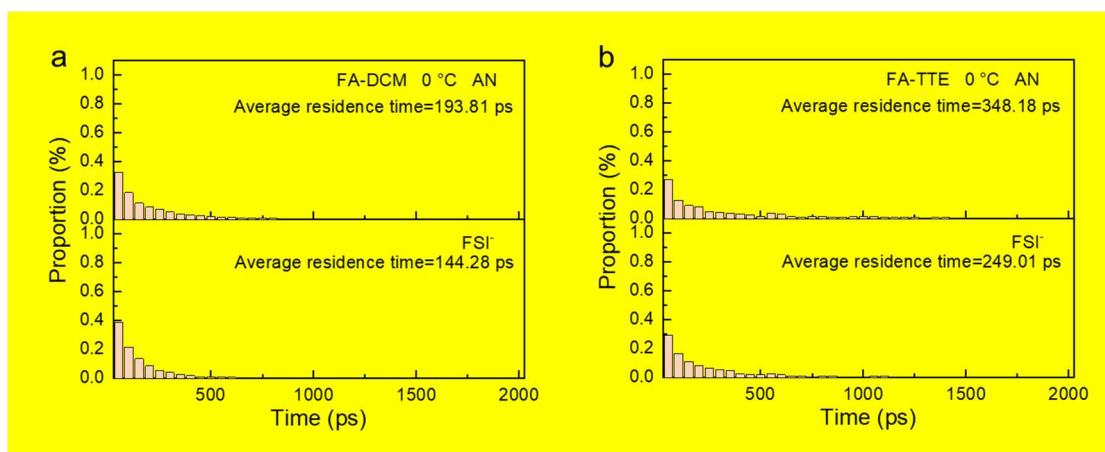


Supplementary Fig. 34 | Li⁺-anion correlated motion in FA-DCM electrolyte (a) and FA-TTE electrolyte (b) at 0 °C.

Importantly, this trend persists at lower temperature (0 °C), indicating that FA-DCM systems (45.86 Å) preserve favorable solvation dynamics even under kinetically demanding conditions, while the interaction between Li^+ -anions in the FA-TTE electrolyte become more heavily (226.13 Å), impeding the transfer of Li^+ .



Supplementary Fig. 35 | Evolution of Li^+ solvation environment in FA-DCM electrolyte (a) and FA-TTE electrolyte (b) from MD simulations at 273K. The vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li^+ in the simulation time of 2,000 ps.



Supplementary Fig. 36 | Residence time distribution of AN and FSI^- in FA-DCM electrolyte (a) and FA-TTE electrolyte (b) at 273K.

3. Under high-rate, transient clustering or "dynamic association" of Li^+ with multiple anions or solvents can occur due to forced ion migration. Has the possibility of such

transient cluster formation been examined in the FA-DCM system? This could impact fast-charging stability and uniformity of Li^+ transport at practical device scales.

Reply: We appreciate the reviewer's thoughtful comment. To examine the possibility of transient clustering under non-equilibrium conditions, we performed MD simulations with increased external electric fields to mimic forced Li^+ migration. The results reveal that as the electric field strength increases, the coordination number of Li^+ decreases, indicating that the immediate solvation environment partially collapses during rapid ion motion (Fig. R8). This dynamic behavior is consistent with the discrete hopping mechanism proposed, wherein Li^+ effectively transitions between solvation clusters rather than dragging anions along. Importantly, such transient coordination reduction facilitates faster and more uniform Li^+ transport, which underlies the excellent fast-charging performance observed experimentally in graphite||NMC811 full cells with FA-DCM electrolyte.

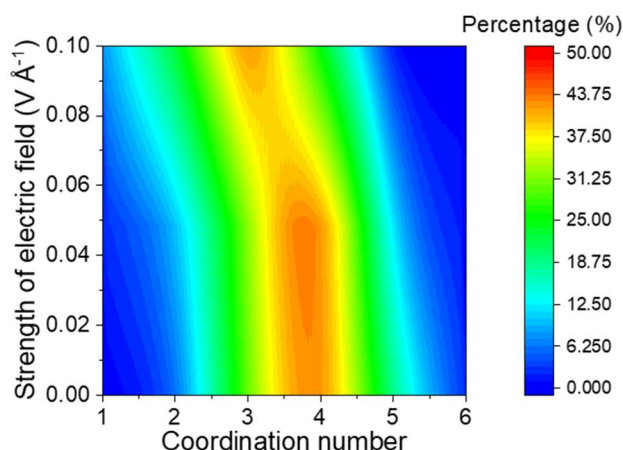


Fig. R8 | Electric field dependence of coordination number in FA-DCM electrolyte.

4. The proposed discrete Li^+ hopping mechanism is shown to be effective in model electrodes. However, in practical electrodes with higher porosity and tortuosity, ion transport limitations are often exacerbated. Could the authors comment on how the observed gains in Li^+ mobility with FA-DCM electrolyte scale with increasing electrode complexity, and whether additional strategies might be required to optimize performance in thick electrodes?

Reply: We appreciate the reviewer's insightful comment. To address the concern, we performed the widely accepted galvanostatic intermittent titration technique (GITT) measurements on graphite electrodes with both low and high areal loadings under small current to evaluate the Li^+ diffusion kinetics under varying electrode complexity (Fig. R9 and R10). Compared with steady-state electrochemical methods, GITT offers a more accurate and physically meaningful measurement of diffusion kinetics, as it decouples thermodynamic and kinetic contributions while preserving the integrity of the electrode–electrolyte interface. The calculated Li^+ diffusion coefficients reveal that the FA-DCM electrolyte ($4.432 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) maintains a diffusivity similar to the baseline carbonate electrolytes (BE, $4.289 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$; BEMP, $4.430 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) and FA-TTE electrolyte ($4.201 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) using graphite electrodes with a low areal loading of 0.53 mAh cm^{-2} (Fig. R9c, d). However, under the more demanding high-loading graphite conditions (3.40 mAh cm^{-2}), the FA-DCM electrolyte exhibits a higher diffusion coefficient ($4.579 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) than the other three electrolytes (FA-TTE, $4.069 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$; BE, $2.876 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$; BEMP, $3.225 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, Fig. R10c, d). This enhancement may be attributed to the superior electrode wettability of the FA-DCM electrolyte and the formation of a LiCl-LiF-rich SEI, which enables faster interfacial Li^+ migration compared to SEIs containing only LiF or organic components¹, thereby influencing the apparent diffusion coefficient.

We agree with the reviewer that in practical, extremely thick electrodes, additional optimization strategies beyond electrolyte design may be required. For example, tailoring the electrode microstructure to reduce tortuosity, optimizing conductive/binder networks, or adopting gradient porosity designs could synergistically enhance Li^+ accessibility. Importantly, our results demonstrate that the FA-DCM electrolyte provides a more favorable Li^+ transport environment, which is critical for achieving high performance in thick electrodes.

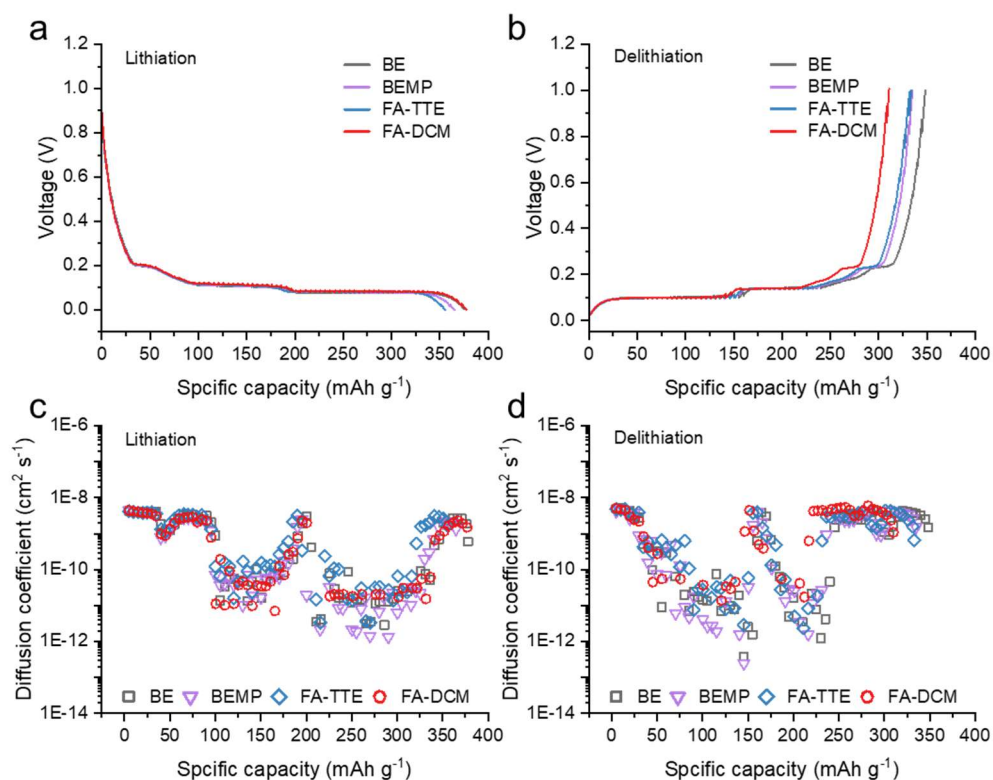


Fig. R9 | GITT evaluations of Li||graphite (0.53 mAh cm⁻²). Curves of the GITT measurements conducted after the 60th cycle of Li||graphite (0.53 mAh cm⁻²) cells with different electrolytes at 0.1 C during lithiation (a) and delithiation (b). The calculated chemical diffusion coefficients of Li⁺ during lithiation (c) and delithiation (d).

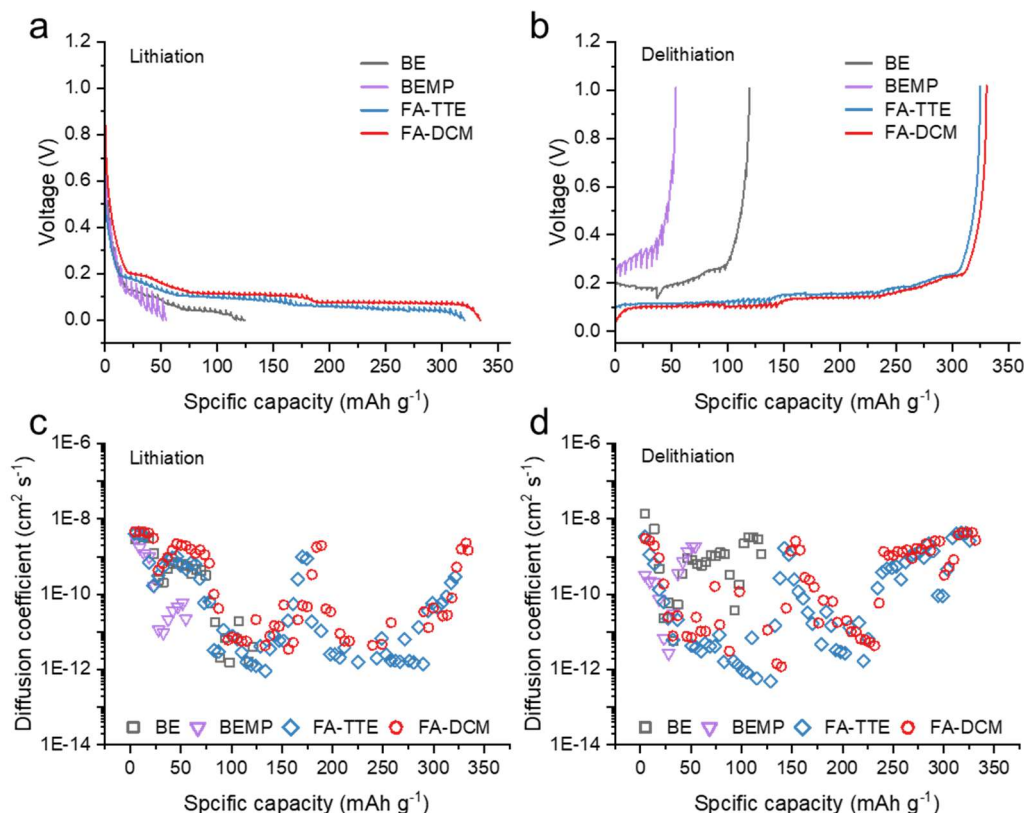
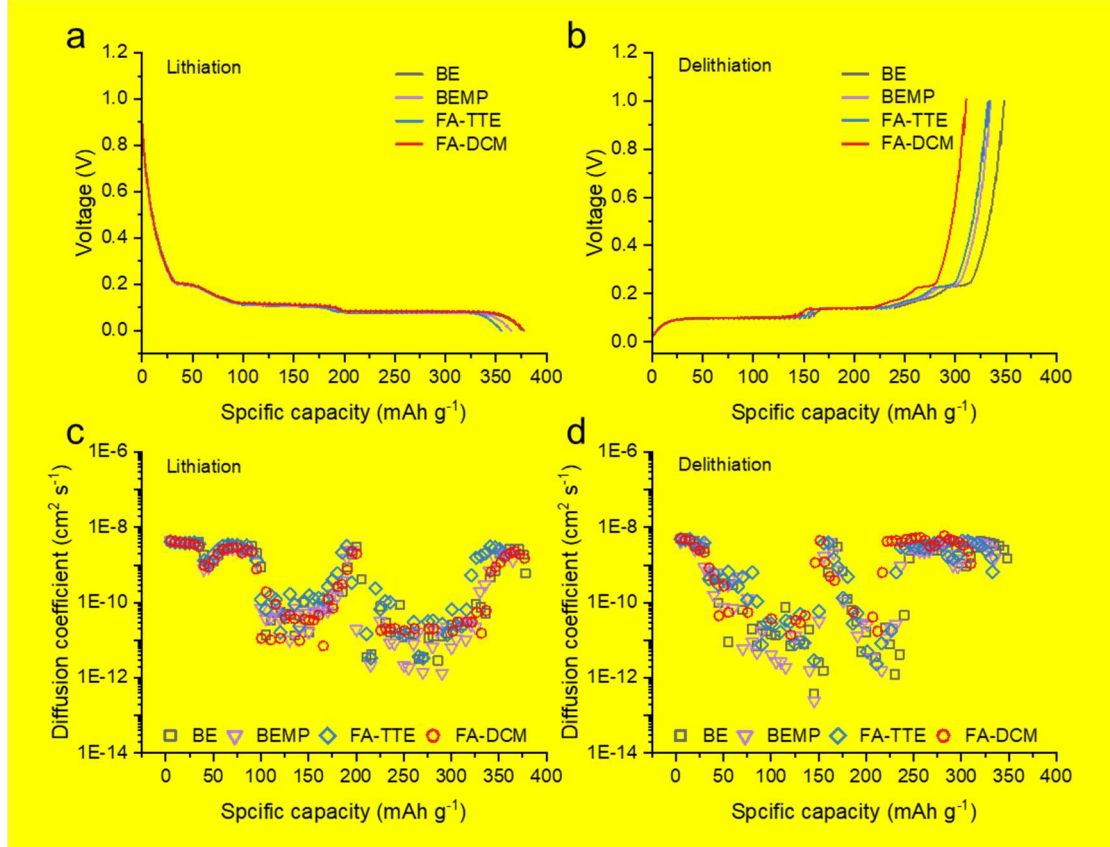


Fig. R10 | GITT evaluations of Li||graphite (3.40 mAh cm⁻²). Curves of the GITT measurements conducted after the 60th cycle of Li||graphite (3.40 mAh cm⁻²) cells with different electrolytes at 0.1 C during lithiation (a) and delithiation (b). The calculated chemical diffusion coefficients of the Li⁺ during lithiation (c) and delithiation (d).

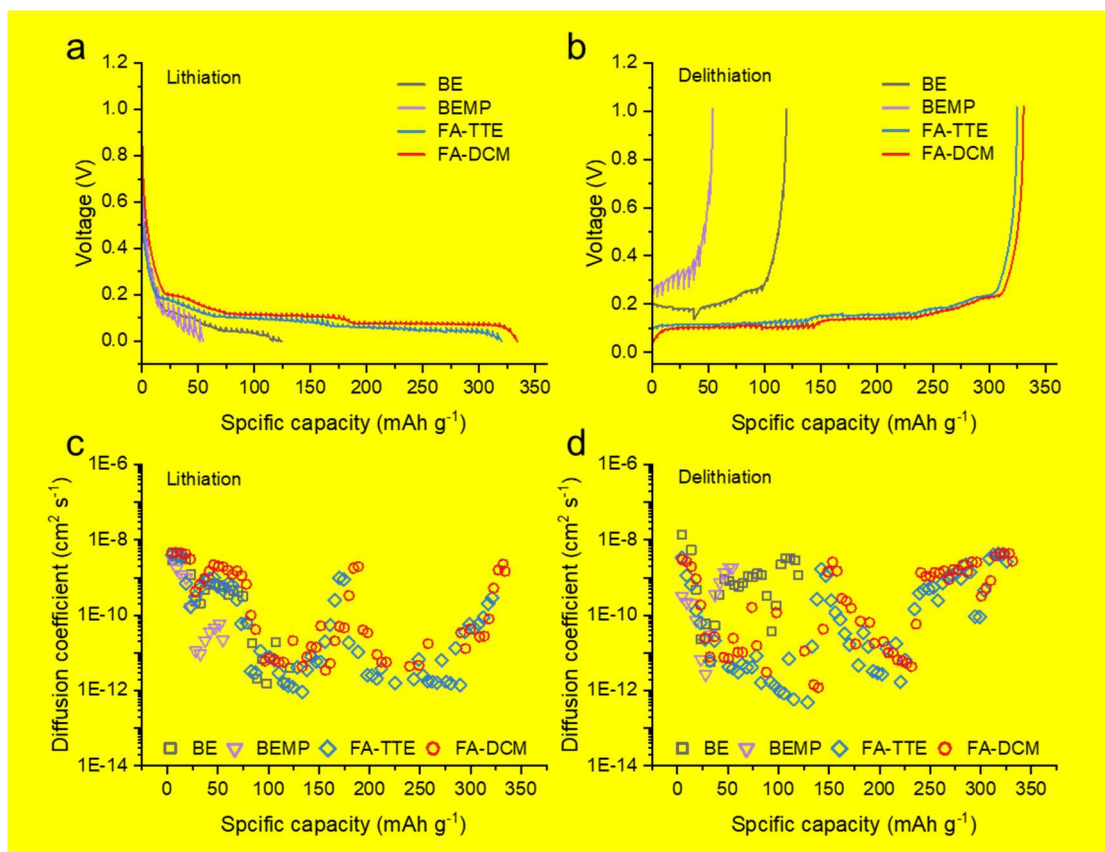
In the revised manuscript (Pages 16), we added the following sentences and highlighted them in yellow:

Moreover, in the low-rate GITT measurements, although the FA-DCM electrolyte exhibits a diffusion coefficient comparable to those of the other three electrolytes when tested with low-loading graphite electrodes, it demonstrates a higher diffusion coefficient under the more demanding high-loading graphite conditions (Supplementary Fig. 28, 29).

In the revised supporting information (Pages 49 and 50), we added Fig. R9 and R10 as Supplementary Fig. 28 and 29, respectively:



Supplementary Fig. 28 | GITT evaluations of Li||graphite (0.53 mAh cm⁻²). Curves of the GITT measurements conducted after the 60th cycle of Li||graphite (0.53 mAh cm⁻²) cells with different electrolytes at 0.1 C during lithiation (a) and delithiation (b). The calculated chemical diffusion coefficients of Li⁺ during lithiation (c) and delithiation (d).



Supplementary Fig. 29 | GITT evaluations of Li||graphite (3.40 mAh cm⁻²). Curves of the GITT measurements conducted after the 60th cycle of Li||graphite (3.40 mAh cm⁻²) cells with different electrolytes at 0.1 C during lithiation (a) and delithiation (b). The calculated chemical diffusion coefficients of Li⁺ during lithiation (c) and delithiation (d).

5. The manuscript highlights an increased population of mobile Li⁺ due to CIP formation. However, a quantitative analysis of the absolute concentration of free (solvent-separated) Li⁺ vs. CIP vs. AGG species is not fully presented. Could the authors provide such a quantitative breakdown from their MD simulations or experimental data to better support their transport enhancement claims?

Reply: We thank the reviewer for this constructive suggestion. In response, we have carried out a quantitative deconvolution of the Raman spectra to extract the relative populations of solvent-separated ion pairs (SSIPs), contact ion pairs (CIPs), and aggregates (AGGs) in the FA-HCE, FA-DCM, and FA-TTE electrolytes (Fig. R11). As

summarized in Table R1, FA-DCM exhibits the highest fraction of CIPs (69.7%) and the lowest fraction of AGGs (18.4%), compared to FA-HCE (CIPs, 33.3%, AGGs, 61.6%) and FA-TTE (CIPs, 33.4%, AGGs, 62.0%). This quantitative comparison demonstrates that DCM effectively disrupts large, immobilized clusters into smaller and more mobile solvation units, thereby increasing the population of transport-active Li^+ . Importantly, these distributions are consistent with molecular dynamics simulations, which independently reproduce the same trend in SSIP/CIP/AGG populations (Table R2). Together, this dual experimental-computational evidence strongly supports our claim that the CIP-dominated solvation structure in FA-DCM is central to its enhanced ion transport properties.

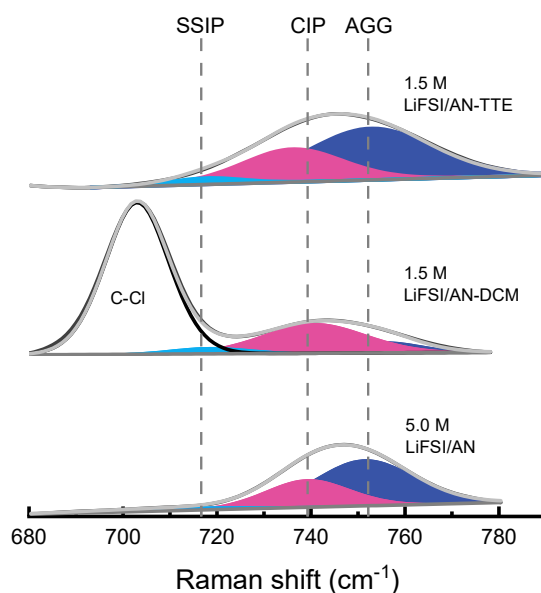


Fig. R11 | Raman spectra of different electrolytes in 680-780 cm^{-1} .

Table R1. Relative percentages of each cluster type for different electrolytes in Fig. R11.

Electrolyte	AGGs propotion (%)	CIPs propotion (%)	SSIP propotion (%)
FAHCE	61.6	33.3	5.1
FA-DCM	18.4	69.7	11.9
FA-TTE	62.0	33.4	4.6

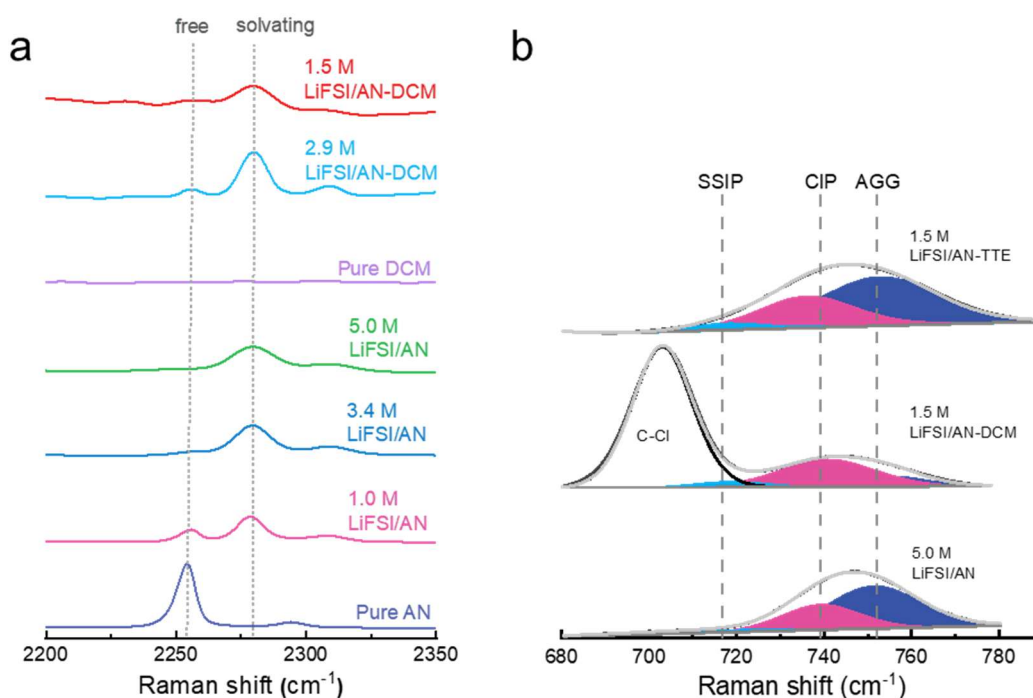
Table R2. Relative percentages of each cluster type for different electrolytes extracted from MD simulation.

FA-DCM	The number of Li ⁺ around FSI ⁻	0	1	2	3	4	5
	Propotion (%)	6	32	28	26	7	1
FAHCE	The number of Li ⁺ around FSI ⁻	0	1	2	3	4	5
	Propotion (%)	2	15	36	31	15	1
FA-TTE	The number of Li ⁺ around FSI ⁻	0	1	2	3	4	5
	Propotion (%)	5	17	38	24	14	2

In the revised manuscript (Pages 9 and 10), we added the following text and highlighted it:

Notably, the chemical environment of Li⁺ in FA-DCM electrolyte (-2.07 ppm) closely resembles that of FALCE electrolyte, as further confirmed by Raman spectroscopy (AGGs, 18.4%; CIPs, 69.7%; SSIPs, 11.9%; Supplementary Fig. 8). However, the FA-TTE electrolyte, due to the large molecular size and high dipole moment of TTE, fails to effectively regulate the solvation structure, retaining a strong Li⁺-anion coordination environment (-1.82 ppm) similar to FAHCE, which corresponds well with the distribution of AGGs (FA-TTE, 62.0%; FAHCE, 61.6%), CIPs, and SSIPs clusters obtained from the deconvolution of the Raman spectra (Supplementary Fig. 8b and Supplementary Table 4).

In the revised supporting information, we added Fig. R11 as Supplementary Fig. 8b (Pages 24) and added Table R1 as Supplementary Table 4 (Pages 9):



Supplementary Fig. 8 | Raman spectra of various concentrations of LiFSI/AN, FA-DCM and FA-TTE electrolytes in different ranges. 2200–2350 cm⁻¹ (a) and 680–780 cm⁻¹ (b), solvent-separated ion pair (SSIP, non-coordinated FSI⁻) locates at ~717 cm⁻¹, contact ion pair (CIP, one FSI⁻ bonding with one Li⁺) locates at 740 cm⁻¹, aggregate (AGG, one FSI⁻ bonding with two or more Li⁺) locates at 751 cm⁻¹.

In Supplementary Fig. 8a, the peak at ~2252 cm⁻¹, assigned to the C≡N stretching vibration of free AN molecules, gradually disappears with the increasing LiFSI concentration. Concurrently, a new peak emerges at ~2280 cm⁻¹, corresponding to the formation of Li⁺-AN coordinated interactions^{16–18}. In Supplementary Fig. 8b, upon adding DCM to the highly concentrated electrolyte (5.0 M LiFSI/AN), a significant portion of AGGs was converted into CIPs, confirming the regulatory role of DCM in tailoring solvation structures. **While with the addition of TTE, the fraction of AGG clusters increases, hindering the facilitation of fast ion conduction.**

Supplementary Table 4. Relative percentages of each cluster type for different electrolytes in Supplementary Fig. 8.

Electrolyte	AGGs propotion (%)	CIPs propotion (%)	SSIP propotion (%)
FAHCE	61.6	33.3	5.1
FA-DCM	18.4	69.7	11.9
FA-TTE	62.0	33.4	4.6

6. The presence of a large fraction of CIP species is proposed to enhance transport. However, CIP species may have different electrochemical stability compared to free solvated Li^+ . Could the authors analyze or comment on whether CIP species are more or less prone to side reactions at high voltages or under fast cycling?

Reply: We thank the reviewer for this important comment. While it is true that CIP species differ from free solvated Li^+ in terms of coordination environment, our results indicate that their presence in the FA-DCM electrolyte is not detrimental but in fact beneficial to electrochemical stability. The smaller solvation cluster of CIP provides better kinetics, thus facilitating the thorough reduction of anion and moderators to form LiF-rich SEI, which in turn stabilizes the interfacial reactions (Fig. R12).

Furthermore, as shown in Table R3, electrochemical impedance spectroscopy (EIS) further supports this conclusion that the FA-DCM electrolyte consistently exhibits lower interfacial resistance compared with BE and FA-TTE electrolytes at different rates. The excellent cycling stability up to 4.5 V coupled with remarkable fast-charging performance (Fig. 4f, g and Fig. 5b-f) collectively demonstrate that the prevalence of CIP species in FA-DCM simultaneously enables favorable interphase formation and rapid ion transport without introducing additional instability.

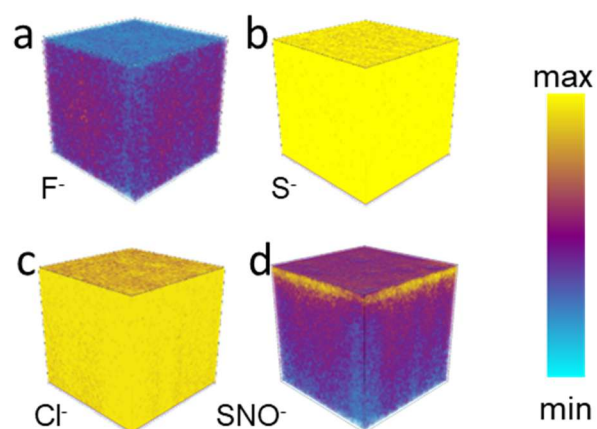


Fig. R12 | 3D-rendering images of F^- (a), S^- (b), Cl^- (c) and SNO^- (d) species on the graphite anode surface cycled in FA-DCM electrolyte

Table R3. Charge-transfer resistance (R_{ct}) and interfacial resistance (R_{SEI}) of Li||graphite cells using different electrolytes at different rates.

Electrolyte	Rate	2 C	4 C	6 C	8 C	10 C
BE	R_{ct} (Ohm)	5.290	8.420	8.790	9.500	12.85
	R_{SEI} (Ohm)	9.035	7.273	7.687	8.717	9.180
FA-TTE	R_{ct} (Ohm)	6.056	7.660	8.720	9.720	10.98
	R_{SEI} (Ohm)	1.438	1.990	3.116	4.651	4.637
FA-DCM	R_{ct} (Ohm)	0.367	0.237	0.366	0.754	0.544
	R_{SEI} (Ohm)	1.757	0.973	1.359	1.670	1.417

In the revised manuscript, we added the following text and highlighted it in yellow (Pages 22), we also added Fig. R12 as Fig. 6g-j (Pages 23):

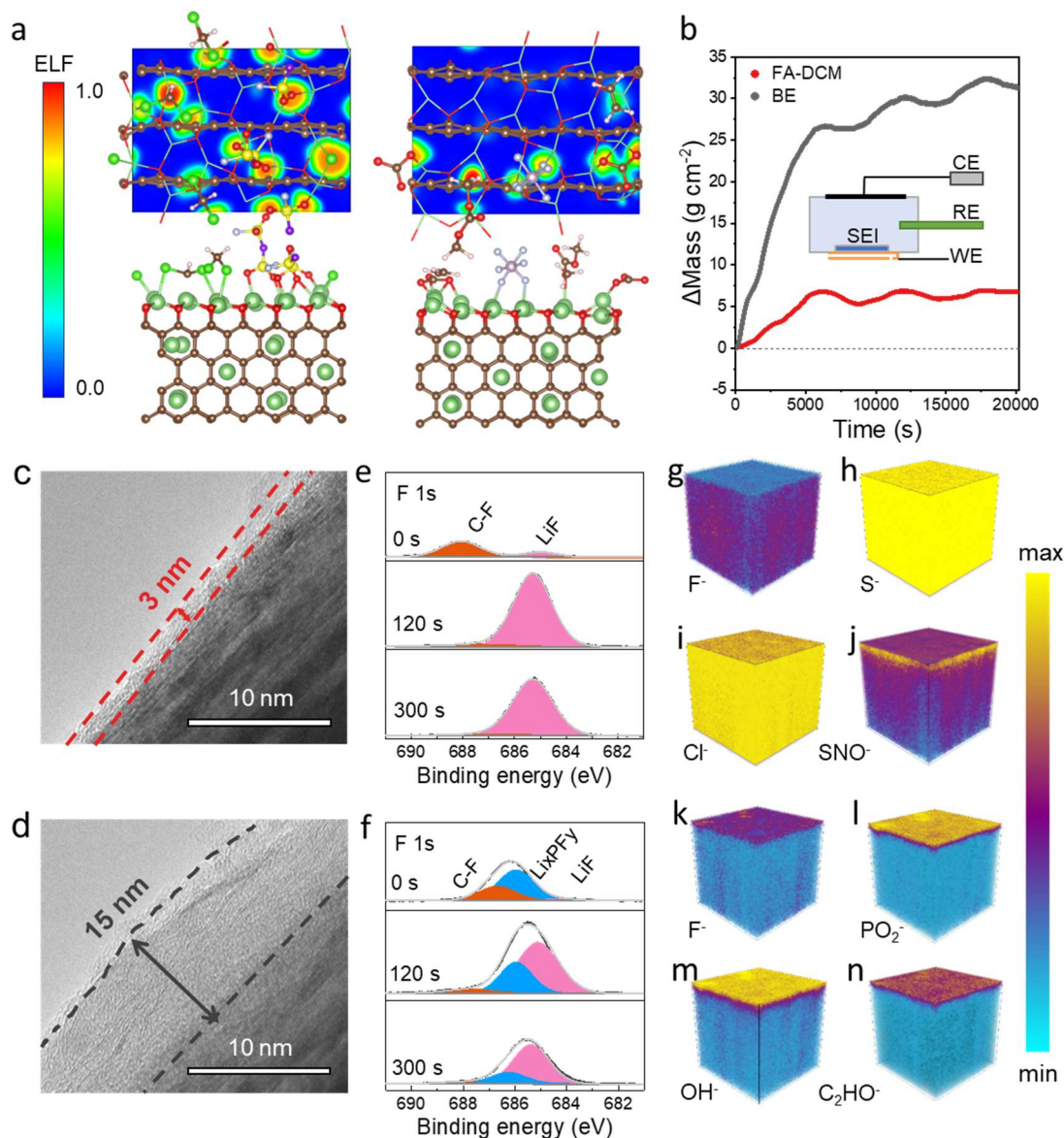


Fig. 6 | Electrolyte/electrode interphase analysis. **a**, The initial decomposition reaction of FA-DCM electrolyte (left) and BE electrolyte (right) on the graphite interphase calculated by *ab initio* molecular dynamics (AIMD). **b**, Electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) profiles of mass change (ΔMass) versus time. (Graphite-sputtered Cu chip resonator is used as the working electrode (WE) and Li metal is used as the counter electrode (CE) and reference electrode (RE). Cells are scanned at a potential window from the 1.50 V to 0.01 V at a scan rate of 5 mV s^{-1} . Frequency is taken at the 3rd overtone ($n = 3$). **c,d**, Transmission electron microscopy (TEM) images of graphite anodes recovered from Li||graphite cells using FA-DCM (**c**) and BE (**d**) electrolyte after 50 cycles, respectively. Scale bars, 10 nm. **e,f**, X-ray photoelectron spectroscopy (XPS) results of the SEI on cycled graphite in FA-DCM electrolyte (**e**) and BE electrolyte (**f**). **g-n**, 3D-rendering images of F⁻ (**g**), S⁻ (**h**), Cl⁻ (**i**) and SNO⁻ (**j**) species on the graphite anode surface cycled in FA-DCM electrolyte and F⁻ (**k**), PO₂⁻ (**l**), OH⁻ (**m**) and C₂HO⁻ (**n**) species on the graphite anode surface cycled in BE electrolytes.

Time of flight secondary ion mass spectrometry (TOF-SIMS) and in-depth X-ray photoelectron spectroscopy (XPS) analysis were conducted to comprehensively explore the chemical composition of electrode-electrolyte interphase (Fig. e-n, Supplementary Fig. 54-58). In the C 1s spectra (Supplementary Fig. 54a), the FA-DCM electrolyte initially forms carbonyl-containing organic compounds (C=O), which diminish with sputtering depth, whereas the LiF signal (Fig. 6f) and N- and S-containing derivatives (Supplementary Fig. 54d, e) increase, indicating preferential decomposition of FSI⁻ anions at graphite interphase. In addition, Cl 2p spectra further reveal the incorporation of LiCl species (Supplementary Fig. 54f), implying the formation of a dual-layer SEI architecture consisting of an inner LiF-LiCl-rich inorganic layer and an outer organic matrix⁵³⁻⁵⁵. 3D-rendering images obtained from TOF-SIMS further confirm the formation of this bilayer structure (Fig. g-j and Supplementary Fig. 57a), which facilitates efficient charge-transfer kinetics and mechanical robustness.

In the revised supporting information (Pages 12), we added Table R3 as Supplementary Table 7:

Supplementary Table 7. Charge-transfer resistance (R_{ct}) and interfacial resistance (R_{SEI}) of Li||graphite cells using different electrolytes at different rates.

Electrolyte	Rate	2 C	4 C	6 C	8 C	10 C
BE	R_{ct} (Ohm)	5.290	8.420	8.790	9.500	12.85
	R_{SEI} (Ohm)	9.035	7.273	7.687	8.717	9.180
FA-TTE	R_{ct} (Ohm)	6.056	7.660	8.720	9.720	10.98
	R_{SEI} (Ohm)	1.438	1.990	3.116	4.651	4.637
FA-DCM	R_{ct} (Ohm)	0.367	0.237	0.366	0.754	0.544
	R_{SEI} (Ohm)	1.757	0.973	1.359	1.670	1.417

7. The authors should include electrolyte stability and performance data at ≥ 60 °C to provide a complete view of the operational window.

Reply: We thank the reviewer for this valuable suggestion. We conducted additional high-temperature electrochemical tests. Specifically, graphite||NMC811 cells with different electrolytes were cycled at 60 °C within the voltage range of 2.8-4.3 V under rates ranging from 1 C to 6 C (each rate for five cycles). The graphite||NMC811 cells using FA-DCM electrolyte exhibited higher capacities (98.3 mAh g^{-1}) compared to the cells assembled with BE (58.5 mAh g^{-1}), BEMP (19.4 mAh g^{-1}) and FA-TTE electrolytes (89.5 mAh g^{-1}) at aggressive 6 C (Fig. R13). These results confirm that FA-DCM electrolyte maintains both electrochemical stability and fast Li^+ transport even at elevated temperature.

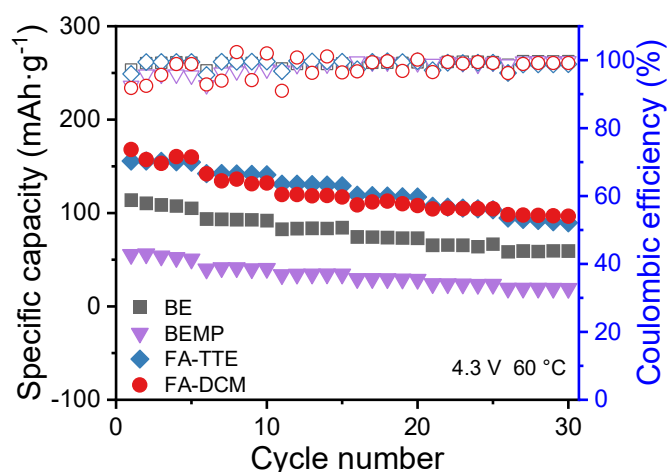


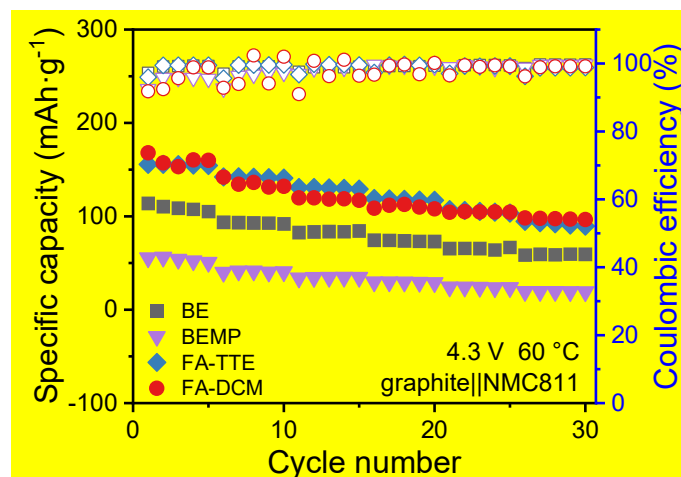
Fig. R13 | Rate performance of graphite||NMC811 cells with different electrolytes in the range of 2.8-4.3 V at 60 °C.

In the revised manuscript (Page 16), we added the following text and highlighted it in yellow:

The graphite||NMC811 full cell with FA-DCM electrolyte delivers a high capacity of 179.8 mAh g^{-1} at a demanding rate of 6 C—higher than that of FA-DCE (158.3 mAh g^{-1}) and FA-HFC (99.3 mAh g^{-1}) (Supplementary Fig. 31), more than double the capacity of the FA-TTE cell (83.2 mAh g^{-1}), and substantially outperforming cells using BE (66.7 mAh g^{-1}) and BEMP (63.9 mAh g^{-1}) electrolytes (Fig. 4f, 4g). This superior

performance extends to high-temperature conditions (Supplementary Fig. 32).

In the revised supporting information (Page 53), we added Fig. R13 as Supplementary Fig. 32:



Supplementary Fig. 32 | Rate performance of graphite||NMC811 cells with different electrolytes in the range of 2.8-4.3 V at 60 °C.

8. The discrete hopping mechanism enables fast bulk Li^+ transport, but may also lead to increased kinetic heterogeneity at the electrode interface (due to asynchronous arrival of Li^+ and counter-ions). Have the authors considered whether the enhanced bulk mobility introduces new challenges for interfacial reaction uniformity, SEI homogeneity, or lithium plating/stripping dynamics?

Reply: We appreciate the reviewer's insightful comment regarding potential interfacial kinetic heterogeneity associated with the discrete Li^+ hopping transport mechanism. To address this, we carried out additional MD simulations under applied electric fields ($E=0.1 \text{ V } \text{\AA}^{-1}$) to directly probe the interfacial behavior of Li^+ and FSI $^-$ in the FA-DCM electrolyte, in comparison with the FA-TTE electrolyte (Fig. R14). The horizontal axis in the Fig. R14 represents the time at which the electric field is applied, after the system has reached equilibrium. The relative number density shown in the Fig. R14 is normalized with respect to the average value of the entire electrolyte system.

Our simulations reveal that in FA-DCM, Li^+ ions indeed migrate rapidly toward

the anode interface, consistent with the enhanced bulk mobility. Meanwhile, although the FSI⁻ concentration at the interface initially decreases due to electrostatic exclusion, it quickly reaches a dynamic equilibrium rather than continuing to diminish. It is also worth noting that the number density of FSI⁻ at the interface is much higher than the average value of the entire electrolyte. This stabilization can be attributed to the rapid accumulation of Li⁺ ions, which effectively screens the interfacial electric field and stabilizes the anion distribution at the interface, thereby suppressing interfacial heterogeneity. As a result, the interfacial environment remains relatively stable instead of exhibiting increasing kinetic heterogeneity.

Furthermore, the observed Li⁺/FSI⁻ distributions suggest that the accelerated Li⁺ transport in FA-DCM does not compromise interfacial uniformity and SEI homogeneity. The balanced arrival of Li⁺ and counter-ions under field conditions supports the formation of a compact and LiF-LiCl-rich SEI, as evidenced by our experimental characterizations (referred to Fig. R12). Both simulation and experimental evidence indicate that the enhanced bulk mobility provided by discrete hopping does not introduce new interfacial instabilities, but instead contributes to improved interfacial robustness.

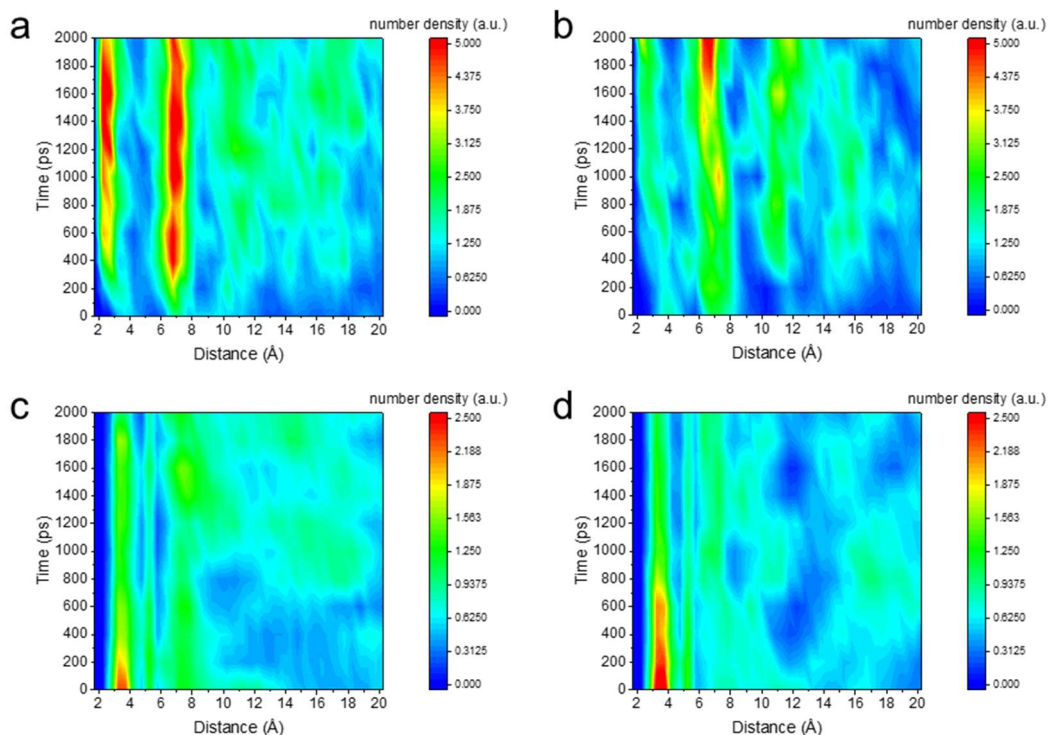


Fig. R14 | Li^+ evolution at the anode interface in FA-DCM electrolyte (a) and FA-DCM electrolyte (b). FSI^- evolution at the anode interface in FA-DCM electrolyte (c) and FA-DCM electrolyte (d), $E=0.1 \text{ V \AA}^{-1}$. The vertical axis in the figure represents the time at which the electric field is applied, following system equilibration, with electrode slabs positioned at both ends of the electrolyte region along the Z-axis. The relative number density shown in the figure is normalized with respect to the average value of the entire electrolyte system.

In the revised manuscript (Page 13 and 14), we added the following text and highlighted it in yellow:

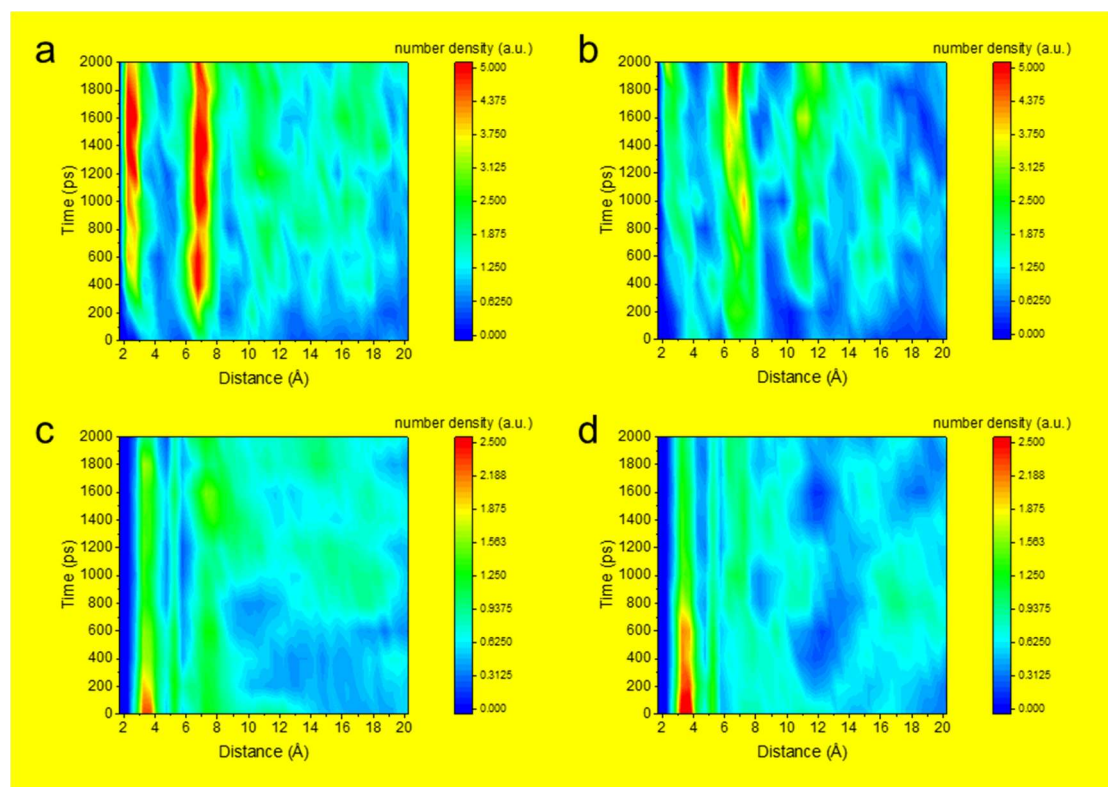
Moreover, to approximate practical conditions, we applied an electric field ($E=0.1 \text{ V \AA}^{-1}$) in the simulations to further clarify the solvation dynamics of the electrolyte under non-equilibrium states. Notably, the interfacial environment remains relatively stable instead of exhibiting increasing kinetic heterogeneity in FA-DCM electrolyte (Supplementary Fig. 17),

In the revised computational method, we added the following text and highlighted it in

yellow (Page 35):

To investigate the effects of electric field and temperature, simulations were conducted under various electric field strengths and temperatures, while all other simulation parameters remained consistent with the procedures described above.

In the revised supporting information (Page 36 and 37), we added the following text and highlighted it in yellow, we also added Fig. R14 as Supplementary Fig. 17:



Supplementary Fig. 17 | Li^+ evolution at the anode interface in FA-DCM electrolyte (a) and FA-TTE electrolyte (b). FSI^- evolution at the anode interface in FA-DCM electrolyte (c) and FA-TTE electrolyte (d), $E=0.1 \text{ V \AA}^{-1}$. The vertical axis in the figure represents the time at which the electric field is applied, following system equilibration, with electrode slabs positioned at both ends of the electrolyte region along the Z-axis. The relative number density shown in the figure is normalized with respect to the average value of the entire electrolyte system.

MD simulations were carried out under applied electric fields ($E=0.1 \text{ V \AA}^{-1}$) to directly probe the interfacial behavior of Li^+ and FSI^- in the FA-DCM electrolyte, in comparison

with the FA-TTE electrolyte. The horizontal axis in the Supplementary Fig. 17 represents the time at which the electric field is applied, after the system has reached equilibrium. The relative number density shown in the figure is normalized with respect to the average value of the entire electrolyte system.

Our simulations reveal that in FA-DCM, Li^+ ions indeed migrate rapidly toward the anode interface, consistent with the enhanced bulk mobility. Meanwhile, although the FSI^- concentration at the interface initially decreases due to electrostatic exclusion, it quickly reaches a dynamic equilibrium rather than continuing to diminish. It is also worth noting that the number density of FSI^- at the interface is much higher than the average value of the entire electrolyte. This stabilization can be attributed to the rapid accumulation of Li^+ ions, which effectively screens the interfacial electric field and stabilizes the anion distribution at the interface, thereby suppressing interfacial heterogeneity. As a result, the interfacial environment remains relatively stable instead of exhibiting increasing kinetic heterogeneity.

Closing remarks

We would like to express our gratitude to Reviewer #1 for dedicating their time to reviewing our paper and providing valuable comments. The reviewer's detailed suggestions significantly improved the presentation and clarity of our paper.

Reviewer #2 (Remarks to the Author):

This manuscript presents a well-executed and insightful study on electrolyte design for lithium ion batteries operating under extreme low temperatures. The authors propose a descriptor driven strategy using a small, low-dipole moment molecule (DCM) to reorganize the Li^+ solvation sheath and enable fast ion transport via a discrete hopping mechanism. The manuscript demonstrates excellent low-temperature cycling performance, including 1.0 Ah pouch cell operation at $-50\text{ }^{\circ}\text{C}$, which is rare in the field. The study is highly relevant to the development of practical, high-performance batteries for cold environments and fast-charging applications. The experimental design is thorough, and the combination of molecular simulations, spectroscopy, and full-cell validation provides a strong foundation for the claims. However, several aspects require clarification and expansion before publication.

Reply: We sincerely thank Reviewer #2 for the highly encouraging and constructive evaluation of our manuscript. We are very pleased that the reviewer recognizes the novelty of our descriptor-driven electrolyte design, the robustness of our combined theoretical and experimental approach, and the significance of the demonstrated low-temperature pouch cell performance. At the same time, we greatly appreciate the reviewer's thoughtful suggestions for clarification and expansion, which we believe will substantially improve the overall clarity, rigor, and impact of the study. We have carefully addressed each of these comments in the revised version of the manuscript, and we hope that our responses and revisions will satisfactorily resolve the reviewer's concerns.

1. The proposed descriptor $D=C/(\mu\cdot V)$ is central to the screening of suitable moderator molecules. However, it remains unclear whether this parameter has been quantitatively correlated with experimentally observed or simulated transport properties. Could the authors provide a quantitative correlation (e.g., regression analysis, R^2 value) between the D value and key ion transport parameters such as ionic conductivity, diffusion coefficient, or Li^+ residence time?

Reply: We thank the reviewer for highlighting this important point. To quantitatively validate the proposed descriptor $D=C/(\mu \cdot V)$, we plotted the correlation between D values and the average Li^+ residence times (both with AN and FSI^-) obtained from MD simulations (Fig. R15a, b). As shown, a negatively correlated linear function relationship is observed: larger D values correspond to shorter residence times, in agreement with our theoretical framework. Pearson's correlation analysis yields $r=-0.785$ for AN and $r=-0.894$ for FSI^- , confirming a strong negative correlation between the descriptor and Li^+ solvation dynamics. While the known dielectric constant does not exhibit a strong linear correlation with solvation dynamics, indicating that these parameters alone are insufficient to capture the complex interplay ion-anion-solvent interactions (Fig. R15c, d). This quantitative analysis supports the predictive capability of the proposed D value in capturing key ion transport characteristics.

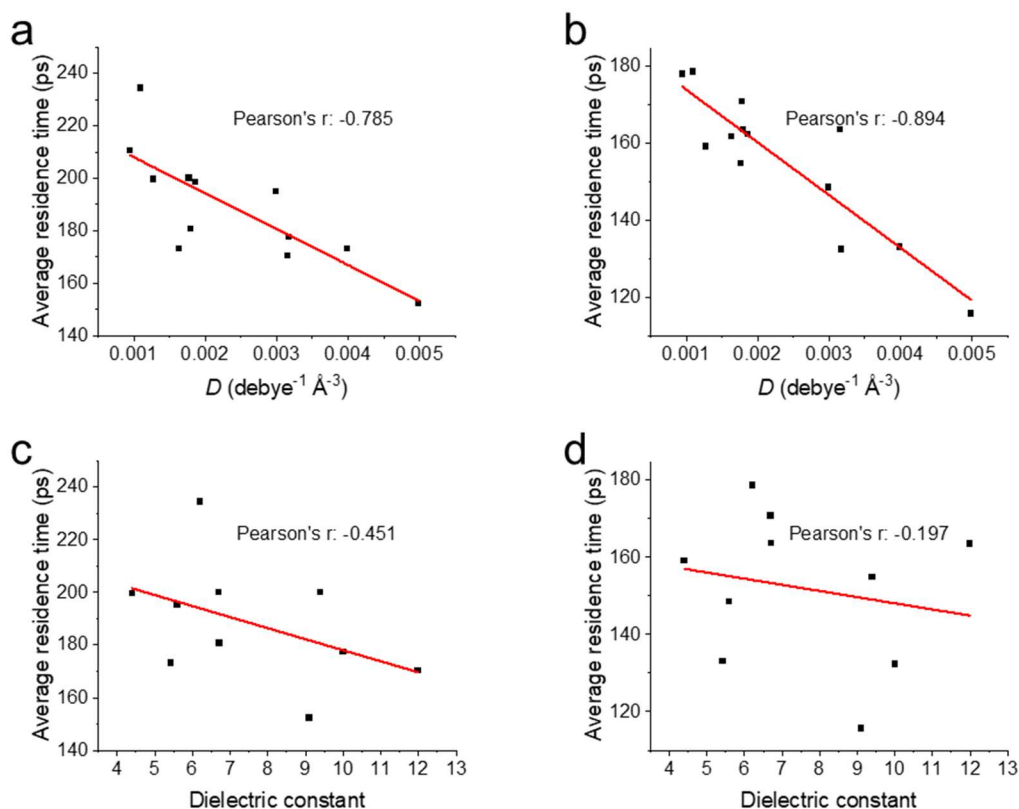
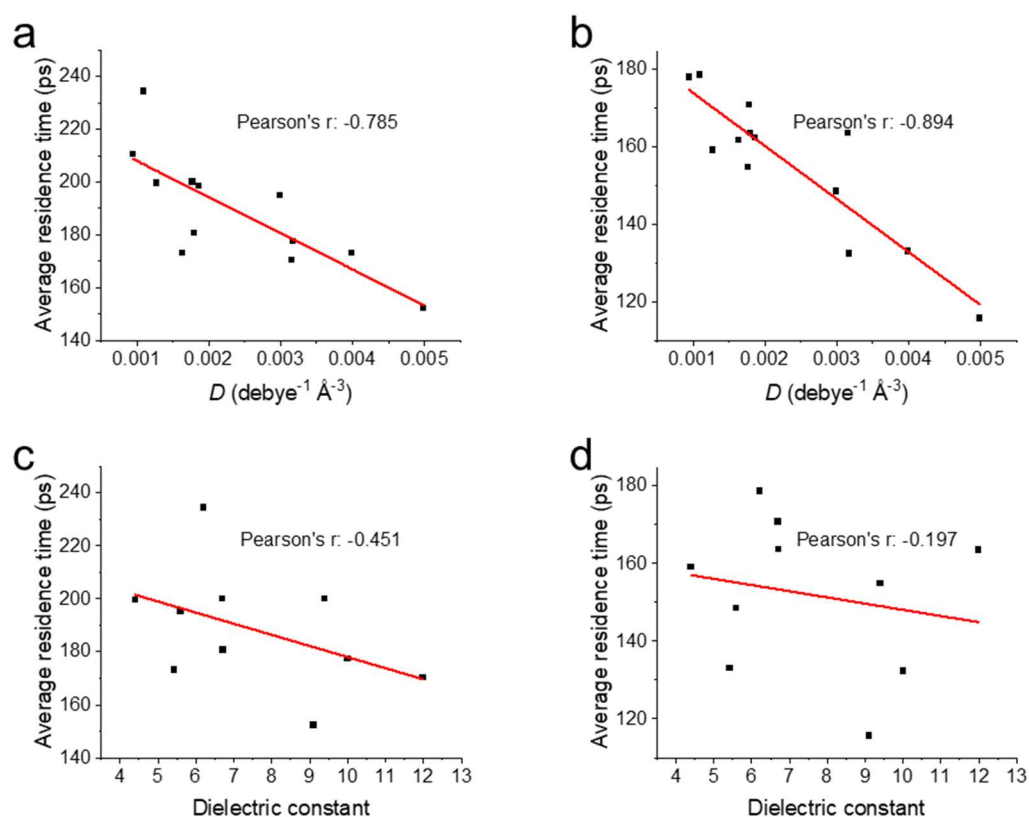


Fig. R15 | Functional relationship between average residence time and the disintegration of solvation structures (D). AN (a) and FSI^- (b). Functional relationship between average residence time and dielectric constant. AN (c) and FSI^- (d).

In the revised manuscript (Page 12 and 13), we added the following sentence and highlighted it in yellow:

Such a linear inverse relationship between the D value and residence time corroborates the effectiveness of this descriptor in predicting ion transport properties (Supplementary Fig. 16).

In the revised supporting information (Page 34 and 35), we added the following sentence and highlighted it in yellow and added Fig. R15 as Supplementary Fig. 16:



Supplementary Fig. 16 | Functional relationship between average residence time and the disintegration of solvation structures (D). AN (a) and FSI $^{-}$ (b). Functional relationship between average residence time and dielectric constant. AN (c) and FSI $^{-}$ (d).

To quantitatively validate the proposed descriptor $D=C/(\mu \cdot V)$, we plotted the correlation between D values and the average Li $^{+}$ residence times (both with AN and

FSI⁻) obtained from MD simulations. As shown, a negatively correlated linear function relationship is observed: larger D values correspond to shorter residence times, in agreement with our theoretical framework. Pearson's correlation analysis yields $r=-0.785$ for AN and $r=-0.894$ for FSI⁻, confirming a strong negative correlation between the descriptor and Li⁺ solvation dynamics. This quantitative analysis supports the predictive capability of the proposed descriptor in capturing key ion transport characteristics. While the known dielectric constant does not exhibit a strong linear correlation with solvation dynamics, indicating that these parameters alone are insufficient to capture the complex interplay ion-anion-solvent interactions.

2. The manuscript claims that DCM does not coordinate with Li⁺, thereby contributing to the breakdown of large solvation clusters. However, the RDF analysis (Supplementary Fig. 24b) indicates possible Li-Cl interactions in the FA-DCM system. How do the authors reconcile this apparent interaction with their claim that DCM is a non-coordinating solvent? Could weak or transient coordination with Li⁺ affect the observed solvation structure or CIP/AGG behavior?

Reply: We thank the reviewer for this insightful comment. We would like to clarify that Supplementary Fig. 24b (Supplementary Fig. 47b, the revised version) shows ab initio molecular dynamics (AIMD) simulation results, reflecting the reactivity of the electrolyte at the graphite interface. The Li-Cl RDF results suggest the formation of LiCl at the electrolyte/graphite interface, rather than Li-Cl coordination. To further illustrate the coordination between Li and Cl, MD simulation was performed on the pure electrolyte system. The RDF curves of Li-Cl reveal no distinct first-shell peak or well-defined coordination plateau, which indicates DCM does not coordinate with Li⁺ (Fig. R16). Therefore, DCM serves as a non-coordinating solvent in the FA-DCM electrolyte by moderating the solvation environment, thereby promoting the disintegration of large Li⁺-anion clusters without directly coordinating to Li⁺.

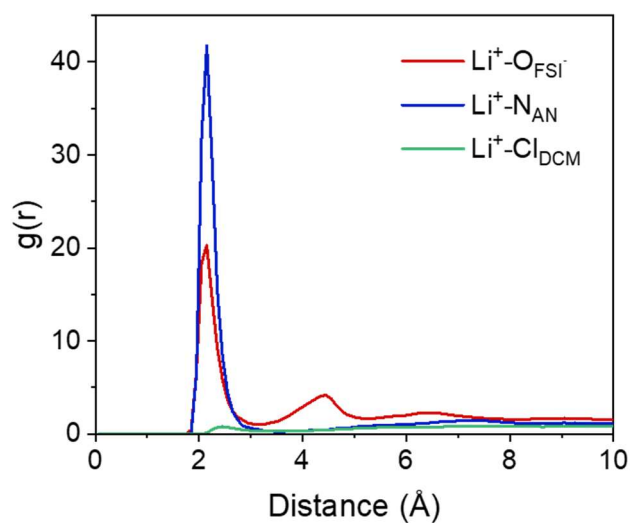


Fig. R16 | MD simulation. RDF curves of FA-DCM electrolyte Li^+ -O (FSI^-) species, Li^+ -N (AN) species and Li-Cl (DCM) species.

3. The proposed Li^+ transport mechanism involves discrete hopping between locally confined solvation domains. This mechanism is inferred from MD simulations showing reduced residence time and increased RMS displacement. Have the authors conducted, or could they consider, experimental validation of this hopping transport mechanism using techniques such as PFG-NMR, isotopic tracer analysis, or neutron scattering?

Reply: We thank the reviewer for this insightful suggestion. We fully agree that direct experimental validation of the proposed hopping-dominated Li^+ transport mechanism is essential. While advanced techniques such as PFG-NMR, isotopic tracer analysis, and neutron scattering are indeed powerful, they are not readily accessible within the scope of this study due to instrumental limitations and the extensive requirements for specialized facilities.

Instead, we employed diffusion ordered spectroscopy (DOSY) NMR, which provides self-diffusion coefficients for different nuclear species within the same electrolyte. Importantly, DOSY NMR can serve as a practical alternative to PFG-NMR, since both methods rely on pulsed field gradient approaches to probe molecular diffusion. By analyzing the diffusion of ^1H , ^7Li and ^{19}F in FA-DCM, FA-TTE and BE

electrolytes, we directly compared the mobilities of solvent molecules, Li^+ and anions (Fig. R17). The self-diffusion coefficients obtained by DOSY NMR of Li^+ , anions and solvent molecules in FA-DCM electrolyte ($3.330 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ of Li^+ , $1.030 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ of FSI^- , $3.825 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ of AN, $1.267 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ of DCM) are higher than those of FA-TTE electrolyte ($1.133 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ of Li^+ , $4.268 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ of FSI^- , $1.514 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ of AN, $9.657 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ of TTE), suggesting the faster Li^+ transport in FA-DCM electrolyte (Table R4).

These experimental findings are in excellent agreement with our MD simulations, which showed reduced Li^+ residence times ($\sim 152.26 \text{ ps}$ at 298 K for AN and $\sim 115.66 \text{ ps}$ at 298 K for FSI^- , Fig. 3c, e) and enhanced root mean square (RMS) displacement (Li^+ exhibits a RMS displacement of $11.7 \text{ \AA}$ over $3,000 \text{ ps}$ at $-40 \text{ }^\circ\text{C}$, Fig. 5a) due to hopping between compact solvation domains, mutually reinforcing evidence for the proposed Li^+ discrete hopping transport mechanism.

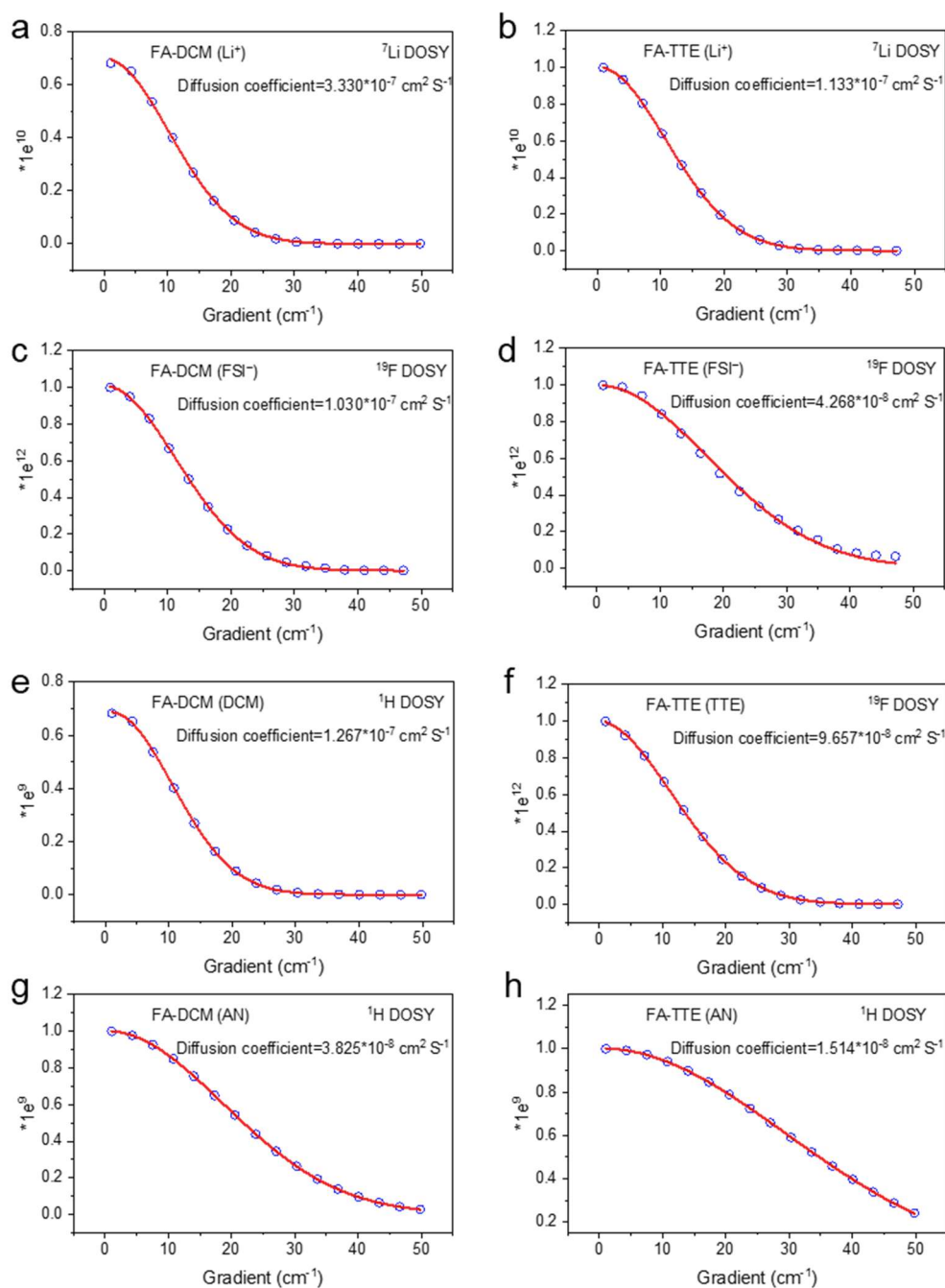


Fig. R17 | Self-diffusion coefficient measurement of different electrolytes. ⁷Li DOSY NMR spectrum of FA-DCM (a) and FA-TTE electrolyte (b). ¹⁹F DOSY NMR spectra of FA-DCM (c) and FA-TTE electrolyte (d, f). ¹H DOSY NMR spectrum of FA-DCM (e, g) and FA-TTE electrolyte (h).

Table R4. Self-diffusion coefficient of different electrolytes at 25 °C.

Electrolyte	FA-DCM	FA-TTE
Self-diffusion coefficient (<i>D</i>) (cm ² s ⁻¹)	$D_{\text{Li}^+}=3.330*10^{-7}$	$D_{\text{Li}^+}=1.133*10^{-7}$
	$D_{\text{FSI}^-}=1.030*10^{-7}$	$D_{\text{FSI}^-}=4.268*10^{-8}$
	$D_{\text{AN}}=3.825*10^{-8}$	$D_{\text{AN}}=1.514*10^{-8}$
	$D_{\text{DCM}}=1.267*10^{-7}$	$D_{\text{TTE}}=9.657*10^{-8}$

In the revised manuscript, we added the following text (Page 10) and highlighted it in yellow:

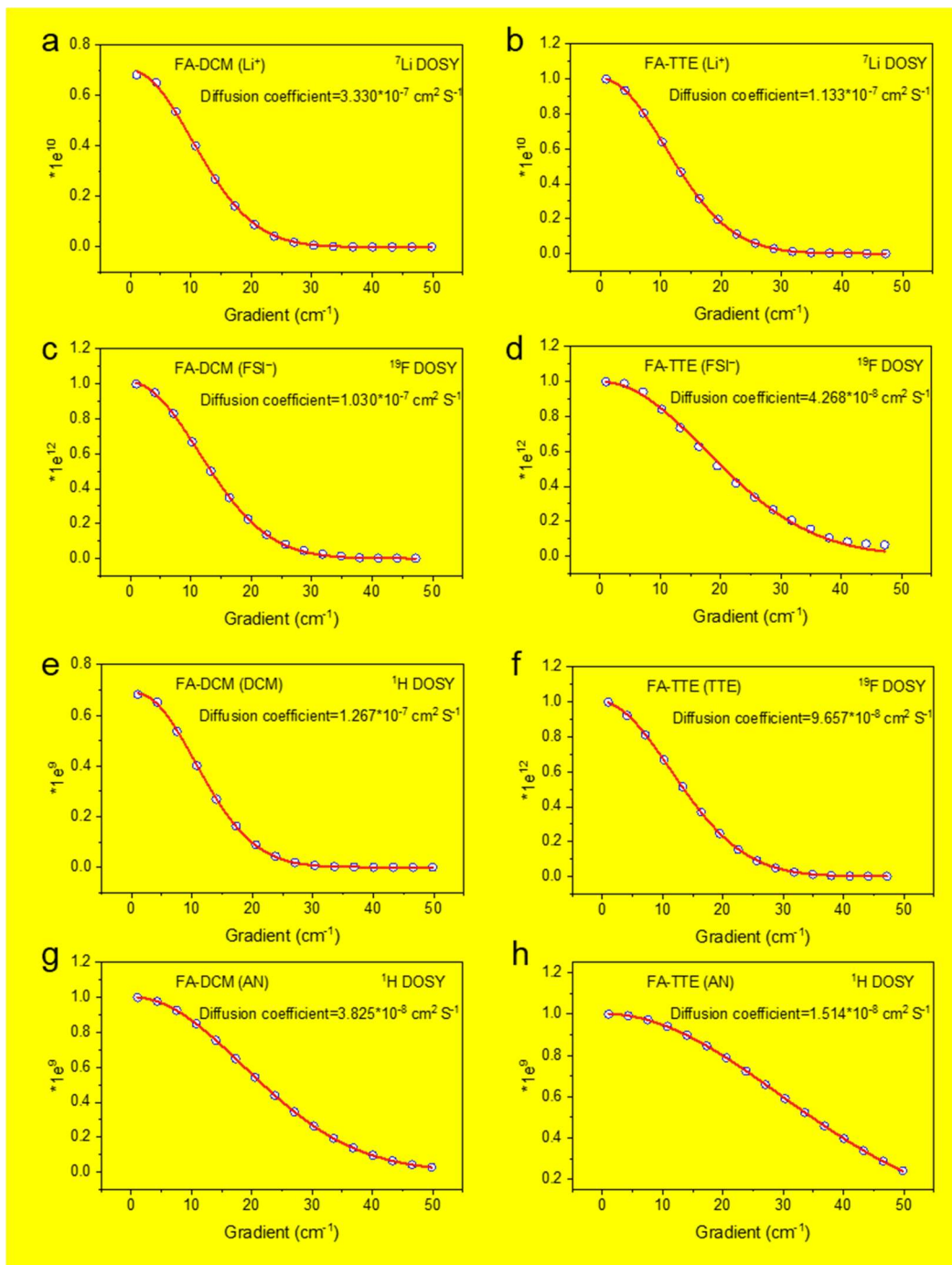
The results of diffusion ordered spectroscopy (DOSY) NMR corroborate the above results, the self-diffusion coefficients obtained by DOSY NMR of Li⁺ in FA-DCM electrolyte ($3.330*10^{-7}$ cm² s⁻¹) are higher than that of FA-TTE electrolyte ($1.133*10^{-7}$ cm² s⁻¹), suggesting the faster Li⁺ transport in FA-DCM electrolyte (Supplementary Fig. 10 and Supplementary Table 5).

In the revised method (Page 33 and 34), we added the following text:

The self-diffusion coefficients of different electrolytes were measured by ¹H, ⁷Li and ¹⁹F diffusion ordered spectroscopy (DOSY) NMR (Bruker 600MHz).

In the revised supporting information, we added the following text and highlighted it in yellow (Page 26 and 27), we also added Fig. R17 as Supplementary Fig. 10 (Page 26) and added Table R4 as Supplementary Table 5 (Page 10):

The self-diffusion coefficients obtained by DOSY NMR of FSI⁻ and solvent molecules in FA-DCM electrolyte ($1.030*10^{-7}$ cm² s⁻¹ of FSI⁻, $3.825*10^{-8}$ cm² s⁻¹ of AN, $1.267*10^{-7}$ cm² s⁻¹ of DCM) are higher than those of FA-TTE electrolyte ($4.268*10^{-8}$ cm² s⁻¹ of FSI⁻, $1.514*10^{-8}$ cm² s⁻¹ of AN, $9.657*10^{-8}$ cm² s⁻¹ of TTE).



Supplementary Fig. 10 | Self-diffusion coefficient measurement of different electrolytes. ^7Li DOSY NMR spectrum of FA-DCM (a) and FA-TTE electrolyte (b). ^{19}F DOSY NMR spectra of FA-DCM (c) and FA-TTE electrolyte (d, f). ^1H DOSY NMR spectrum of FA-DCM (e, g) and FA-TTE electrolyte (h).

Supplementary Table 5. Self-diffusion coefficient of different electrolytes at 25 °C obtained by diffusion ordered spectroscopy NMR in Supplementary Fig. 10.

Electrolyte	FA-DCM	FA-TTE
Self-diffusion coefficient (D) ($\text{cm}^2 \text{ s}^{-1}$)	$D_{\text{Li}^+}=3.330*10^{-7}$	$D_{\text{Li}^+}=1.133*10^{-7}$
	$D_{\text{FSI}}=1.030*10^{-7}$	$D_{\text{FSI}}=4.268*10^{-8}$
	$D_{\text{AN}}=3.825*10^{-8}$	$D_{\text{AN}}=1.514*10^{-8}$
	$D_{\text{DCM}}=1.267*10^{-7}$	$D_{\text{TTE}}=9.657*10^{-8}$

4. DCM has a low boiling point and high volatility, which could pose risks for long-term cell performance and safety, especially in pouch-type configurations. Have the authors investigated the volatility-related stability of DCM-based electrolytes in sealed cells over prolonged storage or cycling? Were there any observations of gas evolution, electrolyte loss, or pressure accumulation?

Reply: We appreciate the reviewer's concern regarding the volatility and long-term stability of DCM-based electrolytes. To specifically address this point, we conducted systematic evaluations on graphite||NMC811 pouch cells cycled with different electrolytes. The volume change of the gas bags after cycled at 25°C and -40°C was obtained through the water displacement method and the results were summarized in Fig. R18.

Although FA-DCM electrolytes (19 mL) exhibited slightly more swelling compared to the carbonate-based systems (BE, 15mL; BEMP, 10mL) after cycling at 25 °C, however, the expansion of the gas bag of the pouch cell using the FA-DCM electrolyte was lower than that of FA-TTE electrolyte (21 mL). A similar situation also occurred after cycling at -40 °C (FA-DCM, 13 mL; BE, 9 mL; BEMP, 7 mL; FA-TTE, 24 mL). Also, the extent of gas evolution remained within the safe operational threshold, without noticeable electrolyte loss, leakage, or abnormal pressure accumulation throughout prolonged cycling, indicating that the FA-DCM system preserves safety under practical pouch-type configurations.

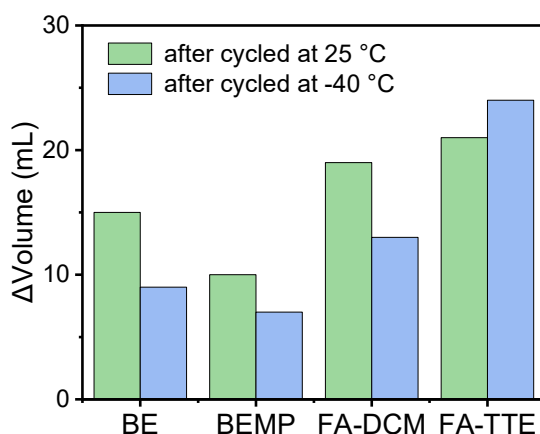
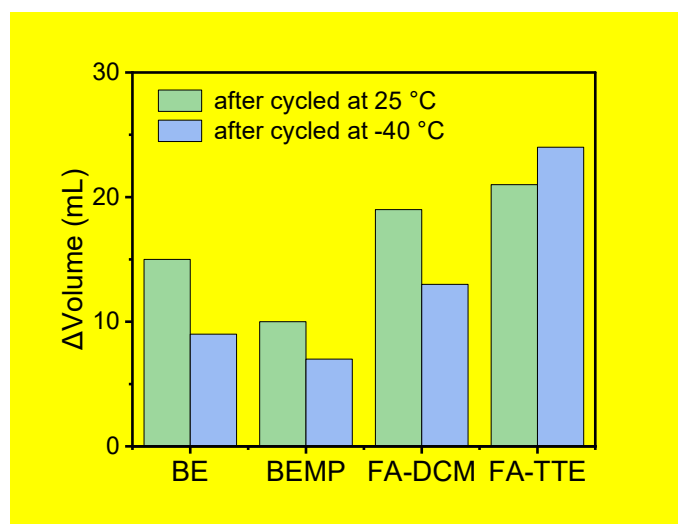


Fig. R18 | The change in volume of gas bag in the pouch cells before and after cycling in different electrolytes.

In the revised manuscript (Page 24), we added the following text and highlighted it in yellow:

It is worth noting that the toxicity and volatility of DCM limit its broader applicability, but the sealed cells using DCM-based electrolyte still demonstrated decent stability and capacity retention under extended cycling or storage (Supplementary Fig. 59-61). More importantly, as a moderator with small molecular size and low dipole moment, DCM successfully tunes the solvation structure, creating a more uniformly distributed and compact solvation clusters, which is essential for ultralow-temperature operation and fast charging. This success validates the feasibility of the concept and paves the way for future electrolytes designed on these principles to be both high-performing and environmentally benign.

In the revised supporting information (Page 81), we added Fig. R18 as Supplementary Fig. 59:



Supplementary Fig. 59 | The change in volume of gas bag in the pouch cells before and after cycling in different electrolytes.

5. XPS depth profiling (Supplementary Fig. 32) indicates a LiF- and LiCl-rich SEI structure, which is proposed to be beneficial for stable cycling. Can the authors provide a more quantitative analysis of the SEI composition? For example, what are the estimated thicknesses or relative volume ratios of the inorganic and organic layers within the SEI?

Reply: We thank the reviewer for this insightful comment. To provide a more quantitative understanding of the SEI composition, we analyzed the XPS depth profiles at a sputtering time of 300 s, where the atomic ratios reach a relatively stable state (Fig. 6e and Supplementary Fig. 54). Based on the atomic concentrations at this depth and the corresponding peak assignments to inorganic (like LiF, LiCl) and organic (like ROCO_2Li , polymeric carbonates) species, we estimated the relative contributions of the inorganic and organic fractions (Supplementary Fig. 32; the revised version, Supplementary Fig. 56). The detailed atomic composition and the calculated organic/inorganic ratio are summarized in Table R5. The results indicate an inorganic-to-organic ratio of ~ 2.4 , confirming that the SEI formed in the FA-DCM electrolyte is dominated by inorganic species (LiF and LiCl), which is consistent with its superior stability and ionic transport properties.

Table R5. The proportion of each atom in SEI and the fraction of organic and inorganic components after cycled in FA-DCM electrolyte.

Elements	N	O	C	S	F	Cl
Atom ratio (%)	3.30	12.48	9.25	4.56	25.9	9.04
Percentage of organic components (%)	0	38	100	0	0	55
Percentage of inorganic components (%)	100	62	0	100	100	45

In the revised supporting information, we added Table R5 as Supplementary Table 9 (Page 14), we also added the following text and highlighted it in yellow (Page 78):

Supplementary Table 9. The proportion of each atom in SEI and the fraction of organic and inorganic components after cycled in FA-DCM electrolyte.

Elements	N	O	C	S	F	Cl
Atom ratio (%)	3.30	12.48	9.25	4.56	25.9	9.04
Percentage of organic components (%)	0	38	100	0	0	55
Percentage of inorganic components (%)	100	62	0	100	100	45

To provide a more quantitative understanding of the SEI composition, we analyzed the XPS depth profiles at a sputtering time of 300 s, where the atomic ratios reach a

relatively stable state. Based on the atomic concentrations at this depth and the corresponding peak assignments to inorganic (like LiF, LiCl) and organic (like ROCO₂Li, polymeric carbonates) species, we estimated the relative contributions of the inorganic and organic fractions. The detailed atomic composition and the calculated organic/inorganic ratio are summarized in Supplementary Table 9. The results indicate an inorganic-to-organic ratio of ~2.4, confirming that the SEI formed in the FA-DCM electrolyte is dominated by inorganic species (LiF and LiCl), which is consistent with its superior stability and ionic transport properties.

6. The study mainly focuses on FA-DCM (high performance) and FA-TTE (poor performance), but Supporting Information includes other moderators with intermediate *D* values (e.g., FB, CLB). Have the authors evaluated the electrochemical performance of these intermediate-*D* systems? Do their results support the general applicability of the *D*-based screening model?

Reply: We thank the reviewer for raising this important point. To further validate the general applicability of the *D*-based screening model, we have investigated an additional electrolyte system using HFC (1,1,2,2,3,3,4-heptafluorocyclopentane) as the moderator, which exhibits an intermediate *D* value between DCM and TTE (electrolyte phase separation was observed upon addition of FB and CLB). Furthermore, to substantiate the universality of the *D* value as a selection parameter, we conducted both simulations and experiments on an electrolyte employing dichloroethane (DCE, with a higher *D* value than HFC, but lower than DCM) and evaluated the corresponding low-temperature and fast-charging performance of the graphite||NMC811 cells (Fig. R19).

According to Fig. R20, Fig. 2b, Supplementary Fig. 3, and Supplementary Fig. 4a, b, the dissociation capability of the solvation structures can be ranked as DCM, DCE, HFC, and TTE, in agreement with the corresponding order of their *D* values. Additionally, MD simulations show that the average Li⁺ residence time of 177.45 ps (AN) and 132.36 ps (FSI⁻) in the FA-DCE electrolyte, and 180.71 ps (AN) and 163.55 ps (FSI⁻) in the FA-HFC electrolyte. These values follow a consistent trend when

referenced against the FA-DCM and FA-TTE systems (Fig. R21-23).

Moreover, under 6 C charge/discharge conditions (Fig. R24), the cells using FA-DCM electrolyte retain 88.2% of its capacity at 1 C, outperforms FA-DCE (80.6%) and FA-HFC (53.1%), which in turn surpasses FA-TTE (43.7%). Similarly, as shown in Fig. R25, at -40 °C, graphite||NMC811 cells assembled with FA-DCM electrolyte deliver the highest capacity (126.7 mAh g⁻¹), while the cells using FA-DCE, FA-HFC electrolyte exhibit lower capacity of 116.6 mAh g⁻¹ and 107.0 mAh g⁻¹, respectively, and FA-TTE shows the poorest performance (75.1 mAh g⁻¹). This quantitative alignment between experimental performance and simulated solvation dynamics provides further support for the predictive capability of the *D*-based screening model. These new results confirm that the correlation between *D* and ion transport properties is not merely a phenomenon observed in isolated cases, but true generality across various systems, thereby reinforcing the broad applicability and robustness of the proposed descriptor.

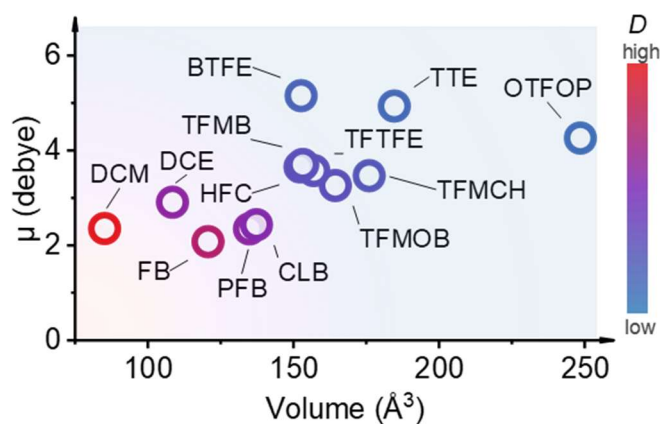


Fig. R19 | $\mu_{\text{moderator}}$ and $V_{\text{moderator}}$ for various moderators.

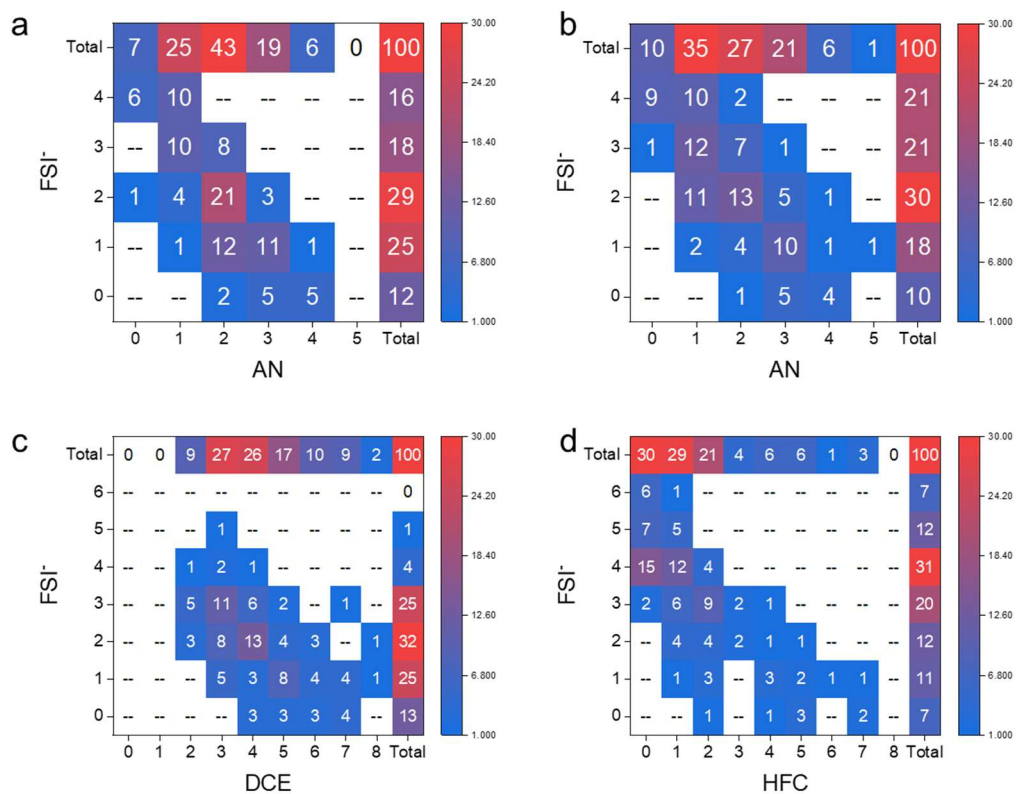


Fig. R20 | Heatmaps of Li^+ solvation sheath in different electrolytes. FA-DCE (a, c) and FA-HFC electrolyte (b, d).

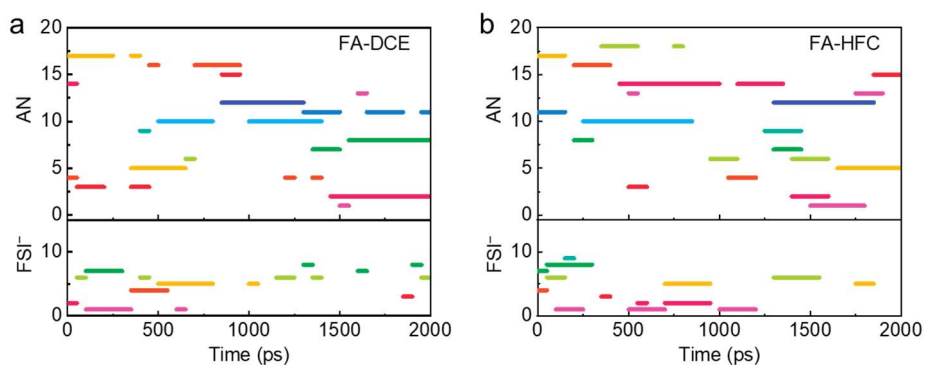


Fig. R21 | Evolution of Li^+ solvation environment in FA-DCE (a) and FA-HFC electrolyte (b) from MD simulations at 298 K. The vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li^+ in the simulation time of 2,000 ps.

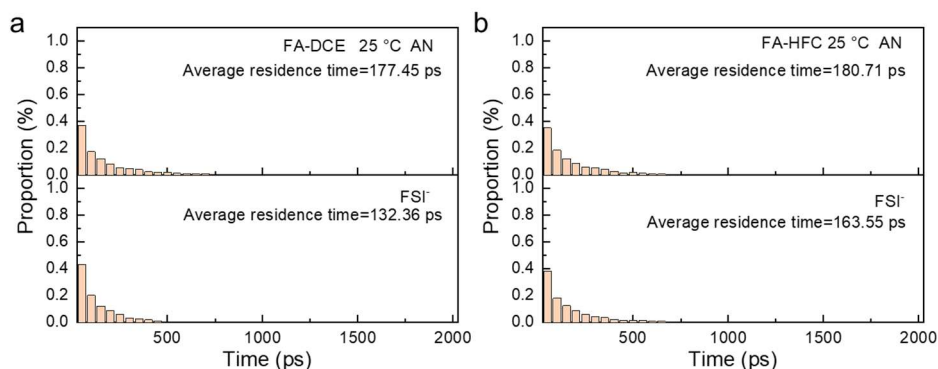


Fig. R22 | Residence time distribution of AN and FSI⁻ in FA-DCE (a) and FA-HFC electrolyte (b) at 298 K.

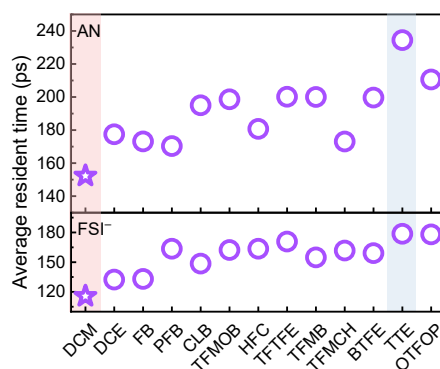


Fig. R23 | The average residence time of Li⁺ in LiFSI/AN-based electrolytes with different moderators.

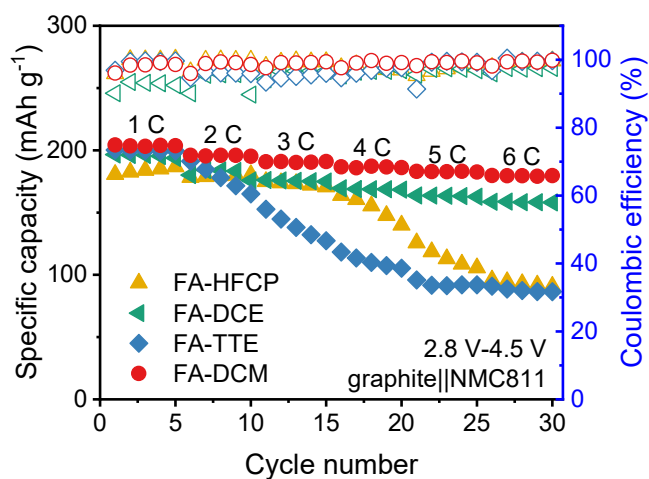


Fig. R24 | Rate performance of graphite||NMC811 cells with different electrolytes in the range of 2.8-4.5 V at 25 °C.

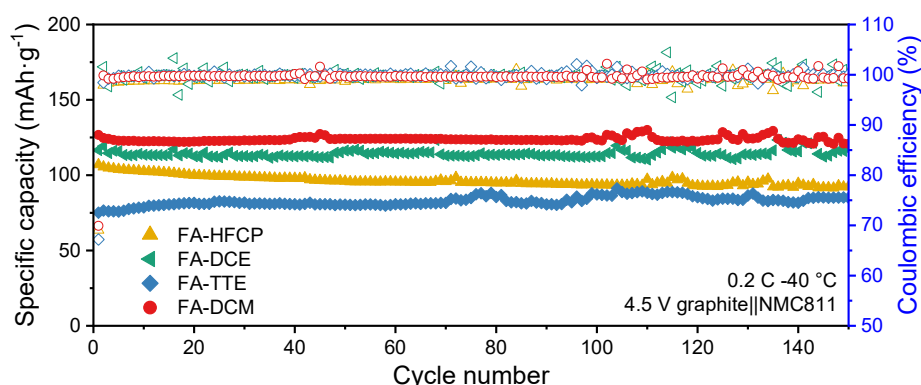


Fig. R25 | Cycling performance with different electrolytes in the range 2.8-4.5 V at 0.2 C under -40 °C.

In the revised manuscript, we added the following sentences and highlighted them, we also added Fig. R19 and Fig. R23 as Fig. 1c and Fig. 3e, respectively.

(Page 9)

Notably, the FA-DCM electrolyte exhibits the highest proportion of CIPs among the **thirteen** analyzed moderator-based electrolytes (Supplementary Fig. 4c-n and Fig. 6).

(Page 12)

Owing to its relatively high D value of dichloroethane (DCE), the 1.5 M LiFSI in an AN-DCE mixture (1:4, vol) (denoted as FA-DCE electrolyte) demonstrates a residence time close to that of FA-DCM (177.45 ps for AN and 132.26 ps for FSI) (Supplementary Fig.14a and Fig. 15f). In contrast, the 1.5 M LiFSI in an AN-1,1,2,2,3,3,4-heptafluorocyclopentane (HFC) mixture (1:4, vol) (denoted as FA-HFC electrolyte), with an intermediate D value, exhibits a significantly longer residence time (180.71 ps for AN and 163.55 ps for FSI) (Supplementary Fig.14b and Fig. 15g).

(Page 16)

The graphite||NMC811 full cell with FA-DCM electrolyte delivers a high capacity of 179.8 mAh g⁻¹ at a demanding rate of 6 C—**higher than that of FA-DCE (158.3 mAh g⁻¹)**

¹) and FA-HFC (99.3 mAh g⁻¹) (Supplementary Fig. 31), more than double the capacity of the FA-TTE cell (83.2 mAh g⁻¹), and substantially outperforming cells using BE

(Page 19)

The graphite||NMC811 full cells based on FA-DCE (large D value), FA-HFC (moderate D value), and FA-TTE (small D value) electrolytes reached 113.3 mAh g⁻¹, 102.4 mAh g⁻¹, and 78.6 mAh g⁻¹, respectively, providing experimental evidence for the universality of adopting the D value as a screening metric.

(Page 7)

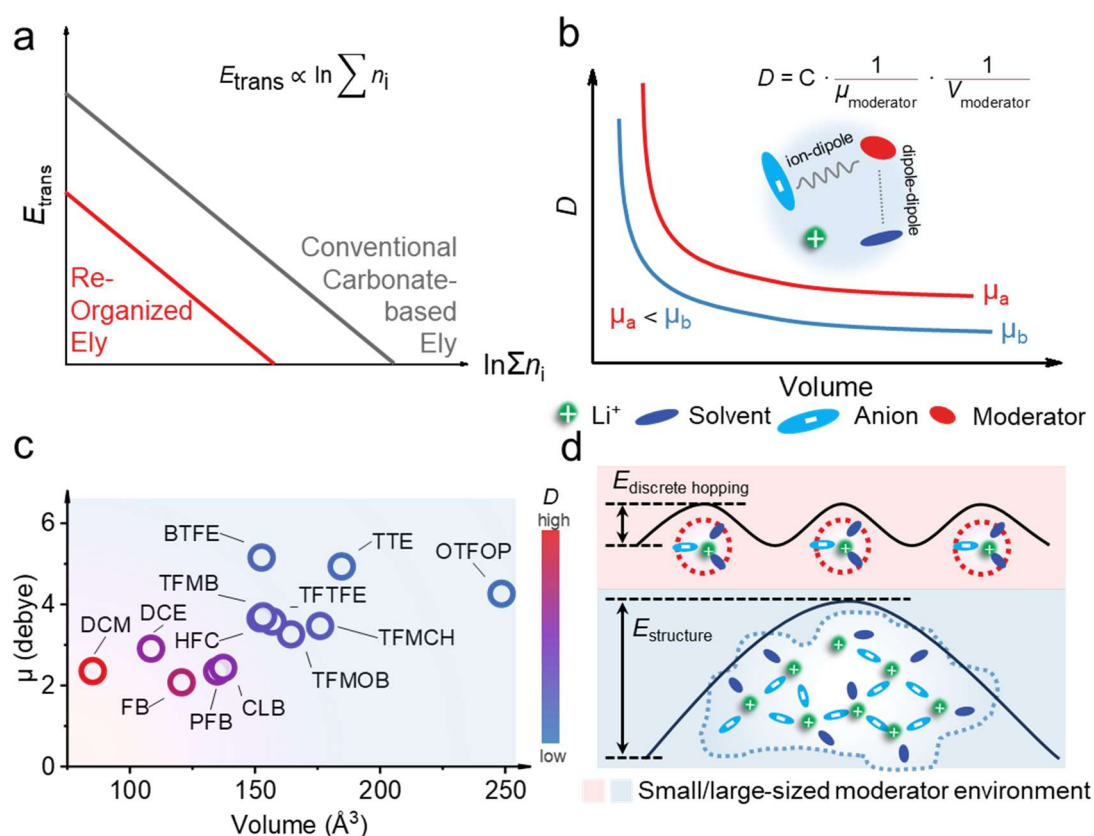


Fig. 1 | Moderator screening strategy. **a**, Variation of Li^+ transfer energy (E_{trans}) as a function of the natural logarithm of the total effective charge carriers ($\sum n_i$) **b**, Functional relationship between the disintegration of solvation structures (D) and moderator properties [dipole moment ($\mu_{\text{moderator}}$) and molecule volume ($V_{\text{moderator}}$)]. **c**, $\mu_{\text{moderator}}$ and $V_{\text{moderator}}$ for various moderators. **d**, Transfer energy barriers for discrete hopping mechanism and structure mechanism in small-sized and large-sized moderator environment, respectively.

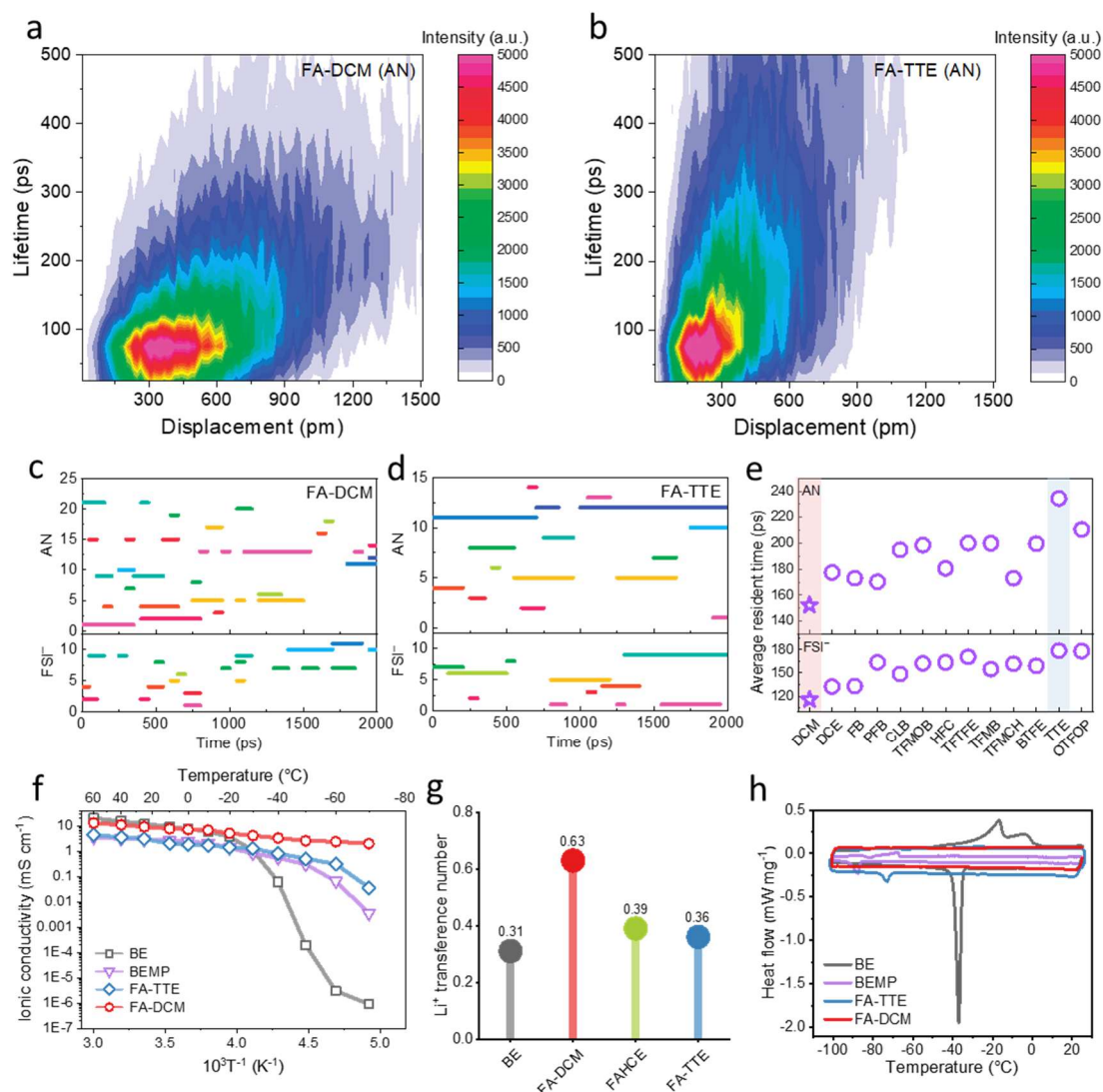
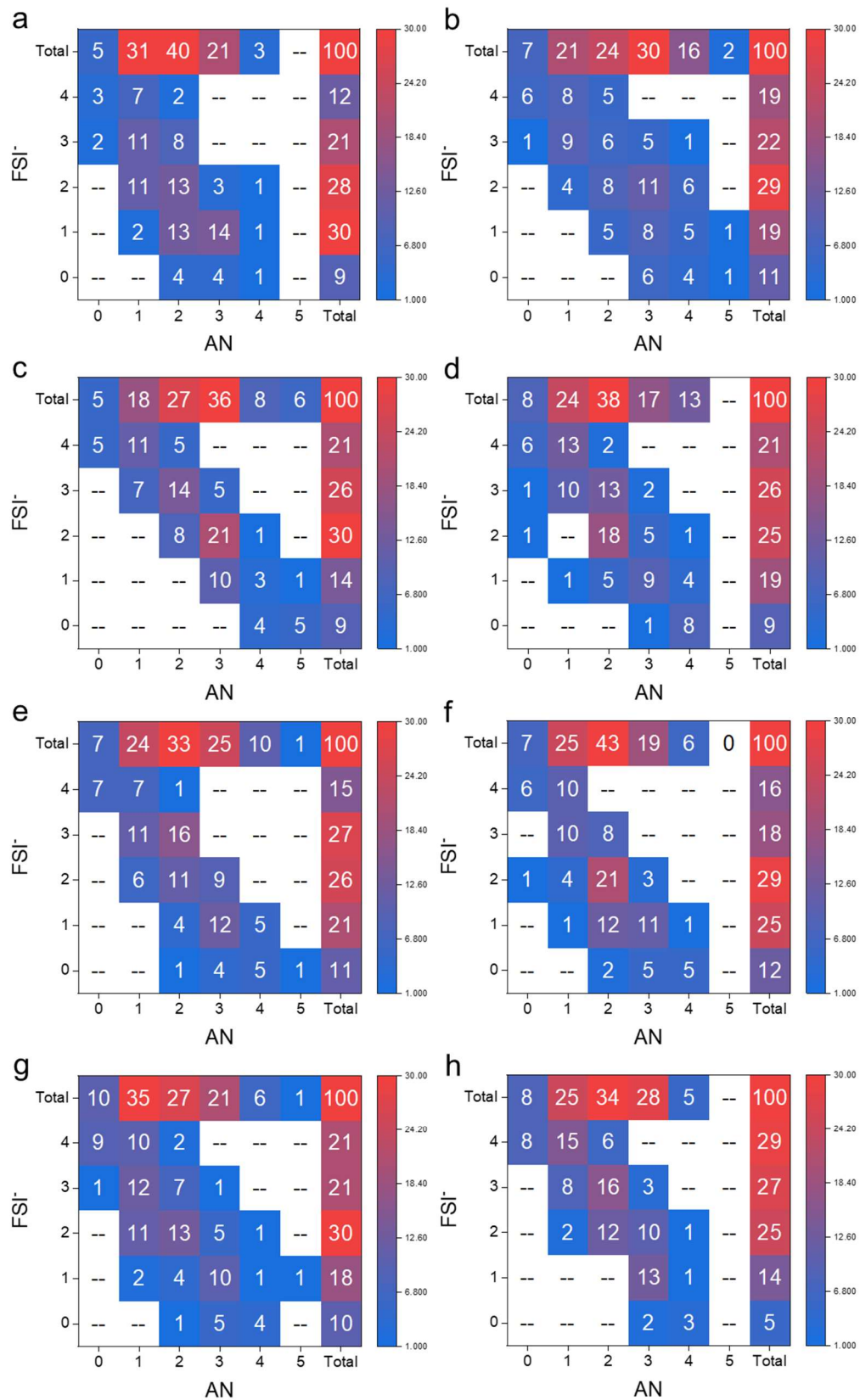
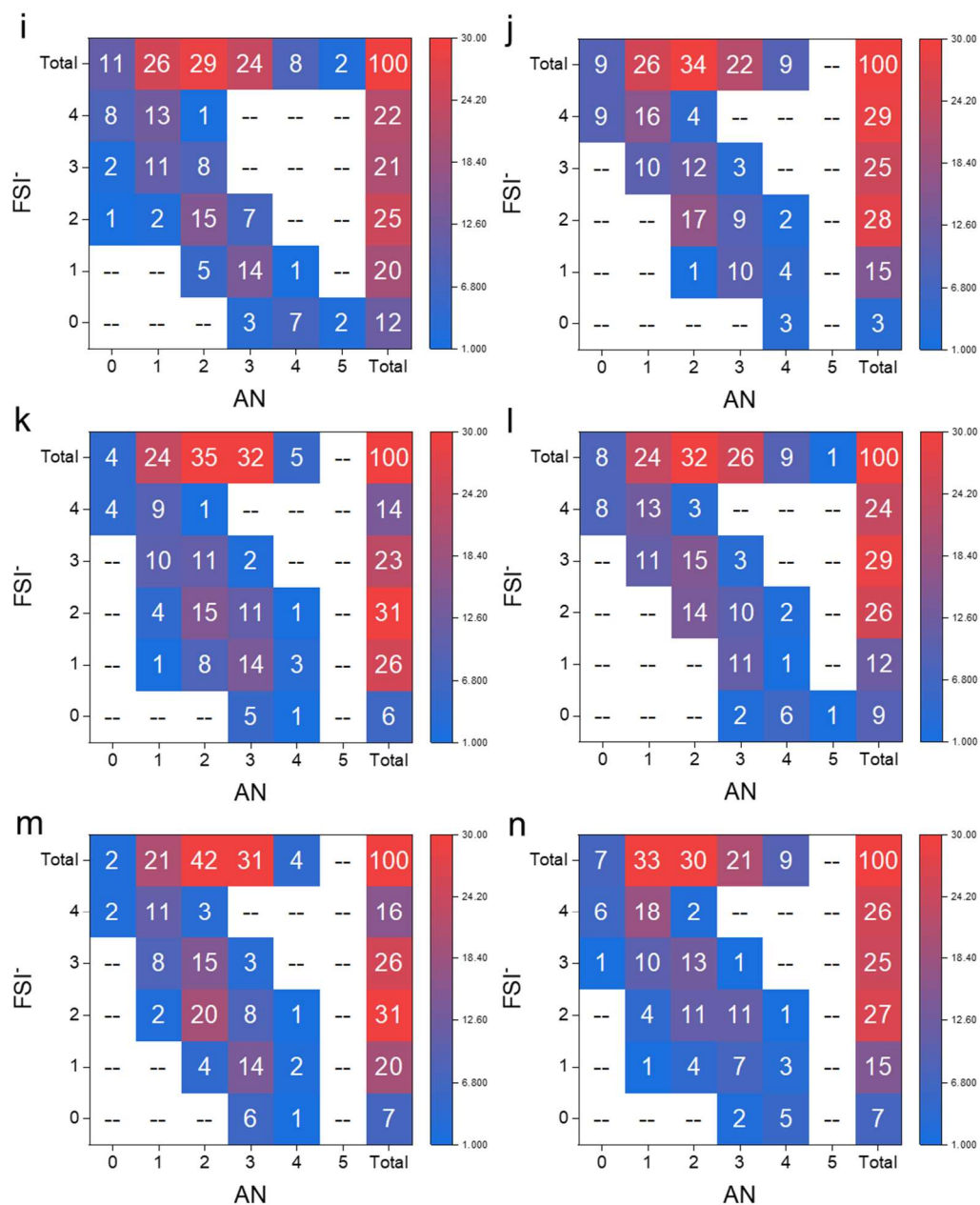


Fig. 3 | Physical properties of the electrolytes. **a,b**, Lifetime/displacement function of AN in FA-DCM electrolyte (**a**) and FA-TTE electrolyte (**b**). **c,d**, Evolution of Li⁺ solvation environment in FA-DCM electrolyte (**c**) and FA-TTE electrolyte (**d**) from MD simulations at 298 K (the vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li⁺ in the simulation time of 2,000 ps). **e**, The average residence time of Li⁺ in LiFSI/AN-based electrolytes with different moderators. **f**, Temperature dependence of the ionic conductivity of different electrolytes. **g**, Li⁺ transference numbers of different electrolytes at 25 °C. **h**, Differential scanning calorimetry cooling and heating curves of different electrolytes.

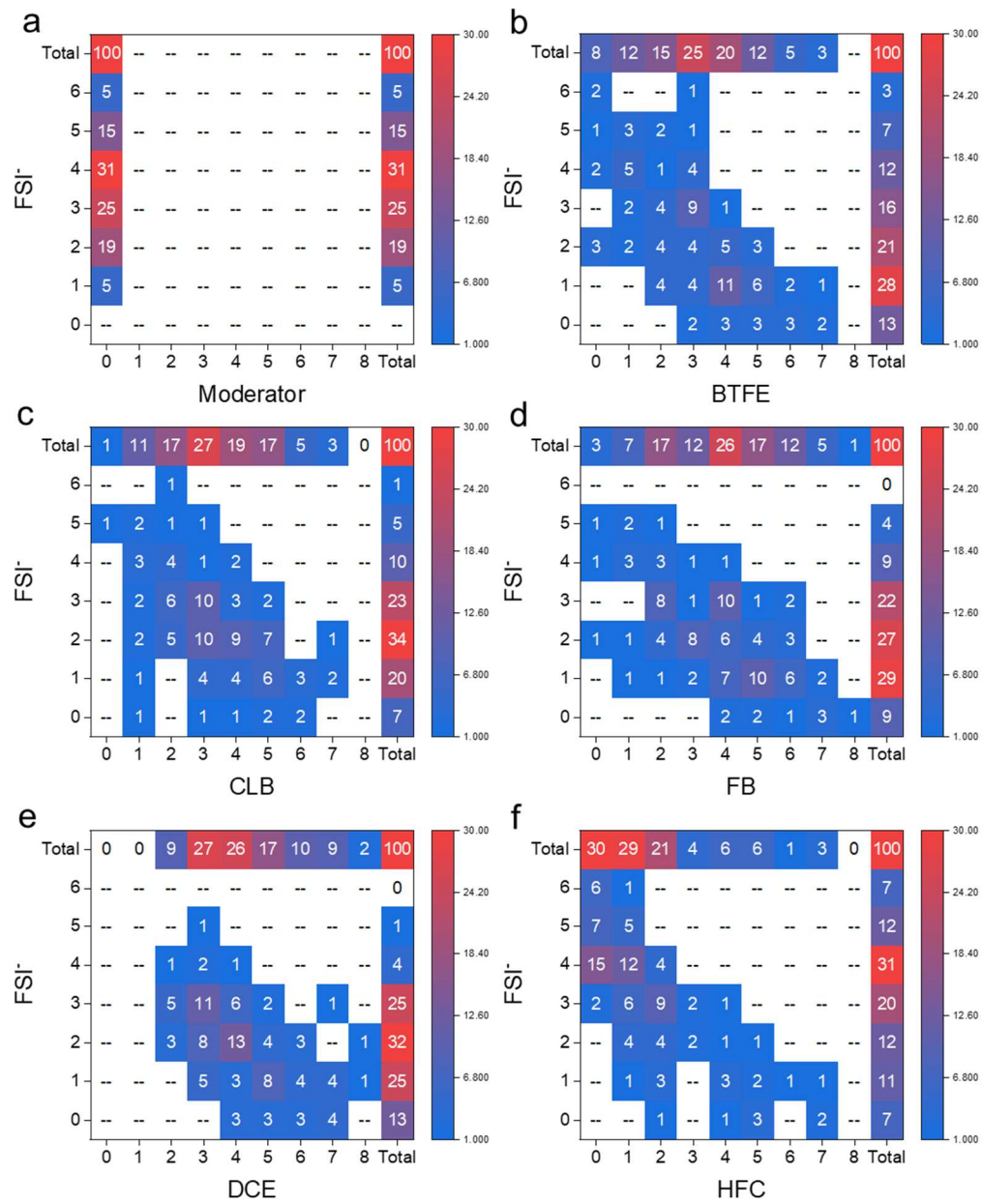
In the revised supporting information, we added Fig. R20a, c, 21, 22, 24 and 25 as Supplementary Fig. 4g, 6e, 14, 15g, 31 and 40.

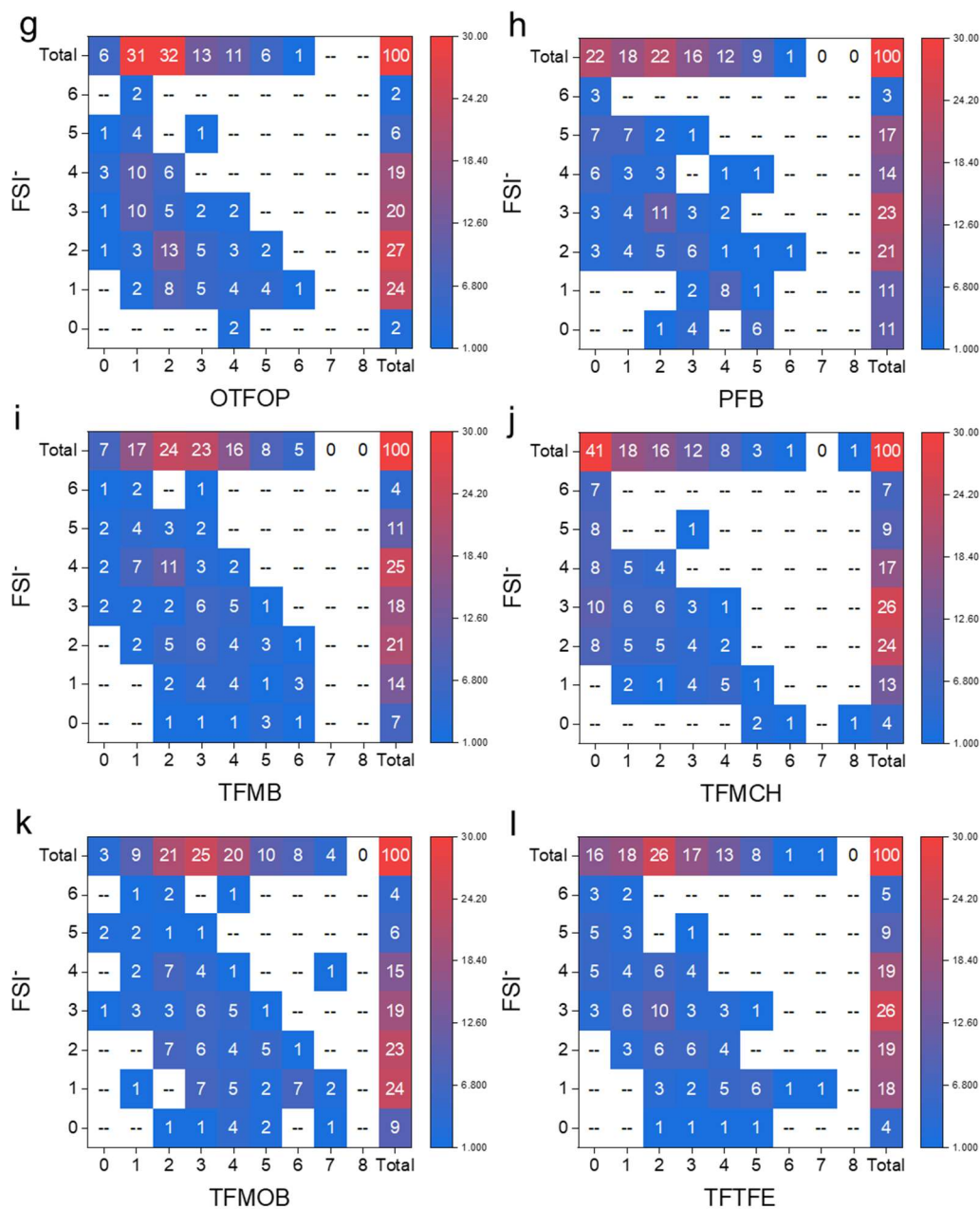




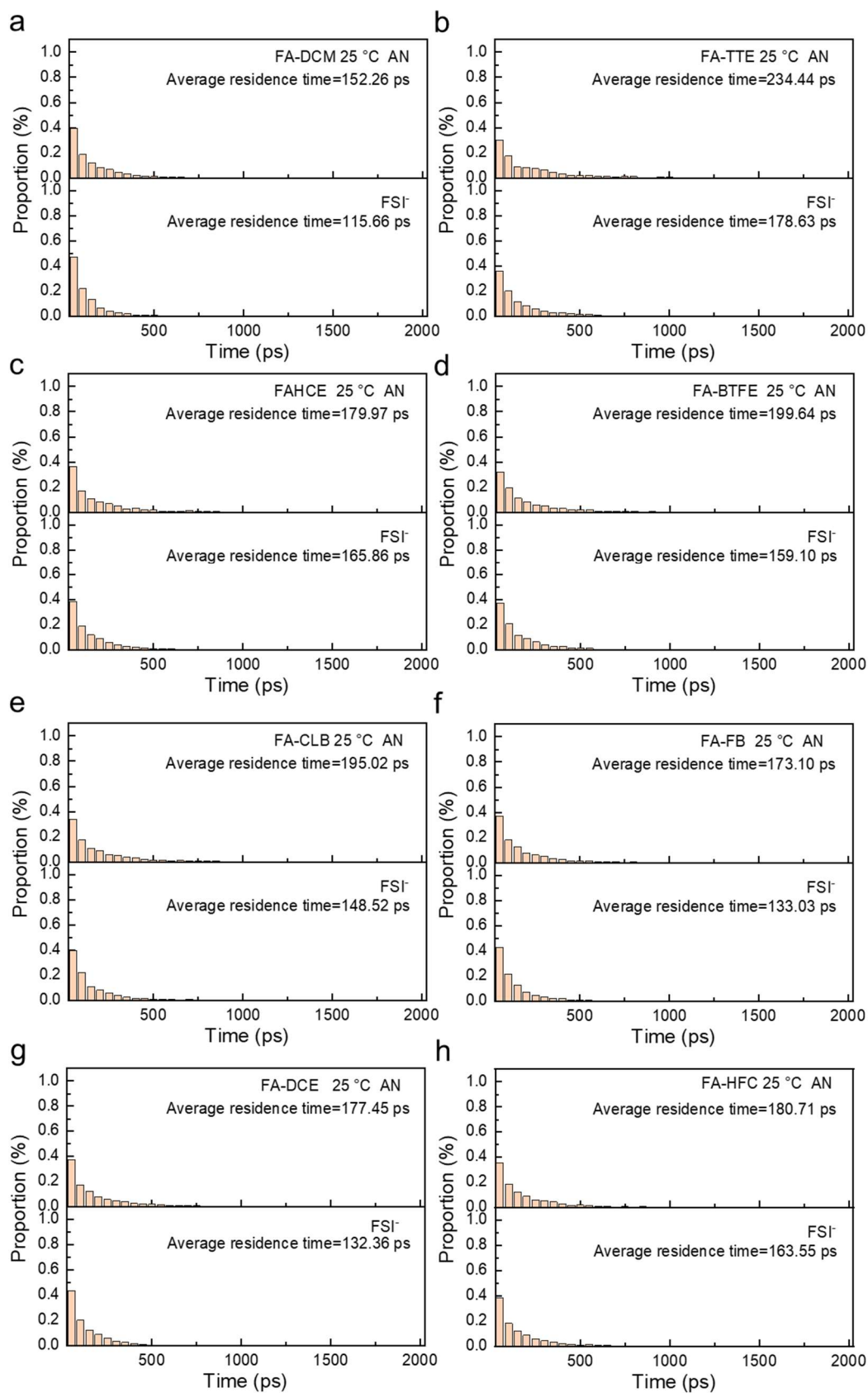
Supplementary Fig. 4 | Heatmaps of Li^+ solvation sheath in different electrolytes.

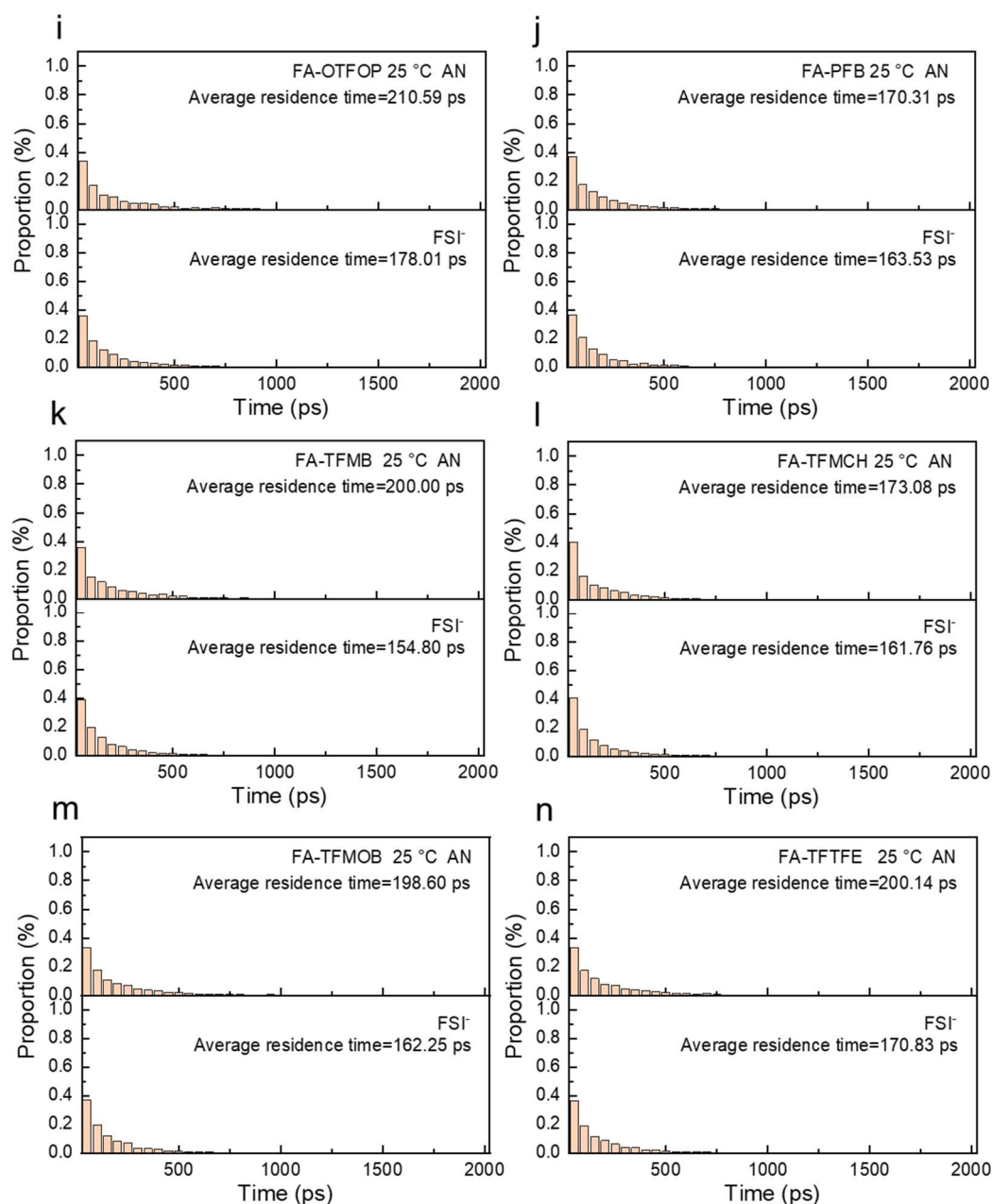
FA-DCM electrolyte (a), FA-TTE electrolyte (b), FAHCE electrolyte (c), FA-BTFE electrolyte (d), FA-CLB electrolyte (e), FA-FB electrolyte (f), **FA-DCE electrolyte (g)**, FA-HFC electrolyte (h), FA-OTFOP electrolyte (i), FA-PFB electrolyte (j), FA-TFMB electrolyte (k), FA-TFMCH electrolyte (l), FA-TFMOB electrolyte (m) and FA-TFTFE electrolyte (n).





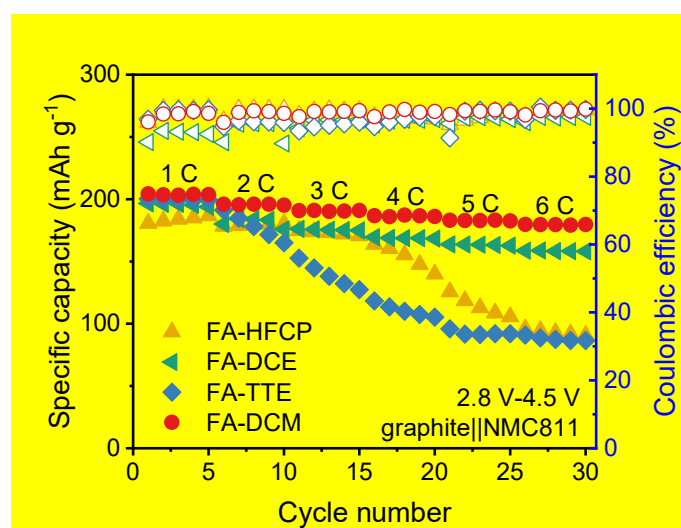
Supplementary Fig. 6 | Heatmaps of Li^+ solvating environment (3 Å to 5 Å) in different electrolytes. FAHCE electrolyte (a), FA-BTFE electrolyte (b), FA-CLB electrolyte (c), FA-FB electrolyte (d), **FA-DCE electrolyte (e)**, FA-HFC electrolyte (f), FA-OTFOP electrolyte (g), FA-PFB electrolyte (h), FA-TFMB electrolyte (i), FA-TFMCH electrolyte (j), FA-TFMOB electrolyte (k) and FA-TFTFE electrolyte (l).





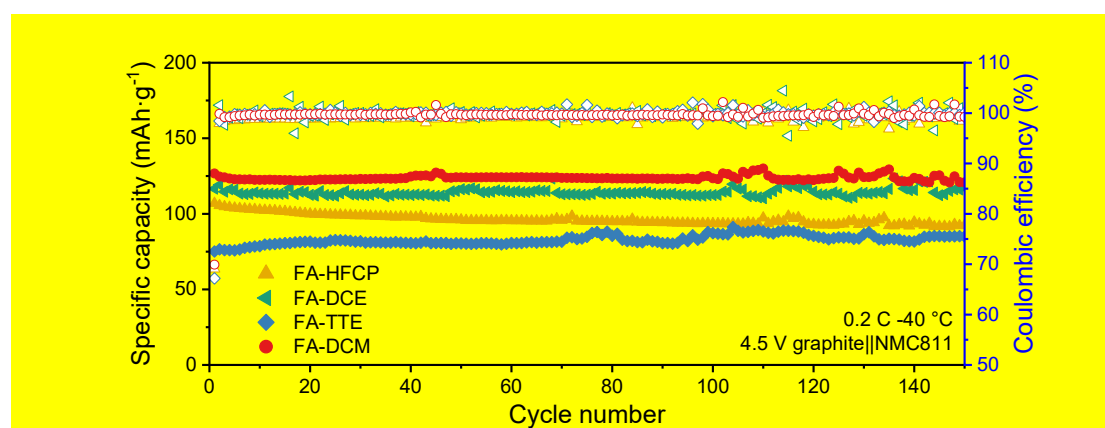
Supplementary Fig. 15 | Residence time distribution of AN and FSI⁻ in different electrolytes. FA-DCM electrolyte (a), FA-TTE electrolyte (b), FAHCE electrolyte (c), FA-BTFE electrolyte (d), FA-CLB electrolyte (e), FA-FB electrolyte (f), **FA-DCE electrolyte (g)**, FA-HFC electrolyte (h), FA-OTFOP electrolyte (i), FA-PFB electrolyte (j), FA-TFMB electrolyte (k), FA-TFMCH electrolyte (l), FA-TFMOB electrolyte (m) and FA-TFTFE electrolyte (n).

(Page 52)



Supplementary Fig. 31 | Rate performance of graphite||NMC811 cells with different electrolytes in the range of 2.8-4.5 V at 25 °C.

(Page 61)



Supplementary Fig. 40 | Cycling performance with different electrolytes in the range 2.8-4.5 V at 0.2 C under -40 °C.

Closing remarks

We would like to extend our sincere appreciation to Reviewer #2 for their invaluable contribution of thought-provoking queries and insightful suggestions, which have significantly enhanced the academic significance of our manuscript. It is our utmost hope that the revised version of our manuscript satisfactorily addresses the concerns raised by Reviewer #2.

Reviewer #3 (Remarks to the Author):

The manuscript titled “Solvation sheath reorganization enables fast ion transfer kinetics” presents a comprehensive study on a novel electrolyte design approach for lithium-ion batteries, employing a low-dipole, small-sized moderator (dichloromethane, DCM) to reorganize the solvation sheath. The authors introduce a descriptor-based framework for selecting such moderators and validate the concept through molecular simulations, electrochemical characterizations, and practical pouch cell demonstrations. Of all the moderators examined, DCM exhibits the smallest molecular volume and lowest dipole. The FA-DCM electrolyte demonstrates outstanding performance in high-rate and low-temperature operations, outperforming state-of-the-art commercial electrolytes. The graphite-NMC full cell electrochemical measurements were carried out at room temperature and a low temperature of -40/-50 °C. The study suggests an alternative to commonly used carbonate-based electrolytes, such as 1 M LiPF₆ in EC: DMC for low-temperature applications because of its high freezing point and elevated activation energy. The authors claim that FA-DCM demonstrates superior compatibility with high-voltage cathodes. The work addresses critical challenges in battery performance under extreme temperatures, a significant bottleneck in LIB deployment for EVs and aerospace. Theoretical study and experimental analysis, such as NMR, XPS, and full/pouch cell testing, strengthen the findings. Demonstration of low-temperature operation down to -75 °C with practical 1.0 Ah pouch cells is impressive.

We suggest a minor revision for the manuscript before it can be published. The following queries should be addressed in the revised version.

Reply: We sincerely thank Reviewer #3 for the thoughtful and positive evaluation of our work. We are very encouraged by the reviewer’s recognition of the significance of our descriptor-based electrolyte design strategy, the comprehensive set of experimental and theoretical analyses, and the demonstration of outstanding low-temperature performance in practical pouch cells. We greatly value the reviewer’s constructive queries and suggestions, which we believe will help further strengthen the clarity and impact of the manuscript. We have carefully addressed each of the comments in detail

and revised the manuscript accordingly. We hope that the changes made will satisfactorily meet the reviewer's expectations.

1. DCM is a halogenated solvent with known toxicity and volatility. The manuscript does not sufficiently address the environmental and safety implications.

Reply: We thank the reviewer for highlighting the important issue of safety and environmental implications associated with DCM. We fully acknowledge that DCM is a halogenated solvent with known toxicity and volatility, which must be carefully considered for any practical application.

Here, DCM is utilized as a proof-of-concept solvent to highlight how solvation structure regulation can substantially facilitate Li^+ transport under demanding low-temperature and high-rate conditions. This approach is designed to reveal the mechanistic principles governing ion transport.

It is important to note that the pouch cells employed in our study possess excellent sealing, which effectively minimizes solvent evaporation and exposure during operation. Moreover, we envision that with further optimization, the unique transport benefits imparted by DCM could be extended to less volatile or less toxic structural analogues, or to mixed formulations with reduced DCM content, thereby improving sustainability.

Taken together, while DCM itself may not be an ideal large-scale solvent candidate, its inclusion here serves to validate the discrete Li^+ hopping mechanism and highlight design principles that can guide the development of safer, environmentally benign electrolyte systems in the future.

In the revised manuscript (Page 24), we added the following text and highlighted it in yellow:

It is worth noting that the toxicity and volatility of DCM limit its broader applicability, but the sealed cells using DCM-based electrolyte still demonstrated decent stability and capacity retention under extended cycling or storage (Supplementary Fig. 59-61). More

importantly, as a moderator with small molecular size and low dipole moment, DCM successfully tunes the solvation structure, creating a more uniformly distributed and compact solvation clusters, which is essential for ultralow-temperature operation and fast charging. This success validates the feasibility of the concept and paves the way for future electrolytes designed on these principles to be both high-performing and environmentally benign.

2. The economic and industrial feasibility of large-scale FA-DCM electrolyte production is not discussed.

Reply: We thank the reviewer for highlighting the importance of discussing the economic and industrial viability of the proposed FA-DCM electrolyte system. While the present work primarily focuses on fundamental solvation structure modulation and its impact on ion transport, we agree that considerations of scale-up feasibility are important, and we have accordingly added the following clarifications and quantitative analysis.

Both DCM and AN are commodity chemicals produced on an industrial scale, with well-established global supply chains. Based on current market prices, DCM (~292.5 \$/t) and AN (~1,016.7 \$/t) are significantly cheaper than other electrolytes (Table R7). The LiFSI used is currently relatively expensive (~55,710.3 \$/t), but is commercially available and used in other high-performance electrolytes (Table R7).

For a typical formulation of 1.5 M LiFSI in AN/DCM (1:4, vol), we estimate the raw material cost to be ~12,374.4 dollars per ton (Table R6). Despite the high unit cost of LiFSI, the combined cost of solvents (AN+DCM) accounts for less than 302.4 dollars per ton, making the system economically competitive compared to advanced electrolytes based on fluorinated ethers or sulfone-based solvents.

All components of the FA-DCM electrolyte are compatible with existing electrolyte manufacturing infrastructure, requiring no special handling beyond conventional dry-room protocols. The solvents are miscible, easily blended, and stable in sealed systems, simplifying scale-up. Additionally, DCM is widely used in other

industrial processes under controlled conditions, suggesting that its inclusion in electrolyte formulation is technologically feasible under standard safety protocols.

The urgent demand for electrolytes capable of enabling reliable low-temperature operation and fast-charging performance underscores the practical relevance of FA-DCM. Given its superior electrochemical performance under these challenging conditions, we believe the slight cost premium compared with the cheapest alternatives is justified by the substantial performance benefits.

Table R6. The costs of various electrolytes.

Electrolyte	Cost (\$/t)	Reference
1.5 M LiFSI/AN-DCM (1:4, vol)	\$12,374.4	This work
1.5 M LiFSI/DME-BTFE (1:2, vol)	\$14,209.2	2
1.8 M LiFSI/DOL	\$15,650.4	3
1.5 M LiFSI/DMK-VC (7:3, vol) + 5wt% FEC	\$18,919.0	4
1 M LiTFSI/ETFA-FEC (7:3, vol)	\$58,721.2	5
LiDFOB/NMTFA (1:5, mol)	\$72,448.0	6
2 M LiTFSI/EA	\$77,710.5	7
1.28 M LiFSI-FEMC/FEC in D2	\$106,075.4	8
4.2 M LiTFSI/AN	\$120,633.6	9
1 M LiTFSI MDFA/MDFSAs-TTE (4:1:5, vol)	\$201,769.3	10
1 M LiDFOB/FEC-IZ (1:10, vol)	\$356,660.0	11
1.3 M LiFSI/FAN	\$19,695,732.4	12

Table R7. The costs of various lithium salts and solvents.

Abbreviation	Name	Cost \$/t
LiDFOB	Lithium difluoro(oxalato)borate	\$13,927.6

LiFSI	Lithium Bis(fluorosulfonyl)imide	\$55,710.3
LiTFSI	Lithium bis(trifluoromethanesulphonyl)imide	\$198,607.2
AN	Acetonitrile	\$1,016.7
BTFE	bis(2,2,2-trifluoroethyl) ether	\$3,899.7
D2	1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane	\$28,830.1
DCM	Dichloromethane	\$292.5
DME	dimethoxyethane	\$1,922.0
DMK	Acetone	\$724.2
DOL	1,3-dioxolane	\$2,924.8
EA	Ethyl acetate	\$752.1
ETFA	Ethyl trifluoroacetate	\$6,267.4
FAN	Fluoroacetonitrile	\$24,889,972.1
FEC	Fuoroethylene carbonate	\$48,746.5
FEMC	Methyl (2,2,2-trifluoroethyl) carbonate	\$480,341.2
IZ	Isoxazole	\$448,468.0
MDFA	Methyl Difluoroacetate	\$192,200.6
MDFSFA	Methyl 2,2-difluoro-2-(fluorosulfonyl)acetate	\$288,348.9
NMTFA	N-methyl-2,2,2-trifluoroacetamide	\$85,689.4
TTE	1,1,2,2-Tetrafluoroethyl-2,2,3,3-tetrafluoropropylether	\$192,200.6
VC	Vinylene carbonate	\$7,242.3

In the revised manuscript (Page 5), we added the following text and highlight it:

The resulting electrolyte, 1.5 M lithium bis(fluorosulfonyl)imide (LiFSI) in an acetonitrile (AN)-DCM mixture (1:4, vol) (denoted as FA-DCM electrolyte), demonstrates exceptional electrochemical performance, combined with cost-

effectiveness (Supplementary Note 3).

In the revised supporting information (Page 5 and 6), we added Supplementary Note 3 and added Table R6, 7 as Supplementary Table 1, 2:

Supplementary Note 3

Supplementary Table 1. The costs of various electrolytes.

Electrolyte	Cost (\$/t)	Reference
1.5 M LiFSI/AN-DCM (1:4, vol)	\$12,374.4	This work
1.5 M LiFSI/DME-BTFE (1:2, vol)	\$14,209.2	4
1.8 M LiFSI/DOL	\$15,650.4	5
1.5 M LiFSI/DMK-VC (7:3, vol)+ 5wt% FEC	\$18,919.0	6
1 M LiTFSI/ETFA-FEC (7:3, vol)	\$58,721.2	7
LiDFOB/NMTFA (1:5, mol)	\$72,448.0	8
2 M LiTFSI/EA	\$77,710.5	9
1.28 M LiFSI-FEMC/FEC in D2	\$106,075.4	10
4.2 M LiTFSI/AN	\$120,633.6	11
1 M LiTFSI MDFA/MDFSFA-TTE (4:1:5, vol)	\$201,769.3	12
1 M LiDFOB/FEC-IZ (1:10, vol)	\$356,660.0	13
1.3 M LiFSI/FAN	\$19,695,732.4	14

Supplementary Table 2. The costs of various lithium salts and solvents.

Abbreviation	Name	Cost \$/t
LiDFOB	Lithium difluoro(oxalato)borate	\$13,927.6
LiFSI	Lithium Bis(fluorosulfonyl)imide	\$55,710.3

LiTFSI	Lithium bis(trifluoromethanesulphonyl)imide	\$198,607.2
AN	Acetonitrile	\$1,016.7
BTFE	bis(2,2,2-trifluoroethyl) ether	\$3,899.7
D2	1,1,2,2-tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane	\$28,830.1
DCM	Dichloromethane	\$292.5
DME	dimethoxyethane	\$1,922.0
DMK	Acetone	\$724.2
DOL	1,3-dioxolane	\$2,924.8
EA	Ethyl acetate	\$752.1
ETFA	Ethyl trifluoroacetate	\$6,267.4
FAN	Fluoroacetonitrile	\$24,889,972.1
FEC	Fuoroethylene carbonate	\$48,746.5
FEMC	Methyl (2,2,2-trifluoroethyl) carbonate	\$480,341.2
IZ	Isoxazole	\$448,468.0
MDFA	Methyl Difluoroacetate	\$192,200.6
MDFSA	Methyl 2,2-difluoro-2-(fluorosulfonyl)acetate	\$288,348.9
NMTFA	N-methyl-2,2,2-trifluoroacetamide	\$85,689.4
TTE	1,1,2,2-Tetrafluoroethyl-2,2,3,3-tetrafluoropropylether	\$192,200.6
VC	Vinylene carbonate	\$7,242.3

Supplementary tables 1 and 2 present the costs of electrolytes for low-temperature and fast-charging conditions, along with the costs of the required lithium salts and moderators. Owing to the low price and ready availability of its constituents, the FA-DCM electrolyte exhibits a lower overall cost, which is conducive to large-scale production and application.

3. Page 14, the incompatibility between acetonitrile, AN, and graphite should be elaborated.

Reply: We appreciate the reviewer's comment and agree that the incompatibility between AN and graphite deserves further clarification. It is well established in the literature that AN exhibits poor compatibility with graphite electrodes due to its tendency to undergo reductive decomposition at low potentials, leading to the formation of unstable interphases and severe capacity degradation^{9,13}.

We also employed graphite||LiFePO₄ (LFP) full cells, in which the high-loading LFP cathode serves primarily as the lithium reservoir. This design circumvents direct contact between AN and metallic lithium, thereby preventing the parasitic side reactions that would otherwise occur¹³. As shown in the Fig. R26, the graphite||LFP cell assembled with the commercial BE electrolyte delivers three characteristic lithiation plateaus, in sharp contrast to the cell using the low-concentration LiFSI/AN electrolyte, which proves incompatible with the graphite electrode.

We believe that these additions provide a clear and thorough explanation of the AN-graphite incompatibility and its impact on anode performance.

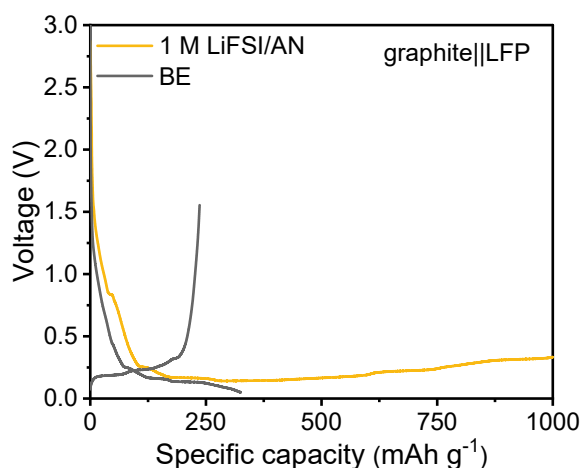


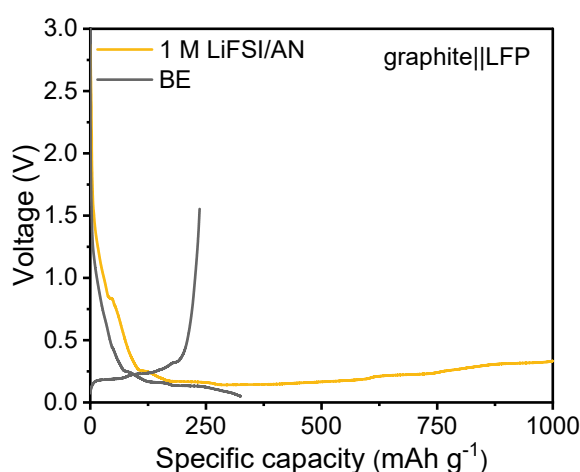
Fig. R26 | The charge/discharge curves of graphite||LFP full cells with different electrolytes.

In the revised manuscript, we added the following text as shown, and highlighted them in yellow (Pages 15), and we have cited the key references (*J. Am. Chem. Soc.* 2014,

136, 5039–5046; *Journal of Power Sources* 384, 2018, 334–341) as ref. 18, 47 in revised manuscript to support our claim.

These results indicate that the previously reported incompatibility between AN and graphite has been effectively resolved, and the sluggish Li^+ desolvation kinetics at the interphases have been significantly improved (Supplementary Fig. 25)^{18, 47}.

In the revised supporting information, we added Fig. R26 as Supplementary Fig. 25, and highlighted them in yellow (Pages 46):



Supplementary Fig. 25 | The charge/discharge curves of graphite||LFP full cells with different electrolytes.

We employed graphite||LiFePO₄ (LFP) full cells, in which the high-loading LFP cathode serves primarily as the lithium reservoir. This design circumvents direct contact between AN and metallic lithium, thereby preventing the parasitic side reactions that would otherwise occur¹⁹. As shown in the Supplementary Fig. 25, the graphite||LFP cell assembled with the commercial BE electrolyte delivers three characteristic lithiation plateaus, in sharp contrast to the cell using the low-concentration LiFSI/AN electrolyte, which proves incompatible with the graphite electrode.

4. Supplementary Information page 28, Figure 17: Please show the fitted line along with the experimental EIS data. Include insets highlighting the region till 10 ohms (Z_{real}) for 17b and 15 ohms (Z_{real}) for 17c.

Reply: We thank the reviewer for the helpful suggestion. As shown in Fig. R27 and Table R8, we have now included the fitted curves along with the experimental EIS data. As recommended, Fig. R27d, f have also been added to highlight the regions up to 10 Ω (Z_{real}) for Fig. 17b and 15 Ω (Z_{real}) for Fig. 17c, respectively, which facilitate a clearer comparison between the fitted and experimental results.

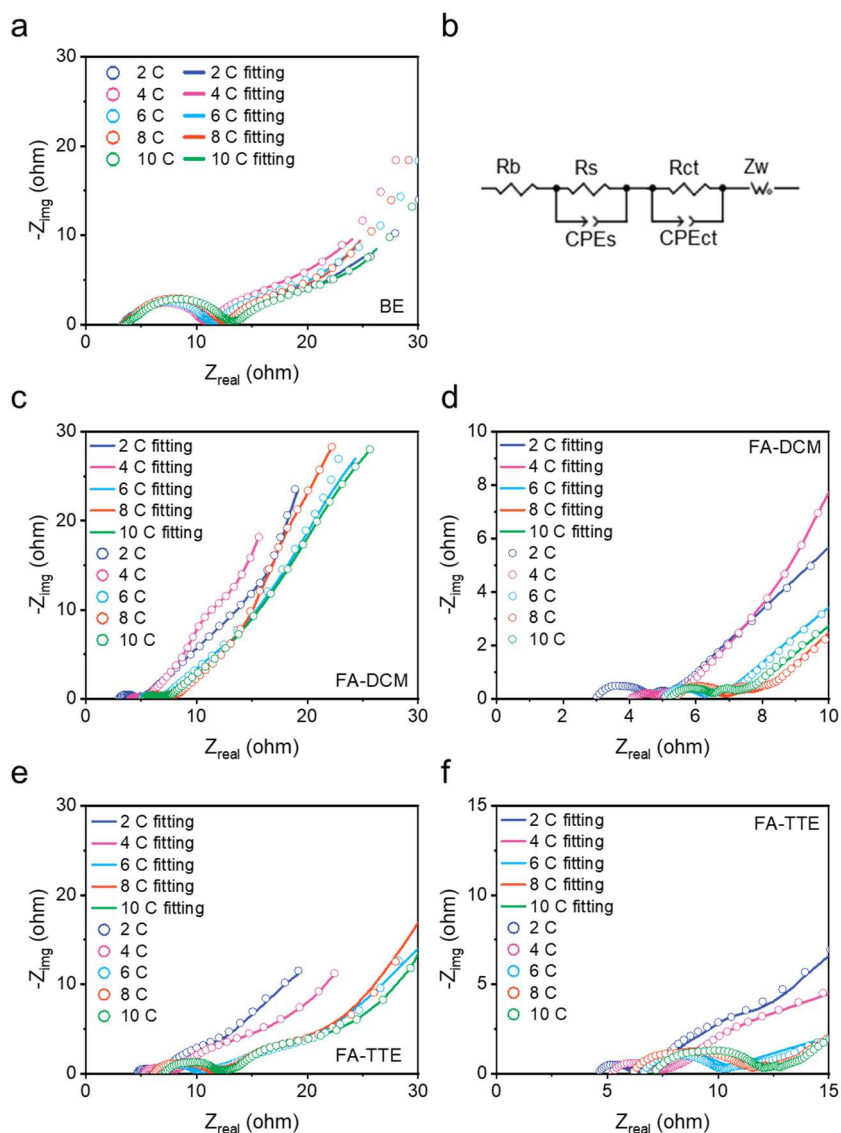


Fig. R27 | Impedance evaluations. Electrochemical impedance spectra of Li||graphite cells at different rates for BE electrolyte (a), FA-DCM electrolyte (c-d) and FA-TTE electrolyte (e-f) at 25 °C. In electrochemical impedance spectra, the solid lines represent the fits using an equivalent circuit (b), EIS were obtained at 0% SOC.

Table R8. Charge-transfer resistance (R_{ct}) and interfacial resistance (R_{SEI}) of

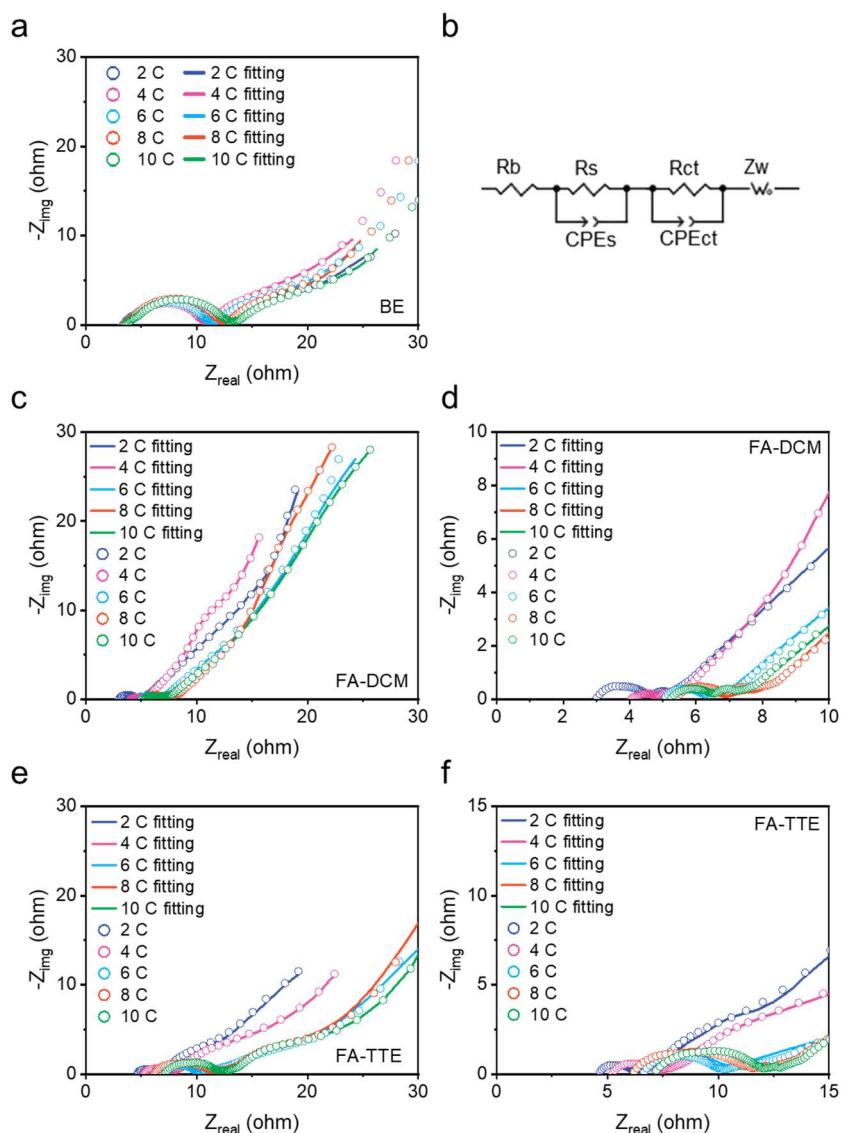
Li||graphite cells using different electrolytes at different rates.

Electrolyte	Rate	2 C	4 C	6 C	8 C	10 C
BE	R_{ct} (Ohm)	5.290	8.420	8.790	9.500	12.85
	R_{SEI} (Ohm)	9.035	7.273	7.687	8.717	9.180
FA-TTE	R_{ct} (Ohm)	6.056	7.660	8.720	9.720	10.98
	R_{SEI} (Ohm)	1.438	1.990	3.116	4.651	4.637
FA-DCM	R_{ct} (Ohm)	0.367	0.237	0.366	0.754	0.544
	R_{SEI} (Ohm)	1.757	0.973	1.359	1.670	1.417

In the revised manuscript (Pages 15), we added the following text and highlighted them in yellow:

The total resistance in the cell primarily comprises bulk resistance (R_b), surface layer resistance (R_{SEI}), and charge transfer resistance (R_{ct}) (Fig. 4c, Supplementary Fig. 26 and Table 7). Notably, the FA-DCM electrolyte exhibits much lower R_{SEI} (1.417 Ohm), and R_{ct} (0.544 Ohm) compared to the BE electrolyte (9.180 Ohm for R_{SEI} and 12.85 Ohm for R_{ct} , respectively) at 10 C, highlighting the its enhanced interfacial reaction kinetics⁴⁷.

In the revised supporting information, we added Fig. R27 as Supplementary Fig. 26 (Page 47), and added Table R8 as Supplementary Table 7 (Page 12):



Supplementary Fig. 26 | Impedance evaluations. Electrochemical impedance spectra of Li||graphite cells at different rates for BE electrolyte (a), FA-DCM electrolyte (c-d) and FA-TTE electrolyte (e-f) at 25 °C. In electrochemical impedance spectra, the solid lines represent the fits using an equivalent circuit (b), EIS were obtained at 0% SOC.

Supplementary Table 7. Charge-transfer resistance (R_{ct}) and interfacial resistance (R_{SEI}) of Li||graphite cells using different electrolytes at different rates.

Electrolyte	Rate	2 C	4 C	6 C	8 C	10 C
BE	R_{ct} (Ohm)	5.290	8.420	8.790	9.500	12.85

	R_{SEI} (Ohm)	9.035	7.273	7.687	8.717	9.180
FA-TTE	R_{ct} (Ohm)	6.056	7.660	8.720	9.720	10.98
	R_{SEI} (Ohm)	1.438	1.990	3.116	4.651	4.637
FA-DCM	R_{ct} (Ohm)	0.367	0.237	0.366	0.754	0.544
	R_{SEI} (Ohm)	1.757	0.973	1.359	1.670	1.417

5. Page 21, The authors report that the FA-DCM electrolyte forms a thinner SEI layer on the graphite anode compared to the base electrolyte, with a higher LiF concentration. Since LiF is known to contribute to the formation of a stable, compact, and ionically conductive SEI, a more in-depth discussion is required on how the increased LiF content correlates with improved interfacial stability and electrochemical performance.

Reply: We appreciate the reviewer’s insightful comment. To provide a more in-depth discussion, we have complemented our X-ray photoelectron spectroscopy (XPS) depth profiling with time of flight secondary ion mass spectrometry (TOF-SIMS) analysis to further elucidate the SEI chemistry. The results confirm that the SEI formed in the FA-DCM electrolyte is predominantly composed of inorganic species such as LiF and LiCl, which originate from the reductive decomposition of FSI⁻ and DCM. These inorganic-rich components contribute to the formation of a thinner, denser, and more uniform SEI compared to that formed in the BE electrolyte (Fig. R28). The higher LiF concentration plays a dual role in stabilizing the electrode-electrolyte interface. First, LiF is chemically robust and electronically insulating, which suppresses parasitic side reactions and minimizes continuous electrolyte decomposition. Second, LiF is ionically conductive to Li⁺, enabling facile Li⁺ transport across the SEI while maintaining its compact and mechanically stable structure.

In contrast, the SEI formed in BE electrolyte contains a higher fraction of organic components and is substantially thicker, which increases interfacial impedance and leads to less efficient Li⁺ transport. This compositional difference correlates with our

EIS results (Supplementary Fig. 24 and Table 7), where graphite||NMC811 cells with FA-DCM exhibits lower interfacial resistance than that with BE, and with the superior rate capability and cycling stability demonstrated by the cells with FA-DCM.

Together, the thinner and LiF-rich SEI in FA-DCM provides both chemical passivation and efficient Li^+ conduction, directly explaining the improved interfacial stability and electrochemical performance compared with BE.

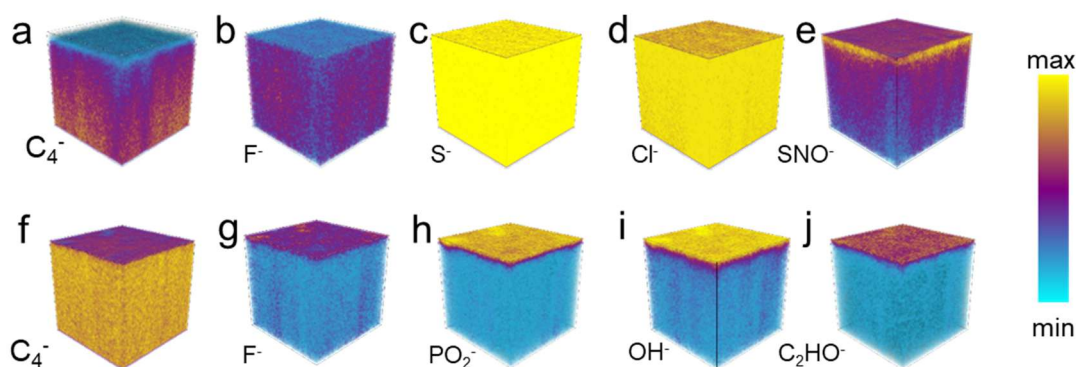


Fig. R28 | 3D-rendering images of C_4^- (a), F^- (b), S^- (c), Cl^- (d) and SNO^- (e) species on the graphite anode surface cycled in FA-DCM electrolyte and C_4^- (f), F^- (g), PO_2^- (h), OH^- (i) and C_2HO^- (j) species on the graphite anode surface cycled in BE electrolytes.

In the revised manuscript, we modified the following sentences and highlighted them in yellow (Page 22), we cited the key references (*Adv. Energy Mater.* 2024, 14, 2400067; *ACS Energy Lett.* 2024, 9, 2545–2553) as ref. 54, 55 in revised manuscript to support our claim. We also added Fig. R28b-e, g-j as Fig. 6g-n (Page 23)

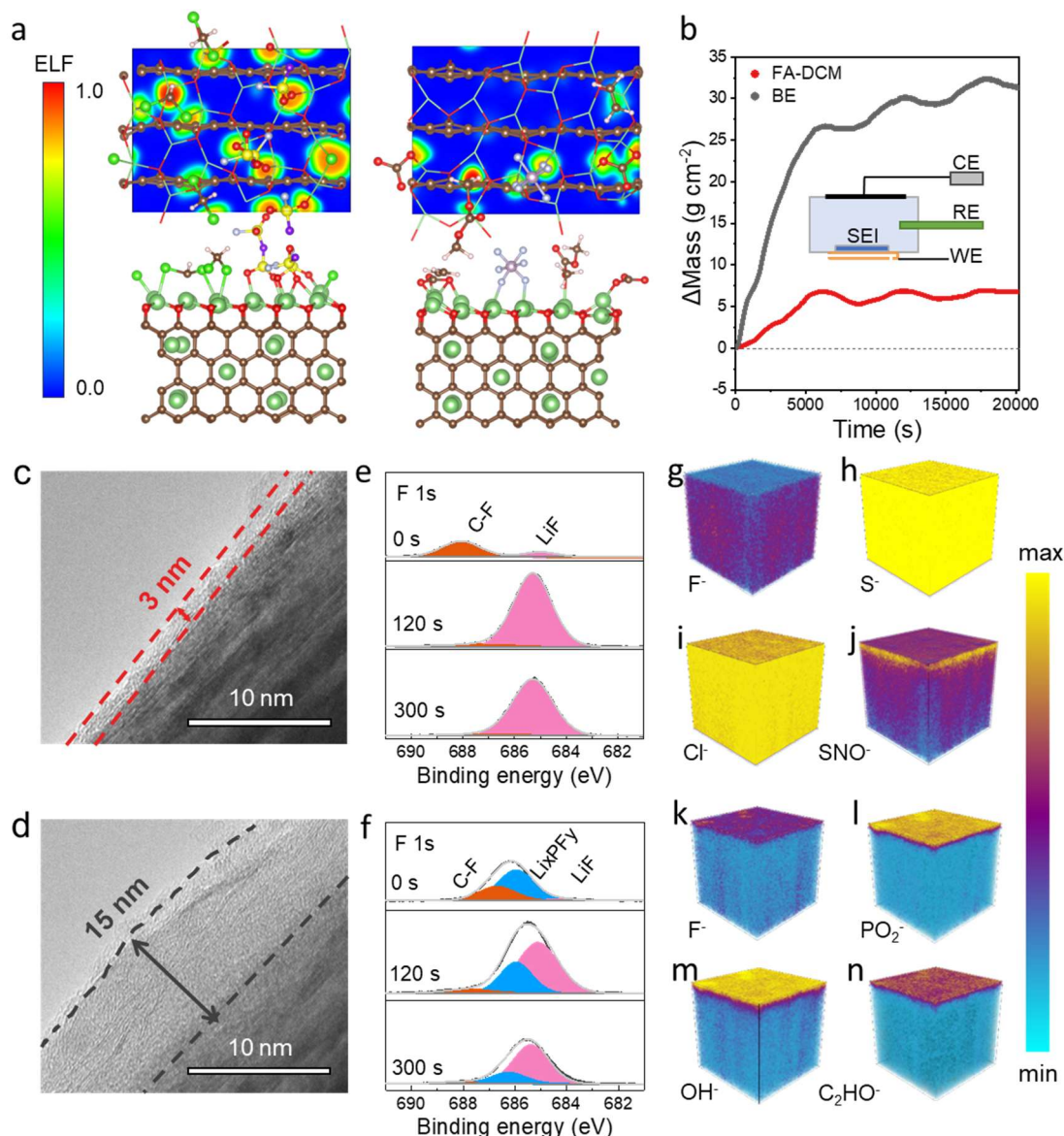


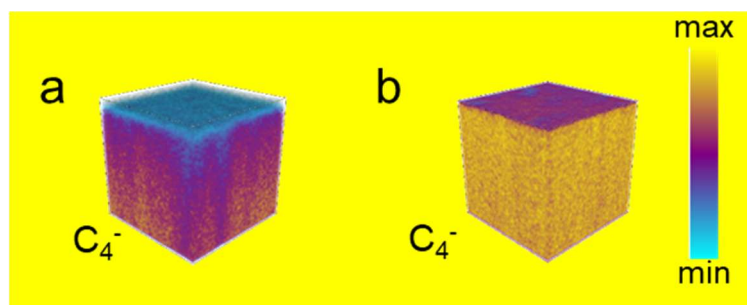
Fig. 6 | Electrolyte/electrode interphase analysis. **a**, The initial decomposition reaction of FA-DCM electrolyte (left) and BE electrolyte (right) on the graphite interphase calculated by *ab initio* molecular dynamics (AIMD). **b**, Electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) profiles of mass change (ΔMass) versus time. (Graphite-sputtered Cu chip resonator is used as the working electrode (WE) and Li metal is used as the counter electrode (CE) and reference electrode (RE). Cells are scanned at a potential window from the 1.50 V to 0.01 V at a scan rate of 5 mV s^{-1} . Frequency is taken at the 3rd overtone ($n = 3$). **c,d**, Transmission electron microscopy (TEM) images of graphite anodes recovered from Li||graphite cells using FA-DCM (**c**) and BE (**d**) electrolyte after 50 cycles, respectively. Scale bars, 10 nm. **e,f**, X-ray photoelectron spectroscopy (XPS) results of the SEI on cycled graphite in FA-DCM electrolyte (**e**) and BE electrolyte (**f**). **g-n**, 3D-rendering images of F^- (**g**), S^- (**h**), Cl^- (**i**) and SNO^- (**j**) species on the graphite anode surface cycled in FA-DCM electrolyte and F^- (**k**), PO_2^- (**l**), OH^- (**m**) and C_2HO^- (**n**) species on the graphite anode surface cycled in BE electrolytes.

Time of flight secondary ion mass spectrometry (TOF-SIMS) and in-depth X-ray photoelectron spectroscopy (XPS) analysis were conducted to comprehensively explore the chemical composition of electrode-electrolyte interphase (Fig. e-n, Supplementary Fig. 54-58). In the C 1s spectra (Supplementary Fig. 54a), the FA-DCM electrolyte initially forms carbonyl-containing organic compounds (C=O), which diminish with sputtering depth, whereas the LiF signal (Fig. 6f) and N- and S-containing derivatives (Supplementary Fig. 54d, e) increase, indicating preferential decomposition of FSI⁻ anions at graphite interphase. In addition, Cl 2p spectra further reveal the incorporation of LiCl species (Supplementary Fig. 54f), implying the formation of a dual-layer SEI architecture consisting of an inner LiF-LiCl-rich inorganic layer and an outer organic matrix⁵³⁻⁵⁵. 3D-rendering images obtained from TOF-SIMS further confirm the formation of this bilayer structure (Fig. g-j and Supplementary Fig. 57a), which facilitates efficient charge-transfer kinetics and mechanical robustness.

In the revised method (Page 34), we added the following text and highlighted it in yellow:

X-ray photoelectron spectroscopy (XPS) (Thermo Scientific ESCALAB 250Xi) and time of flight secondary ion mass spectrometry (TOF-SIMS) (ToF.SIMS 5-100 instrument IONTOF GmbH).

In the revised supporting information (Page 79), we added the following text and highlighted it in yellow, we added Fig. R28a, f as Supplementary Fig. 57.



Supplementary Fig. 57 | TOF-SIMS. 3D-rendering images of C₄⁻ species on the graphite anode surface cycled in FA-DCM electrolyte (a) and BE electrolyte (b).

On the graphite surface cycled in the FA-DCM electrolyte, a dense SEI layer is formed, and with increasing depth, partial derivatives are also detected between the graphite layers; in contrast, graphite cycled in the BE electrolyte predominantly exhibits a strong C signal.

6. Advanced Li-ion batteries use Si-based anodes. It would be interesting to discuss applicability of solvation sheath reorganization using DCM moderator to Si-based anodes.

Reply: We thank the reviewer for raising this important point regarding the applicability of our solvation sheath reorganization strategy to Si-based anodes. To directly address this, we assembled SiC||NMC811 (with an areal capacity of 3.60 mAh cm^{-2} for the cathode) full cells with FA-DCM electrolyte in the range of 2.8-4.3 V. As shown in Fig. R29, after 100 cycles, the cells retained 91.8% of their initial capacity with an average Coulombic efficiency of 99.7%. These results clearly demonstrate that the FA-DCM electrolyte can effectively stabilize the Si-based anode interface, thereby extending the applicability of our DCM-mediated solvation strategy beyond graphite to high-capacity Si anodes. This finding further underscores the general relevance of solvation sheath reorganization in improving the electrochemical performance of next-generation anode chemistries.

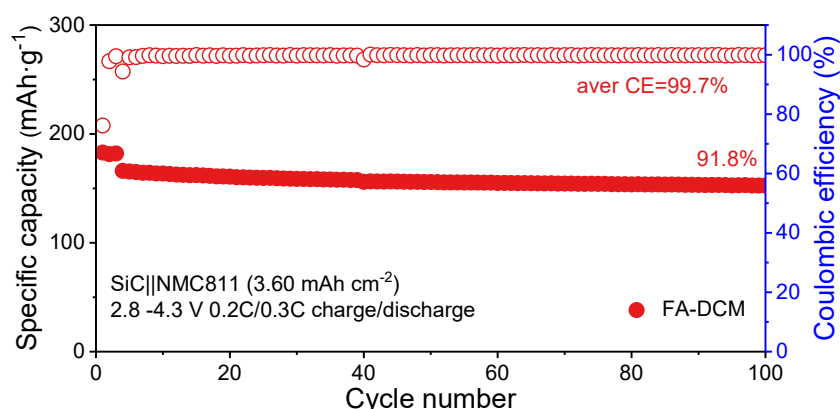
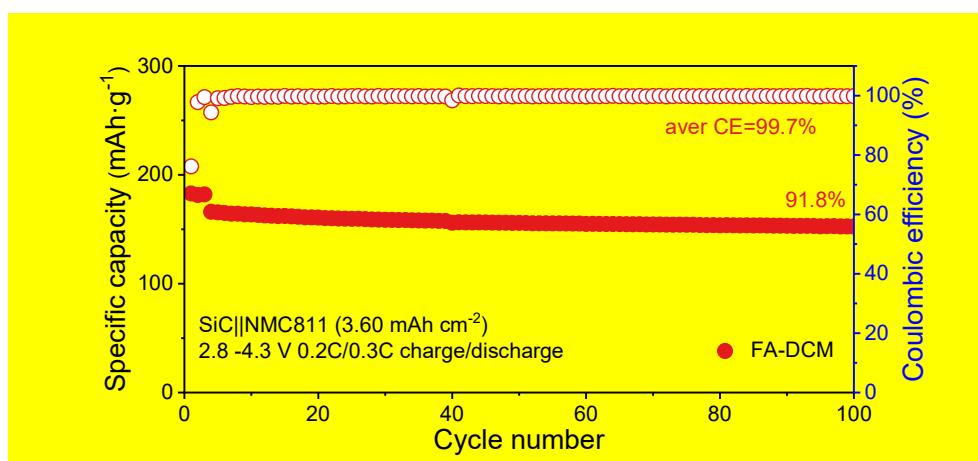


Fig. R29 | Cycling performance of SiC||NMC811 (3.60 mAh cm^{-2}) cell with FA-DCM electrolytes in the range of 2.8-4.3 V.

In the revised manuscript, we added the following text and highlighted it in yellow (Page 21):

Moreover, FA-DCM electrolyte can also effectively stabilize the Si-based anode interface (Supplementary Fig. 42).

In the revised supporting information, we added Fig. R29 as Supplementary Fig. 42, we also added the following text and highlighted it in yellow (Page 63):



Supplementary Fig. 42 | Cycling performance of SiC||NMC811 (3.60 mAh cm⁻²) cell with FA-DCM electrolytes in the range of 2.8-4.3 V.

The applicability of our DCM-mediated solvation strategy can be extended beyond graphite to high-capacity Si anodes. As shown in Supplementary Fig. 42, after 100 cycles, the cells retained 91.8% of their initial capacity with an average Coulombic efficiency of 99.7%.

Minor comments:

1. Page 4, put a space before cm⁻¹ and references 28, 29.
2. Page 9, start a new paragraph when NMR is discussed.

Reply: We have corrected the typos, which have been highlighted in the revised manuscript.

In Page 4, we modified the sentences:

(1) ultimately suppressing the ionic conductivity to below 5.00 mS cm⁻¹ ^{14,15}.

In Page 9, we modified the sentences:

(2) Coaxial nuclear magnetic resonance (NMR) spectroscopy was employed to further investigate the solvation structures across different electrolytes (Fig. 2d).

Closing remarks

We would like to express our sincere gratitude to Reviewer #3 for their constructive feedback and insightful comments. Their suggestions have helped us refine both the clarity and the scientific depth of our work. We have carefully addressed all the concerns raised, and we hope that the revised manuscript meets the reviewer's expectations and standards.

Reviewer #4 (Remarks to the Author):

Although the work proposes a descriptor-based screening strategy and reports promising low-temperature battery performance, several fundamental and scientific concerns undermine the strength of the central claims and limit the impact and generalizability of the study.

Reply: We greatly appreciate Reviewer #4's thorough evaluation and candid comments. We have carefully considered each of the reviewer's points and provide detailed, point-by-point responses in the revised manuscript. We sincerely hope that the revisions and clarifications we have made will satisfactorily address the concerns raised and meet the reviewer's expectations.

The comments and suggestions for improving this work are as follows:

1) The manuscript frequently claims improved "fast ion transfer kinetics." However, the improvements are primarily in liquid-phase transport and interfacial desolvation, not in solid-state diffusion, which is typically the rate-limiting step in battery operation. The terminology should be clarified and limited to the electrolyte domain.

Reply: We appreciate the reviewer's constructive comment and agree that the term "fast ion transfer kinetics" should be used with greater precision. In this work, the improvements we describe arise primarily from two domains: (i) enhanced Li^+ mobility in the liquid electrolyte due to solvation shell disruption, and (ii) facilitated Li^+ desolvation at the electrolyte/electrode interface. We acknowledge that solid-state Li^+ diffusion within the active electrode material is a key determinant of practical performance, though it was not the focus of the present study.

Accordingly, we have revised the manuscript to clarify our terminology. We believe this clarification strengthens the mechanistic accuracy of our claims while keeping the emphasis on the electrolyte design strategy.

In page 5, we modified the sentences:

which significantly increase the population of mobile Li^+ and reduced the Li^+ hopping

time, thereby enabling fast Li^+ transfer kinetics in liquid-phase transport and interfacial desolvation through a discrete hopping mechanism^{34, 35}.

In page 12, we modified the sentence:

MD simulations were performed to analyze Li^+ transport behavior, focusing on solvated sheath transport kinetics in the bulk electrolyte and the solvent/anion residence times around the Li cations (Fig. 3c, 3d and Supplementary Fig. 12-15).

In page 14, we modified the sentence:

These findings highlight the DCM's ability to fine-tune the interactions between Li^+ and FSI⁻/AN, leading to fast ion transport in liquid-phase.

In page 17, we modified the sentence:

These results validate the effectiveness of the small-moderator-regulated discrete hopping mechanism in enabling fast ion kinetics in liquid-phase transport and interfacial desolvation.

2) The authors do not measure or analyze Li^+ diffusion within the solid electrodes (e.g., graphite, NMC811), where kinetic bottlenecks often lie. Techniques such as GITT-based diffusion coefficient extraction or operando XRD would help separate bulk limitations from interfacial ones.

Reply: We appreciate the reviewer's suggestion regarding the importance of probing Li^+ diffusion within the solid electrodes. Following this recommendation, we have performed galvanostatic intermittent titration technique (GITT) measurements under small current perturbations on graphite electrodes with both low and high areal loadings (Fig. R30, 31). The calculated Li^+ diffusion coefficients reveal that the FA-DCM electrolyte ($4.432 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) maintains a diffusivity similar to the baseline carbonate electrolytes (BE, $4.289 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$; BEMP, $4.430 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) and FA-TTE electrolyte ($4.201 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) using graphite electrodes with a low areal loading of

0.53 mAh cm⁻² (Fig. R30c, d). However, under the more demanding high-loading graphite conditions (3.40 mAh cm⁻²), the FA-DCM electrolyte exhibits a higher diffusion coefficient (4.579*10⁻⁹ cm² s⁻¹) than the other three electrolytes (FA-TTE, 4.069*10⁻⁹ cm² s⁻¹; BE, 2.876*10⁻⁹ cm² s⁻¹; BEMP, 3.225*10⁻⁹ cm² s⁻¹, Fig. R31c, d). This enhancement may originate from the superior wettability of the FA-DCM electrolyte toward the porous and tortuous electrode structure, as well as the formation of a LiCl-LiF-rich SEI, which enables faster interfacial Li⁺ migration compared to SEI containing only LiF or organic components¹, thereby influencing the apparent diffusion coefficient. These results confirm that the enhanced Li⁺ mobility observed with FA-DCM is not limited to the electrolyte phase but also translates into improved solid-state diffusion within the electrodes.

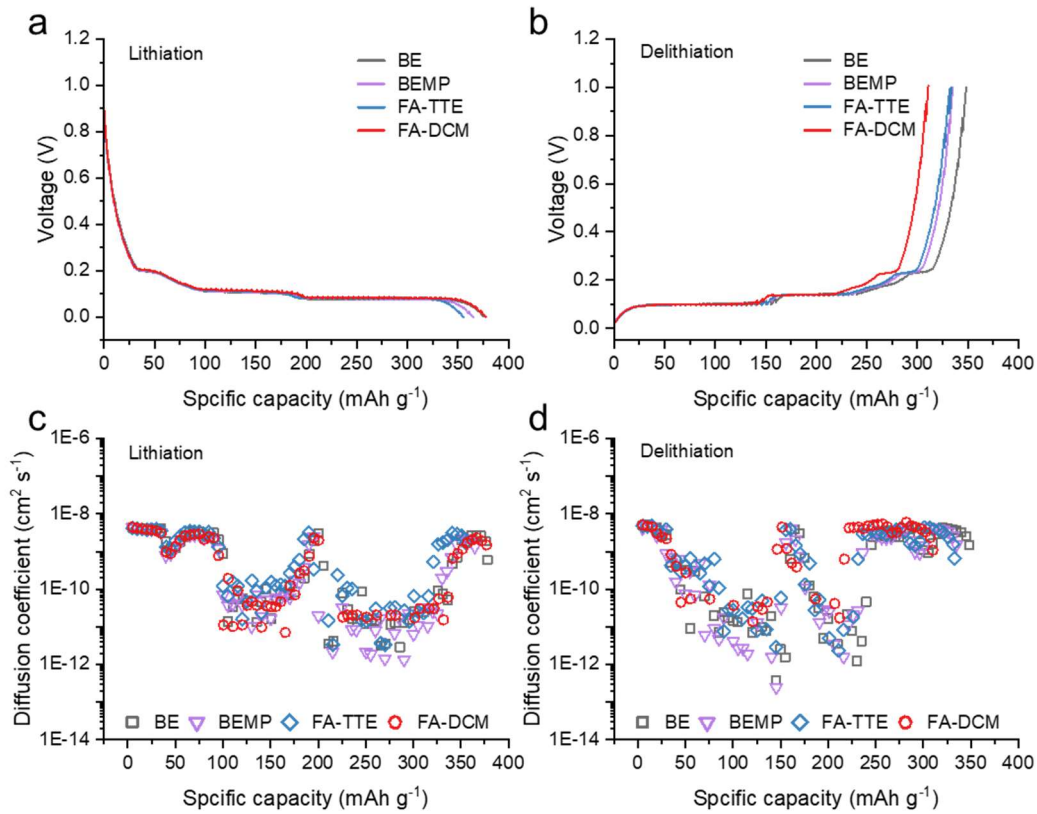


Fig. R30 | GITT evaluations of Li||graphite (0.53 mAh cm⁻²). Curves of the GITT measurements conducted after the 60th cycle of Li||graphite (0.53 mAh cm⁻²) cells with different electrolytes at 0.1 C during lithiation (a) and delithiation (b). The calculated chemical diffusion coefficients of Li⁺ during lithiation (c) and delithiation (d).

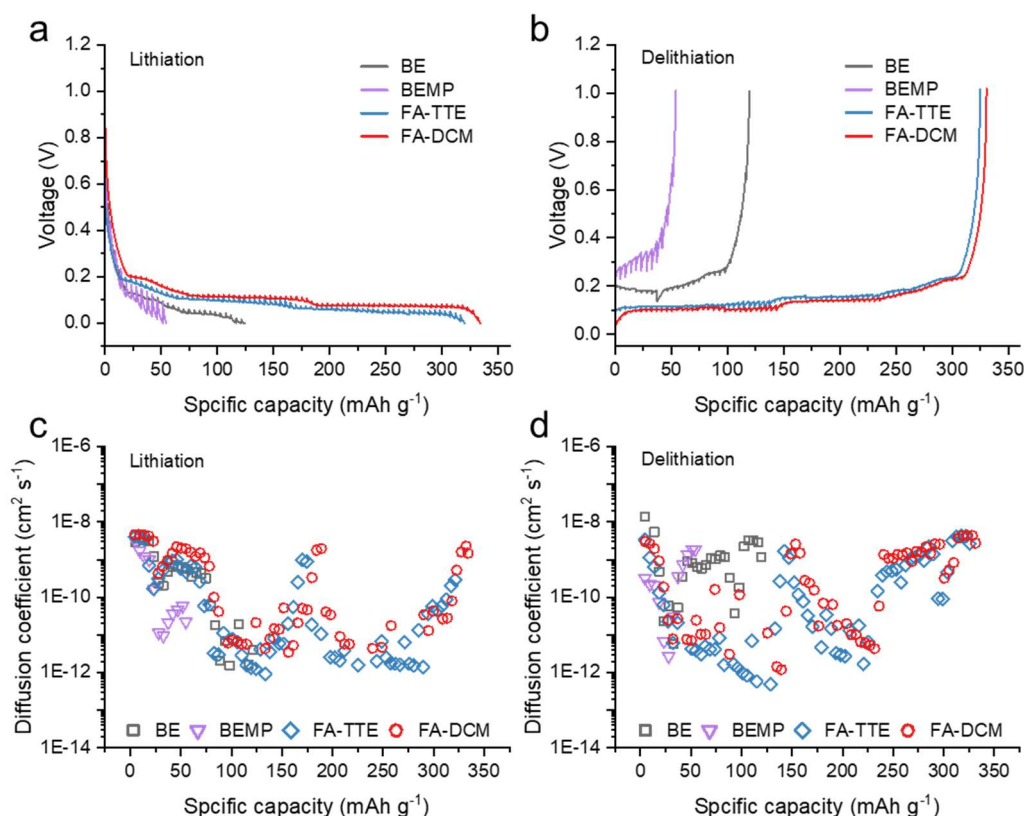
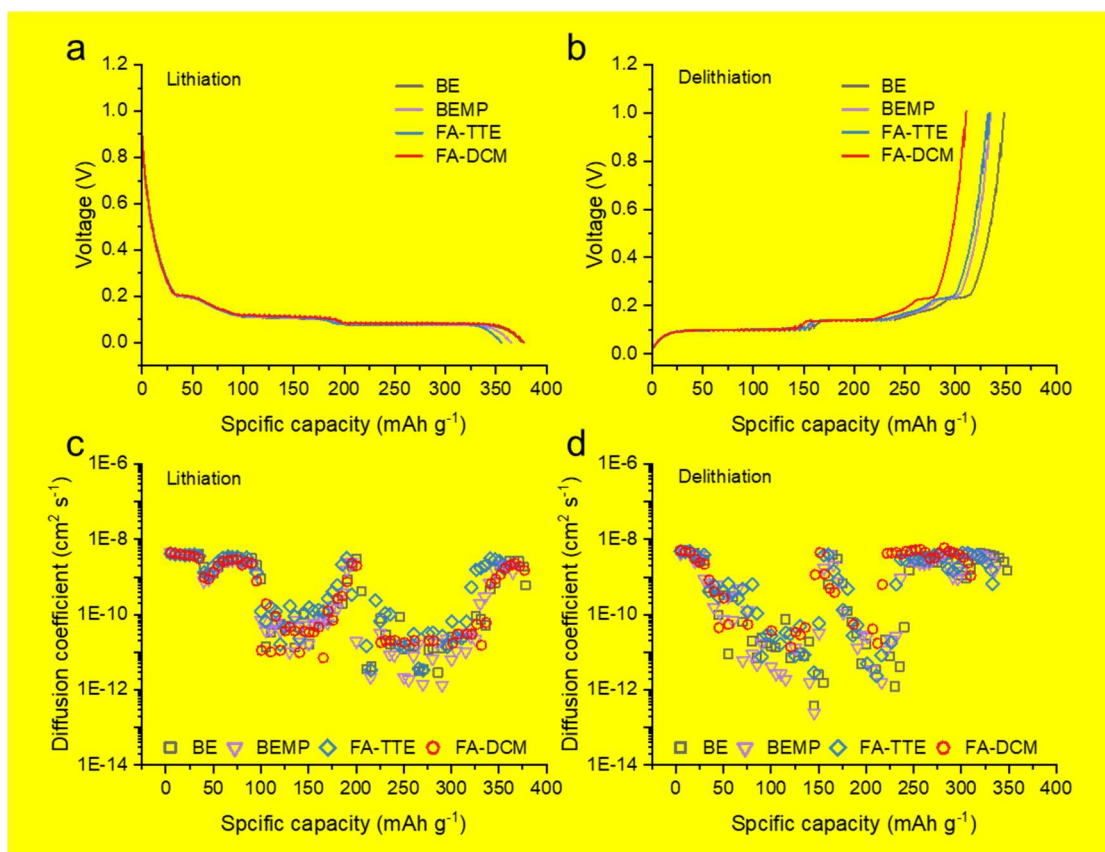


Fig. R31 | GITT evaluations of Li||graphite (3.40 mAh cm⁻²). Curves of the GITT measurements conducted after the 60th cycle of Li||graphite (3.40 mAh cm⁻²) cells with different electrolytes at 0.1 C during lithiation (a) and delithiation (b). The calculated chemical diffusion coefficients of Li⁺ during lithiation (c) and delithiation (d).

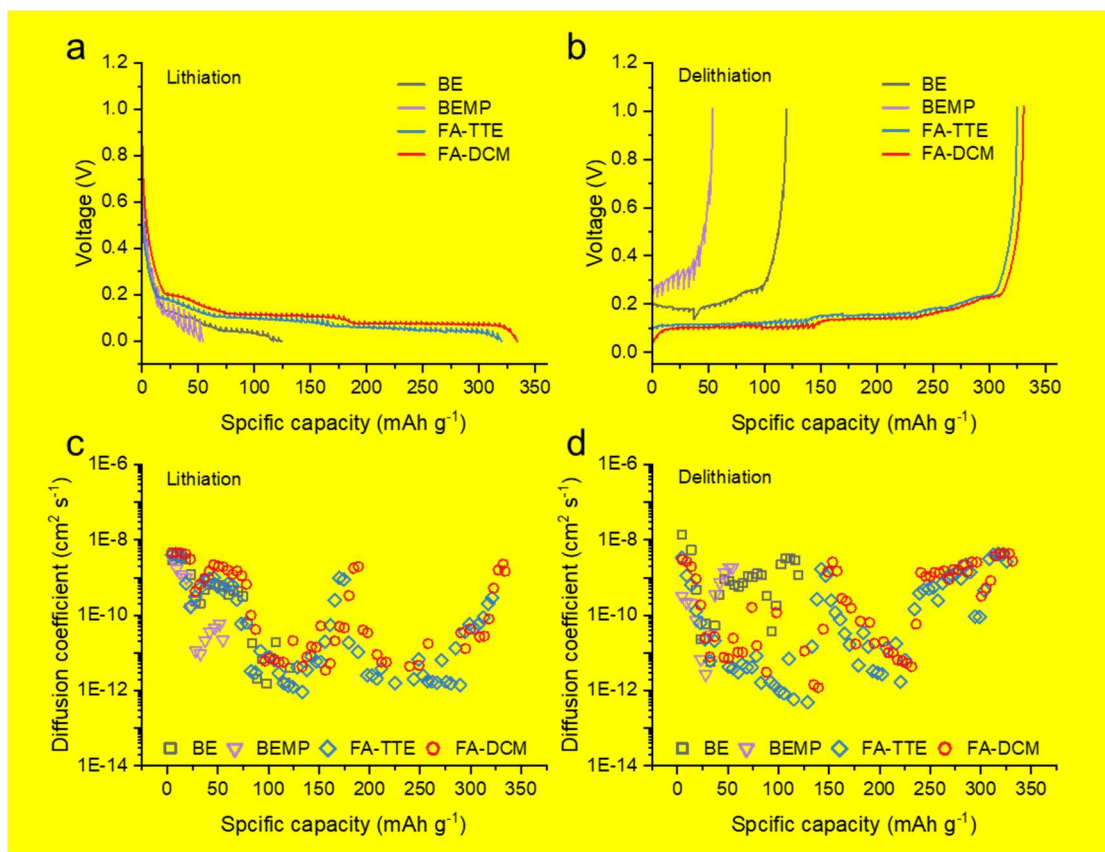
In the revised manuscript, we added the following text and highlighted it in yellow (Page 16):

Moreover, in the low-rate GITT measurements, although the FA-DCM electrolyte exhibits a diffusion coefficient comparable to those of the other three electrolytes when tested with low-loading graphite electrodes, it demonstrates a higher diffusion coefficient under the more demanding high-loading graphite conditions (Supplementary Fig. 28, 29).

In the revised supporting information (Pages 49 and 50), we added Fig. R30 and R31 as Supplementary Fig. 28 and 29, respectively:



Supplementary Fig. 28 | GITT evaluations of Li||graphite (0.53 mAh cm⁻²). Curves of the GITT measurements conducted after the 60th cycle of Li||graphite (0.53 mAh cm⁻²) cells with different electrolytes at 0.1 C during lithiation (a) and delithiation (b). The calculated chemical diffusion coefficients of Li⁺ during lithiation (c) and delithiation (d).



Supplementary Fig. 29 | GITT evaluations of Li||graphite (3.40 mAh cm⁻²). Curves of the GITT measurements conducted after the 60th cycle of Li||graphite (3.40 mAh cm⁻²) cells with different electrolytes at 0.1 C during lithiation (a) and delithiation (b). The calculated chemical diffusion coefficients of Li⁺ during lithiation (c) and delithiation (d).

3) The central mechanistic claim—enhanced ion mobility due to solvation shell disruption—should be supported by ⁷Li DOSY NMR to quantify Li⁺ diffusion. ¹H and ¹⁹F DOSY could further confirm the dynamic solvation exchange involving DCM and FSI. This experimental validation is currently missing and would greatly strengthen the work.

Reply: We thank the reviewer for this valuable suggestion. In response, we have performed ⁷Li, ¹H and ¹⁹F diffusion ordered spectroscopy (DOSY) NMR measurements on FA-DCM, FA-TTE and BE electrolytes (Fig. R32 and Table R9). The self-diffusion coefficients obtained by DOSY NMR of Li⁺ and solvent molecules in FA-DCM

electrolyte ($3.330 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ of Li^+ , $1.030 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ of FSI^- , $3.825 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ of AN, $1.267 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ of DCM) are higher than those of FA-TTE electrolyte ($1.133 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ of Li^+ , $4.268 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ of FSI^- , $1.514 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ of AN, $9.657 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ of TTE), suggesting the faster Li^+ transport in FA-DCM electrolyte. These results are consistent with the MD simulation results (Fig. 3c-d), in which the Li^+ is frequently solvated by AN molecules ($\sim 152.26 \text{ ps}$ at 298 K) and FSI^- anions ($\sim 115.66 \text{ ps}$ at 298 K) with ultra-fast hopping frequencies, conjointly confirming the discrete hopping mechanism of FA-DCM electrolyte.

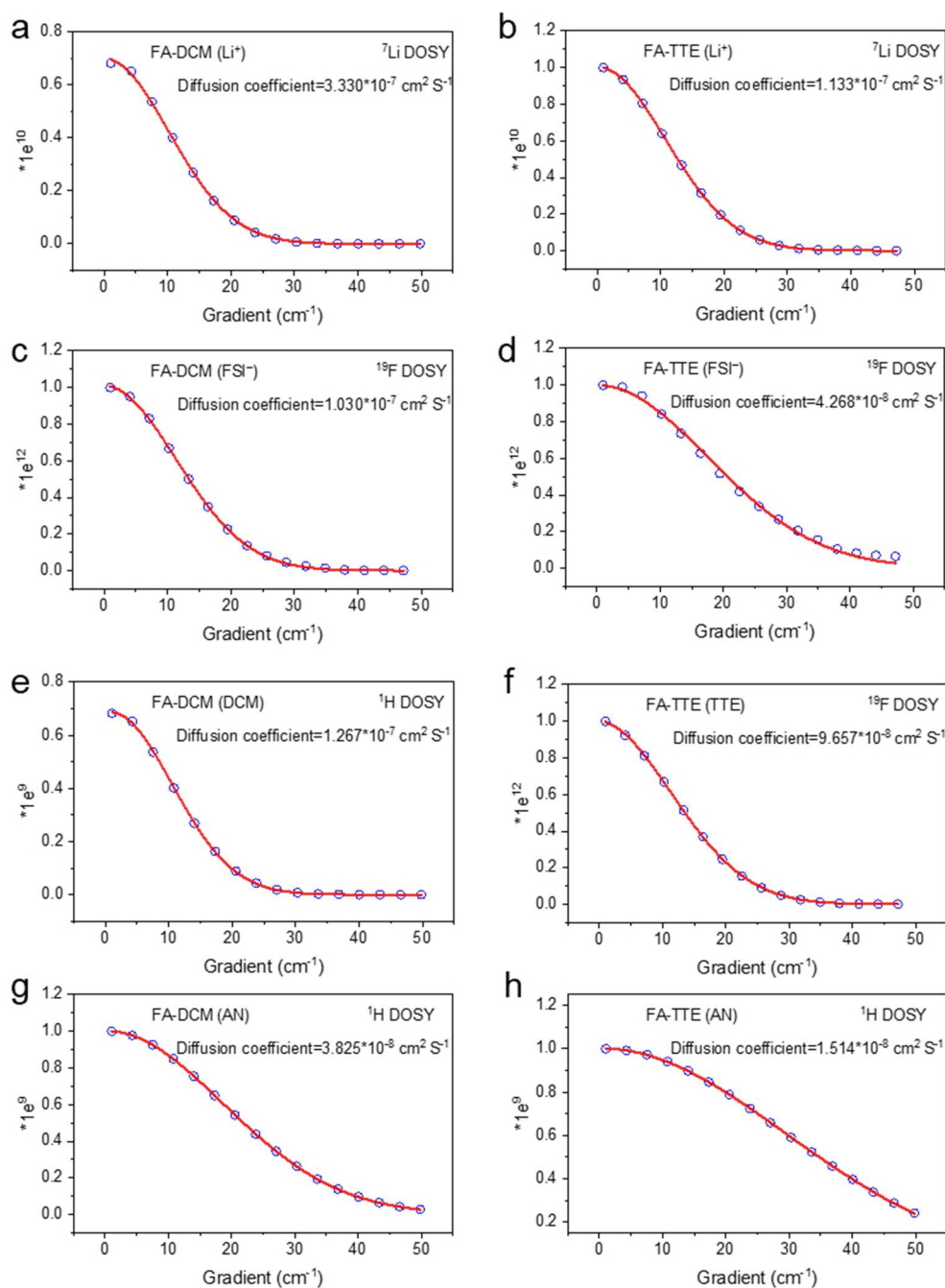


Fig. R32 | Self-diffusion coefficient measurement of different electrolytes. ^7Li DOSY NMR spectrum of FA-DCM (a) and FA-TTE electrolyte (b). ^{19}F DOSY NMR spectra of FA-DCM (c) and FA-TTE electrolyte (d, f). ^1H DOSY NMR spectrum of FA-DCM (e, g) and FA-TTE electrolyte (h).

Table R9. Self-diffusion coefficient of different electrolytes at 25 °C.

Electrolyte	FA-DCM	FA-TTE
Self-diffusion coefficient (<i>D</i>) (cm ² s ⁻¹)	$D_{\text{Li}^+}=3.330*10^{-7}$	$D_{\text{Li}^+}=1.133*10^{-7}$
	$D_{\text{FSI}^-}=1.030*10^{-7}$	$D_{\text{FSI}^-}=4.268*10^{-8}$
	$D_{\text{AN}}=3.825*10^{-8}$	$D_{\text{AN}}=1.514*10^{-8}$
	$D_{\text{DCM}}=1.267*10^{-7}$	$D_{\text{TTE}}=9.657*10^{-8}$

In the revised manuscript, we added the following text (Page 10) and highlighted it in yellow:

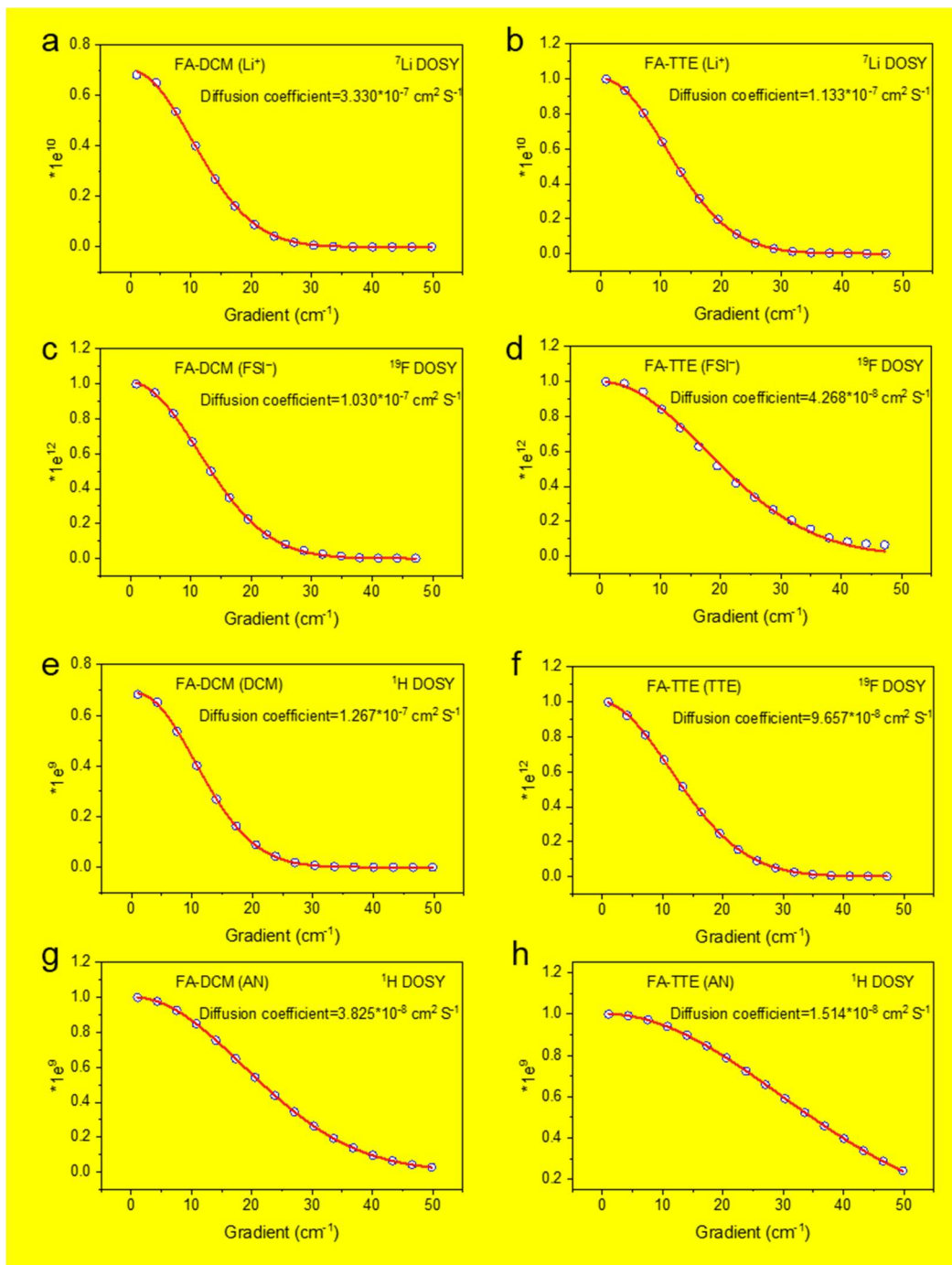
The results of diffusion ordered spectroscopy (DOSY) NMR corroborate the above results, the self-diffusion coefficients obtained by DOSY NMR of Li⁺ in FA-DCM electrolyte ($3.330*10^{-7}$ cm² s⁻¹) are higher than that of FA-TTE electrolyte ($1.133*10^{-7}$ cm² s⁻¹), suggesting the faster Li⁺ transport in FA-DCM electrolyte (Supplementary Fig. 10 and Supplementary Table 5).

In the revised method (Page 33 and 34), we added the following text:

The self-diffusion coefficients of different electrolytes were measured by ¹H, ⁷Li and ¹⁹F diffusion ordered spectroscopy (DOSY) NMR (Bruker 600MHz).

In the revised supporting information, we added the following text and highlighted it in yellow (Page 26 and 27), we also added Fig. R32 as Supplementary Fig. 10 (Page 26) and added Table R4 as Supplementary Table 5 (Page 10):

The self-diffusion coefficients obtained by DOSY NMR of FSI⁻ and solvent molecules in FA-DCM electrolyte ($1.030*10^{-7}$ cm² s⁻¹ of FSI⁻, $3.825*10^{-8}$ cm² s⁻¹ of AN, $1.267*10^{-7}$ cm² s⁻¹ of DCM) are higher than those of FA-TTE electrolyte ($4.268*10^{-8}$ cm² s⁻¹ of FSI⁻, $1.514*10^{-8}$ cm² s⁻¹ of AN, $9.657*10^{-8}$ cm² s⁻¹ of TTE).



Supplementary Fig. 10 | Self-diffusion coefficient measurement of different electrolytes. ⁷Li DOSY NMR spectrum of FA-DCM (a) and FA-TTE electrolyte (b). ¹⁹F DOSY NMR spectra of FA-DCM (c) and FA-TTE electrolyte (d, f). ¹H DOSY NMR spectrum of FA-DCM (e, g) and FA-TTE electrolyte (h).

Supplementary Table 5. Self-diffusion coefficient of different electrolytes at 25 °C obtained by diffusion ordered spectroscopy NMR in Supplementary Fig. 10.

Electrolyte	FA-DCM	FA-TTE
Self-diffusion coefficient (D) ($\text{cm}^2 \text{ s}^{-1}$)	$D_{\text{Li}^+}=3.330*10^{-7}$	$D_{\text{Li}^+}=1.133*10^{-7}$
	$D_{\text{FSI}^-}=1.030*10^{-7}$	$D_{\text{FSI}^-}=4.268*10^{-8}$
	$D_{\text{AN}}=3.825*10^{-8}$	$D_{\text{AN}}=1.514*10^{-8}$
	$D_{\text{DCM}}=1.267*10^{-7}$	$D_{\text{TTE}}=9.657*10^{-8}$

4) While improved SEI/CEI composition is discussed (LiF-LiCl-rich), the quantitative interfacial impedance analysis (e.g., R_{SEI} vs R_{ct} from EIS fitting) is limited. More robust correlation between interphase composition and electrochemical impedance would help establish cause–effect relationships.

Reply: We thank the reviewer for this constructive comment. Following the suggestion, we have carried out equivalent-circuit fitting of the electrochemical impedance spectra to quantitatively separate the SEI resistance (R_{SEI}) and the charge-transfer resistance (R_{ct}). The results confirm that the FA-DCM electrolyte achieves lower R_{SEI} and R_{ct} values than the baseline carbonate electrolyte and FA-TTE electrolyte (Fig. R33 and Table R10). And it can be inferred from the XPS analysis (Fig. 6f and Supplementary Fig. 54) and TEM images (Fig. 6d) that conventional carbonate-based electrolytes typically form SEI that is thick, heterogeneous, and rich in organic decomposition products such as alkyl carbonates and polymeric species. These organic-rich components possess poor ionic conductivity and limited mechanical robustness, which impede efficient Li^+ transport across the electrode-electrolyte interface. Moreover, the continuous reactivity of carbonate solvents with the electrode surface leads to unstable SEI growth and accumulation of resistive species over cycling, further increasing interfacial impedance. While the FA-TTE electrolyte forms LiF-rich SEI on the graphite the generally exhibits low interfacial impedance owing to its high chemical stability and dense morphology. The presence of LiF provides an electronically insulating yet ionically conductive matrix that effectively suppresses continuous electrolyte decomposition while allowing facile Li^+ migration across the interphase^{8,10,16}.

Moreover, when LiCl is co-formed with LiF, the resulting dual-halide (LiF-LiCl) interphase further achieve superior Li^+ transport kinetics due to the low energy barrier of grain boundaries for LiCl, leading to lower overall impedance and faster charge-transfer kinetics¹⁷⁻²⁰. Consequently, SEIs composed of both LiF and LiCl (FA-DCM) exhibit superior interfacial stability and ion-transport efficiency compared to those containing only LiF (FA-TTE) or organic-rich components (BE).

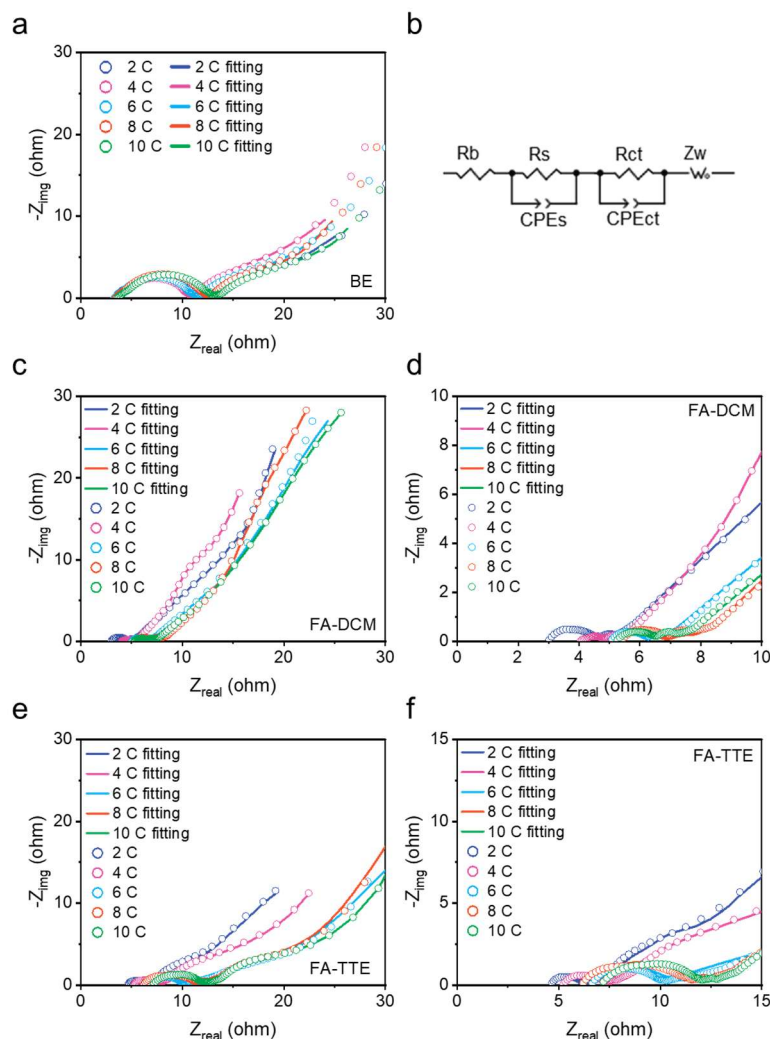


Fig. R33 | Impedance evaluations. Electrochemical impedance spectra of Li||graphite cells at different rates for BE electrolyte (a), FA-DCM electrolyte (c-d) and FA-TTE electrolyte (e-f) at 25 °C. In electrochemical impedance spectra, the solid lines represent the fits using an equivalent circuit (b), EIS were obtained at 0% SOC.

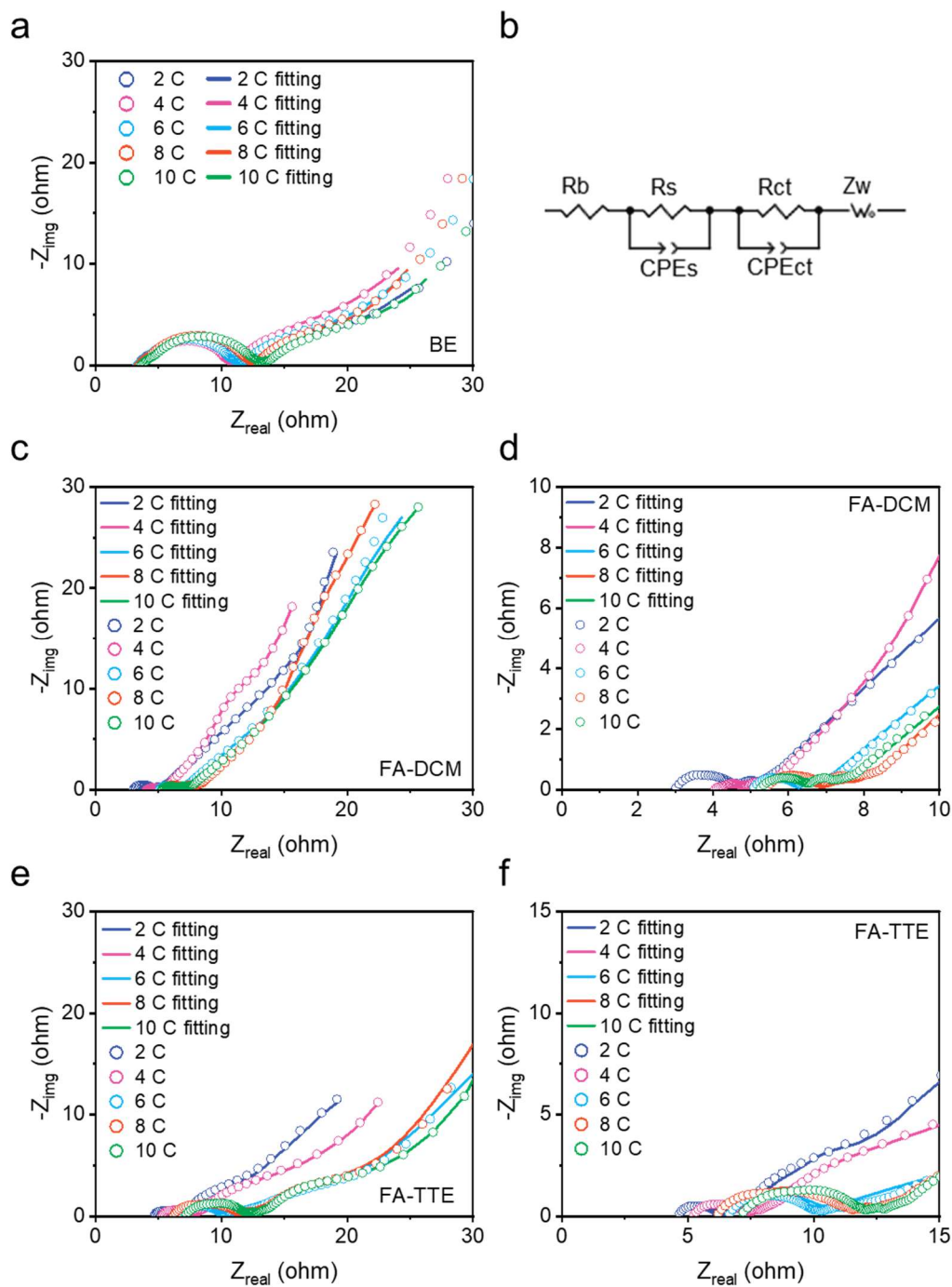
Table R10. Charge-transfer resistance (R_{ct}) and interfacial resistance (R_{SEI}) of Li||graphite cells using different electrolytes at different rates.

Electrolyte	Rate	2 C	4 C	6 C	8 C	10 C
BE	R_{ct} (Ohm)	5.290	8.420	8.790	9.500	12.85
	R_{SEI} (Ohm)	9.035	7.273	7.687	8.717	9.180
FA-TTE	R_{ct} (Ohm)	6.056	7.660	8.720	9.720	10.98
	R_{SEI} (Ohm)	1.438	1.990	3.116	4.651	4.637
FA-DCM	R_{ct} (Ohm)	0.367	0.237	0.366	0.754	0.544
	R_{SEI} (Ohm)	1.757	0.973	1.359	1.670	1.417

In the revised manuscript, we added the following text and highlighted them in yellow (Pages 15):

The total resistance in the cell primarily comprises bulk resistance (R_b), surface layer resistance (R_{SEI}), and charge transfer resistance (R_{ct}) (Fig. 4c, [Supplementary Fig. 26](#) and Table 7). Notably, the FA-DCM electrolyte exhibits much lower R_{SEI} (1.417 Ohm), and R_{ct} (0.544 Ohm) compared to the BE electrolyte (9.180 Ohm for R_{SEI} and 12.85 Ohm for R_{ct} , respectively) at 10 C, highlighting the its enhanced interfacial reaction kinetics⁴⁷.

In the revised supporting information, we added Fig. R33 as Supplementary Fig. 26 (Page 46), and added Table R8 as Supplementary Table 7 (Page 12):



Supplementary Fig. 26 | Impedance evaluations. Electrochemical impedance spectra of Li||graphite cells at different rates for BE electrolyte (a), FA-DCM electrolyte (c-d) and FA-TTE electrolyte (e-f) at 25 °C. In electrochemical impedance spectra, the solid lines represent the fits using an equivalent circuit (b), EIS were obtained at 0% SOC.

Supplementary Table 7. Charge-transfer resistance (R_{ct}) and interfacial resistance (R_{SEI}) of Li||graphite cells using different electrolytes at different rates.

Electrolyte	Rate	2 C	4 C	6 C	8 C	10 C
BE	R_{ct} (Ohm)	5.290	8.420	8.790	9.500	12.85
	R_{SEI} (Ohm)	9.035	7.273	7.687	8.717	9.180
FA-TTE	R_{ct} (Ohm)	6.056	7.660	8.720	9.720	10.98
	R_{SEI} (Ohm)	1.438	1.990	3.116	4.651	4.637
FA-DCM	R_{ct} (Ohm)	0.367	0.237	0.366	0.754	0.544
	R_{SEI} (Ohm)	1.757	0.973	1.359	1.670	1.417

5) Dichloromethane (DCM) has low boiling point and is environmentally concerning. The paper lacks discussion on volatility, flammability, and toxicity, which may limit practical applicability despite performance advantages.

Reply: We appreciate the reviewer’s thoughtful comment regarding the safety and environmental implications of DCM. We fully acknowledge that DCM has a low boiling point and is associated with volatility, flammability, and toxicity, which warrant careful consideration for any practical deployment.

In this study, however, the use of DCM is intended primarily as a proof-of-concept to demonstrate how tailoring the solvation structure can fundamentally enhance Li^+ mobility under demanding low-temperature and high-rate conditions. The relatively high proportion of DCM was chosen to clearly reveal the mechanistic advantages. Importantly, the pouch cells employed in our experiments provide excellent sealing, which effectively mitigates solvent evaporation and exposure during operation.

Looking forward, we envision that the mechanistic insights gained here can guide the rational design of next-generation electrolytes based on less volatile and less toxic solvents, or on mixed formulations with substantially reduced DCM content. Thus,

while DCM itself may not represent a practical large-scale solution, its inclusion in this work establishes fundamental design principles that can be translated to safer and more sustainable electrolyte systems.

In the revised manuscript (Page 24), we added the following text and highlighted it in yellow:

It is worth noting that the toxicity and volatility of DCM limit its broader applicability, but the sealed cells using DCM-based electrolyte still demonstrated decent stability and capacity retention under extended cycling or storage (Supplementary Fig. 59-61). More importantly, as a moderator with small molecular size and low dipole moment, DCM successfully tunes the solvation structure, creating a more uniformly distributed and compact solvation clusters, which is essential for ultralow-temperature operation and fast charging. This success validates the feasibility of the concept and paves the way for future electrolytes designed on these principles to be both high-performing and environmentally benign.

6) The proposed $D = 1/(\mu \cdot V)$ descriptor is interesting but lacks theoretical foundation. Why should this specific functional form (inverse product) correlate with solvation disruption? Comparative performance against known Gutmann donor number, dielectric constant, or Lewis basicity is not shown.

Reply: We thank the reviewer for this constructive comment. The interactions between moderators and anions, as well as between moderator and solvents, are described by equations as shown in Supplementary Note 4. To disrupt the solvation structure, it is necessary to strengthen the interaction between the moderators and the anions (thereby weakening the lithium-anion interaction) and to reduce the interaction between the moderators and the solvents (thereby strengthening the lithium-solvent interaction). According to the results derived from the formula in the Supplementary Note 4, reducing μ enhances the effectiveness of the moderators, whereas reducing V increases the number of moderators actions. To benchmark the proposed descriptor against

conventional parameters, we analyzed the correlation of average Li^+ residence times with D value, Gutmann donor number and dielectric constant. As shown in Fig. R34-36, neither donor number nor dielectric constant exhibits a strong linear correlation with solvation dynamics, indicating that these parameters alone are insufficient to capture the complex interplay ion-anion-solvent interactions.

In contrast, the descriptor $D = 1/(\mu \cdot V)$ provides a significantly stronger correlation with Li^+ residence time (Pearson's $r=-0.785$ for AN, Pearson's $r=-0.894$ for FSI $^-$), reflecting its ability to capture both electronic and steric effects in the system. It is grounded in the physical rationale that moderators of small dipole moment and compact molecular volume help to adjust the intermolecular interactions, thereby promoting disruption of large ion-anion clusters and facilitating Li^+ hopping.

In brief, these results suggest that the D descriptor more effectively rationalizes solvation structure regulation than conventional donor number or dielectric constant, providing a practical screening criterion for moderator design.

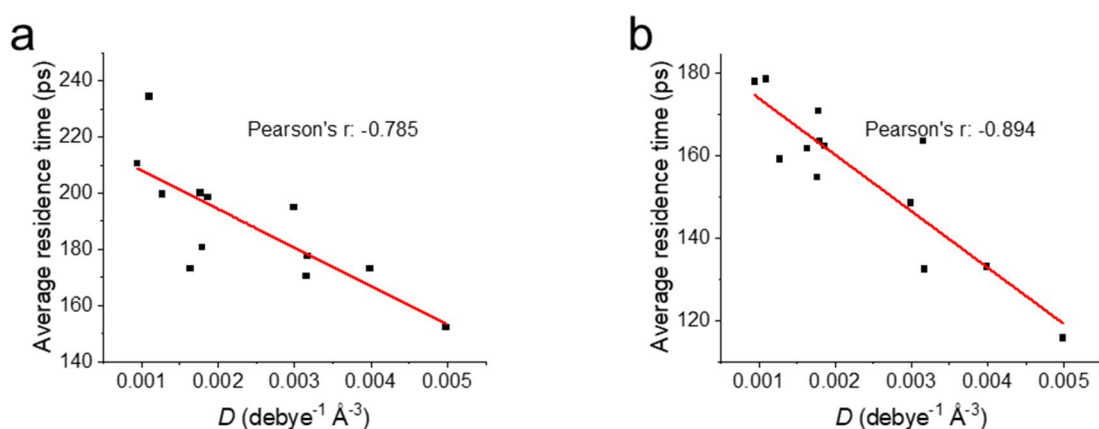


Fig. R34 | Functional relationship between average residence time and the disintegration of solvation structures (D). AN (a) and FSI $^-$ (b).

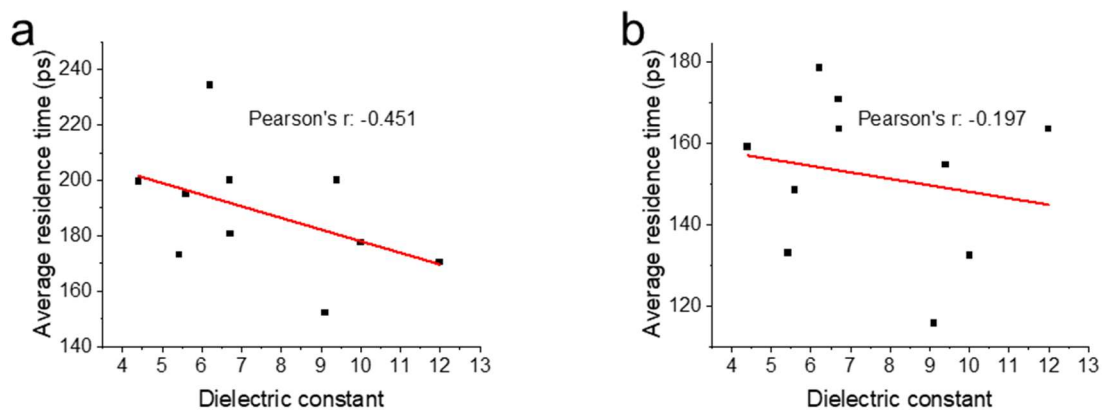


Fig. R35 | Functional relationship between average residence time and dielectric constant. AN (a) and FSI (b).

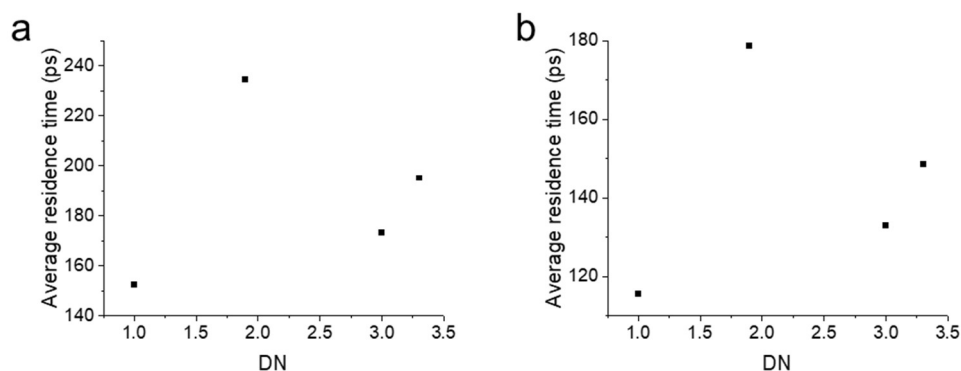
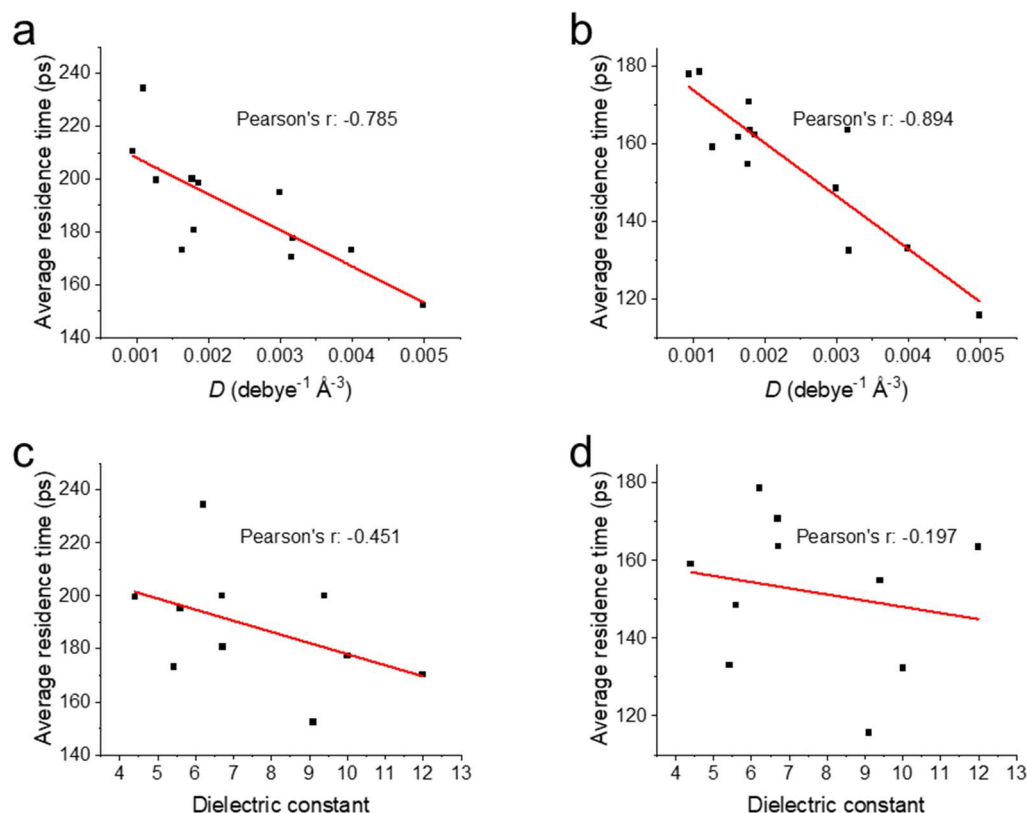


Fig. R36 | Functional relationship between average residence time and donor number. AN (a) and FSI (b).

In the revised manuscript (Page 12), we added the following text and highlighted it in yellow:

Such a linear inverse relationship between the D value and residence time corroborates the effectiveness of this descriptor in predicting ion transport properties (Supplementary Fig. 16).

In the revised supporting information (Page 34 and 35), we added the following text and highlighted it in yellow and add Fig. R34 and Fig. R35 as Supplementary Fig. 16.



Supplementary Fig. 16 | Functional relationship between average residence time and the disintegration of solvation structures (D). AN (a) and FSI⁻ (b). Functional relationship between average residence time and dielectric constant. AN (c) and FSI⁻ (d).

To quantitatively validate the proposed descriptor $D=C/(\mu \cdot V)$, we plotted the correlation between D values and the average Li⁺ residence times (both with AN and FSI⁻) obtained from MD simulations. As shown, a negatively correlated linear function relationship is observed: larger D values correspond to shorter residence times, in agreement with our theoretical framework. Pearson's correlation analysis yields $r=-0.785$ for AN and $r=-0.894$ for FSI⁻, confirming a strong negative correlation between the descriptor and Li⁺ solvation dynamics. This quantitative analysis supports the predictive capability of the proposed descriptor in capturing key ion transport characteristics. While the known dielectric constant does not exhibit a strong linear correlation with solvation dynamics, indicating that these parameters alone are insufficient to capture the complex interplay ion-anion-solvent interactions.

7) Although ionic conductivity is reported at $-70\text{ }^{\circ}\text{C}$ to $25\text{ }^{\circ}\text{C}$, activation energy (E_a) for ion transport is not extracted. Arrhenius or VTF plots would provide a clearer understanding of temperature-dependent kinetics.

Reply: We thank the reviewer for this valuable suggestion. Following the comment, we have extracted the activation energy (E_a) for ion transport by fitting the ionic conductivity data using both Arrhenius and Vogel-Tammann-Fulcher (VTF) equations. In Fig. R37, the FA-DCM electrolyte exhibits a substantially lower E_a compared to the carbonate-based BE electrolyte and the FA-TTE electrolyte employing a bulky moderator.

This reduced activation barrier highlights the more facile Li^+ transport enabled by FA-DCM, particularly at sub-zero temperatures, and provides further quantitative support for the discrete Li^+ hopping mechanism proposed in this work. The consistency between conductivity-temperature fitting and the electrochemical performance results strengthens the mechanistic conclusions.

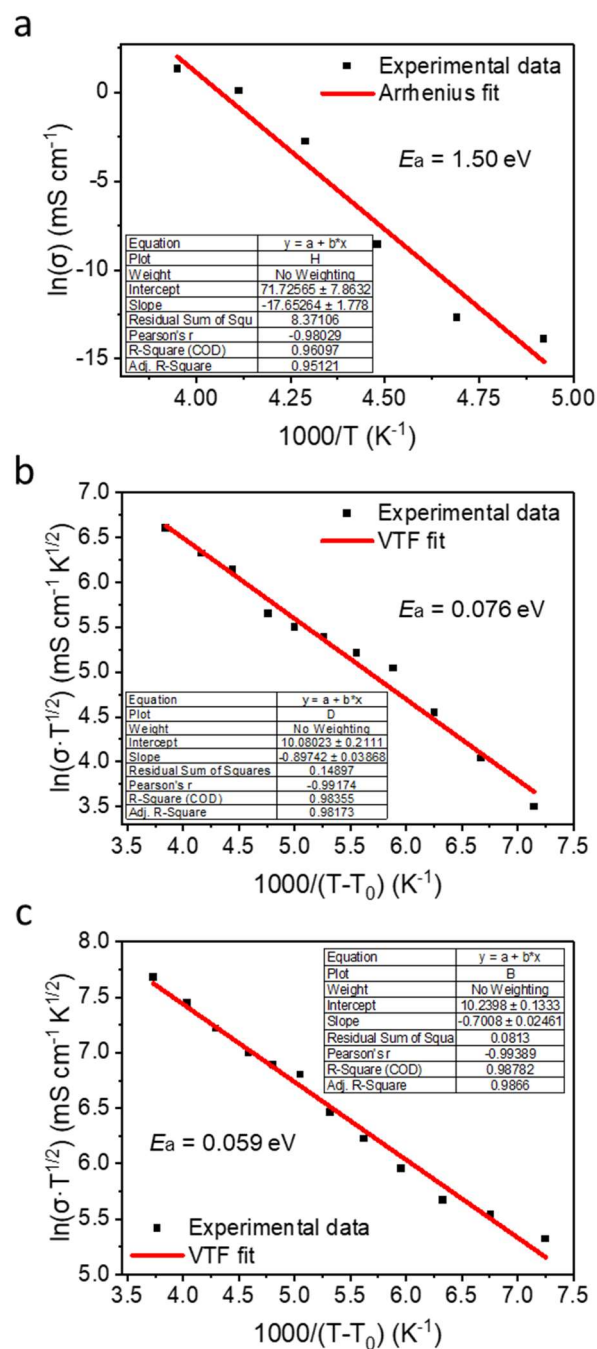
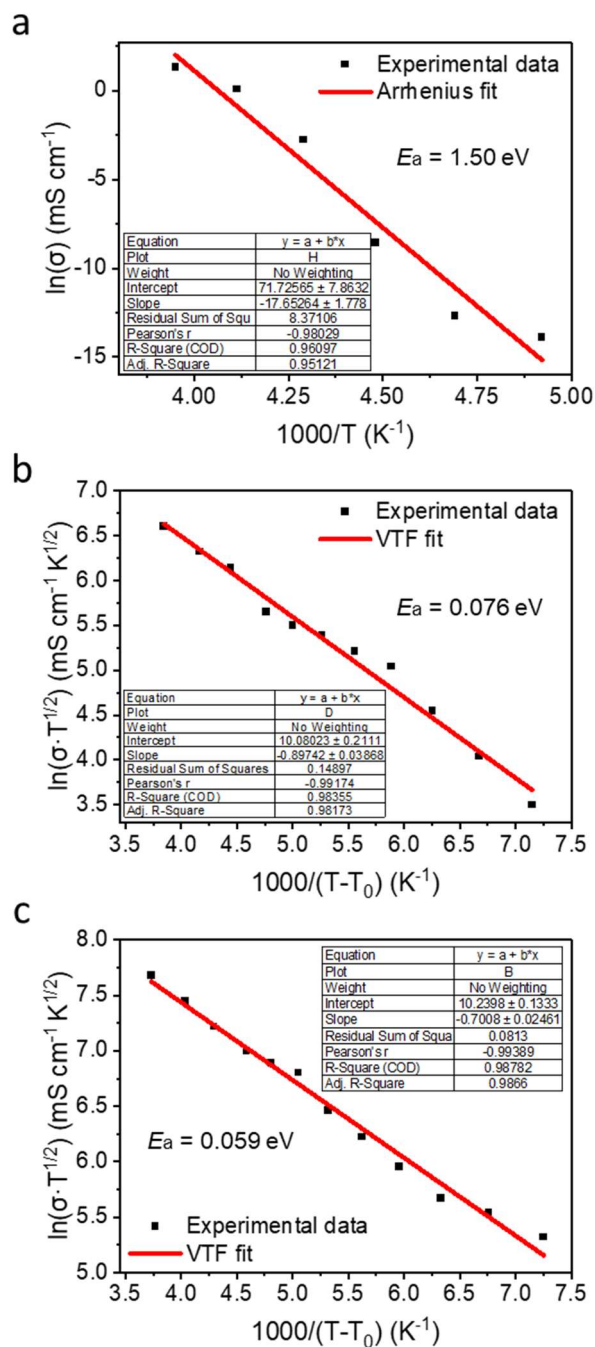


Fig. R37 | Ionic conductivity-temperature fitting. The fitting results for BE electrolyte (a), FA-TTE electrolyte (b) and FA-DCM electrolyte (c).

In the revised manuscript, we added the following sentence and highlighted it in yellow on Pages 14:

Even at an ultra-low temperature of -70 °C, the FA-DCM electrolyte, with its lower activation energy (0.059 eV), maintains an impressive ionic conductivity of 2.01 mS cm⁻¹, ensuring adequate low-temperature ion transfer kinetics²⁶ (Supplementary Fig. 22). In contrast, the commercial carbonate-based electrolyte of 1.0 M LiPF₆ in an EC-dimethyl carbonate (DMC) mixture (1:1, vol) (denoted as BE electrolyte) exhibits slightly higher ionic conductivity at room temperature (12.00 mS cm⁻¹) but suffers a sharp decline at -38 °C (0.06 mS cm⁻¹) due to its high freezing point and elevated activation energy (1.50 eV), making it unsuitable for low-temperature applications (Fig. 3h).

In the revised supporting information (Pages 42), we added Fig. R37 as Supplementary Fig. 22.



Supplementary Fig. 22 | Ionic conductivity-temperature fitting. The fitting results for BE electrolyte (a), FA-TTE electrolyte (b) and FA-DCM electrolyte (c).

8) Is the effect of DCM reversible or stable over time and cycling? The paper does not show long-term aging or electrolyte stability under extended cycling or storage.

Reply: We thank the reviewer for raising this important point regarding the long-term stability of the DCM-containing electrolyte. To directly address this concern, we

performed storage and post-aging electrochemical tests on pouch cells assembled with BE, BEMP, FA-TTE, and FA-DCM electrolytes. The pouch cells were stored at 45 °C for 7 days, after which we obtained the volume change of the gas bag through the water displacement method. Moreover, we also evaluated the capacity retention by comparing the discharge capacity before and after storage.

As shown in Fig. R38, the swelling of graphite||NMC811 pouch cells assembled with the FA-DCM electrolyte was minimal and highly acceptable. Importantly, the capacity retention of FA-DCM is acceptable among the four electrolytes (FA-DCM, 90.7%; FA-TTE, 86.5%; BE, 96.9%; BEMP, 97.2%, Fig. R39). These results confirm that the volatility of DCM, while contributing to slight swelling, remains within safe limits without inducing catastrophic failure.

These findings demonstrate that the effect of DCM is not only reversible but also reasonably stable under extended storage at elevated temperature. The pouch cells assembled with FA-DCM electrolyte maintain capacity retention comparable to conventional systems, indicating that the molecular-level benefits of solvation sheath reorganization are preserved over time and cycling.

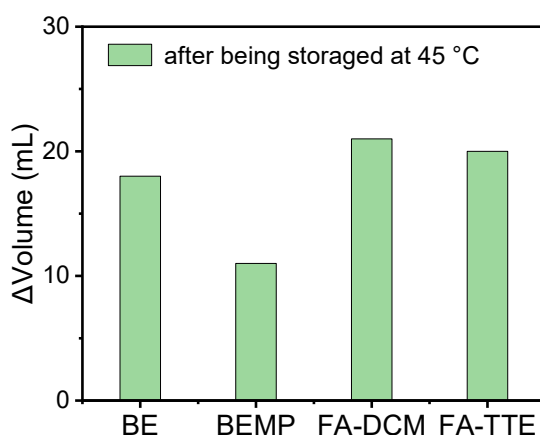


Fig. R38 | The change in volume of gas bag in the pouch cells before and after being stored at 45 °C in different electrolytes.

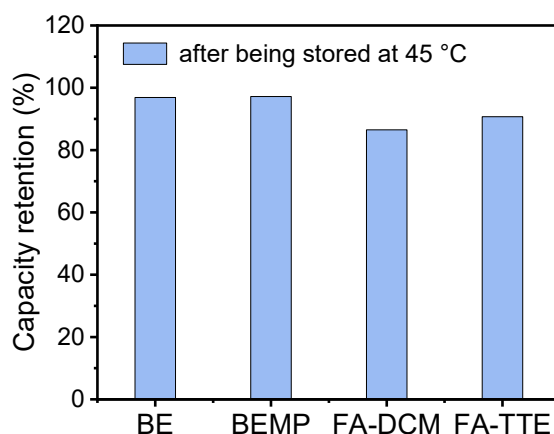
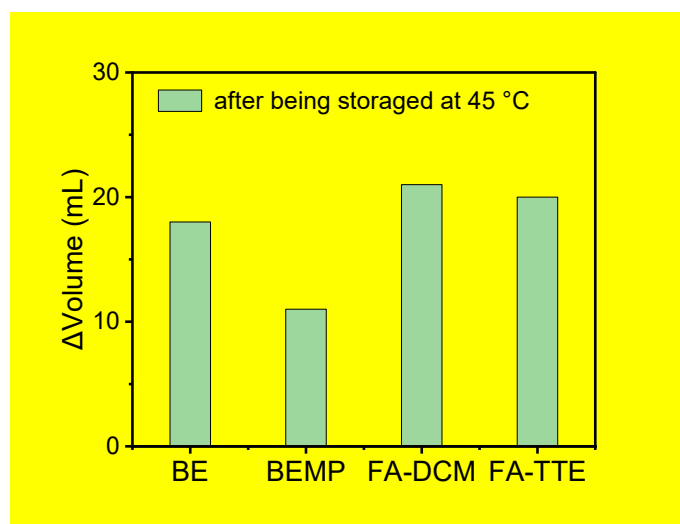


Fig. R39 | Capacity retention of the pouch cells after being stored at 45 °C in different electrolytes.

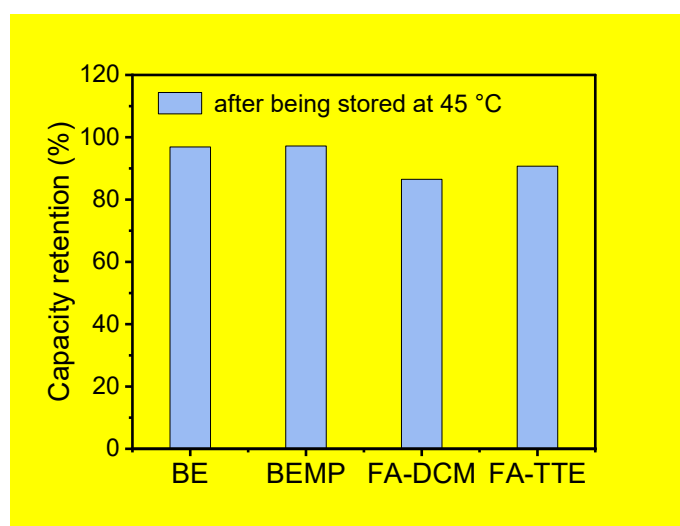
In the revised manuscript (Page 24), we added the following sentences and highlighted them in yellow:

It is worth noting that the toxicity and volatility of DCM limit its broader applicability, but the sealed cells using DCM-based electrolyte still demonstrated decent stability and capacity retention under extended cycling or storage (Supplementary Fig. 59-61). More importantly, as a moderator with small molecular size and low dipole moment, DCM successfully tunes the solvation structure, creating a more uniformly distributed and compact solvation clusters, which is essential for ultralow-temperature operation and fast charging. This success validates the feasibility of the concept and paves the way for future electrolytes designed on these principles to be both high-performing and environmentally benign.

In the revised supporting information (Page 82 and 83), we added Fig. R38 and Fig. R39 as Supplementary Fig. 60, 61, respectively.



Supplementary Fig. 60 | The change in volume of gas bag in the pouch cells before and after being stored at 45 °C in different electrolytes.



Supplementary Fig. 61 | Capacity retention of the pouch cells after being stored at 45 °C in different electrolytes.

9) The comparison is mainly between FA-TTE and FA-DCM. A control using FA alone or other small molecule moderators would clarify whether DCM is uniquely effective or if the result is generalizable.

Reply: We appreciate the reviewer's suggestion. To clarify whether the observed effect is unique to DCM or generalizable to other small-molecule moderators, we additionally investigated an FA-dichloroethane (DCE) system. And to further validate the general

applicability of the D -based screening model, we have investigated an additional electrolyte system using 1,1,2,2,3,3,4-heptafluorocyclopentane (HFC) as the moderator, which exhibits an intermediate D value between DCM and TTE. Furthermore, to substantiate the universality of the D value as a selection parameter, we conducted both simulations and experiments on an electrolyte employing DCE (a higher D value than HFC, but lower than DCM) and evaluated the corresponding low-temperature and fast-charging performance of the graphite||NMC811 cells (Fig. R40).

According to Fig. R41, Fig. 2b, Supplementary Fig. 3, and Supplementary Fig. 4a, b, the dissociation capability of the solvation structures can be ranked as DCM, DCE, HFC, and TTE, in agreement with the corresponding order of their D values. Additionally, MD simulations show that the average Li^+ residence time of 177.45 ps (AN) and 132.36 ps (FSI^-) in the FA-DCE electrolyte, and 180.71 ps (AN) and 163.55 ps (FSI^-) in the FA-HFC electrolyte. These values follow a consistent trend when referenced against the FA-DCM and FA-TTE systems (Fig. R42-44).

Moreover, under 6 C charge/discharge conditions (Fig. R45), the cells using FA-DCM electrolyte retain 88.2% of its capacity at 1 C, outperforms FA-DCE (80.6%) and FA-HFC (53.1%), which in turn surpasses FA-TTE (43.7%). Similarly, as shown in Fig. R46, at -40 °C, graphite||NMC811 cells assembled with FA-DCM electrolyte deliver the highest capacity (126.7 mAh g⁻¹), while the cells using FA-DCE, FA-HFC electrolyte exhibit lower capacity of 116.6 mAh g⁻¹ and 107.0 mAh g⁻¹, respectively, and FA-TTE shows the poorest performance (75.1 mAh g⁻¹). This quantitative alignment between experimental performance and simulated solvation dynamics provides further support for the predictive capability of the D -based screening model. These new results confirm that the correlation between D and ion transport properties is not merely a phenomenon observed in isolated cases, but true generality across various systems, thereby reinforcing the broad applicability and robustness of the proposed descriptor.

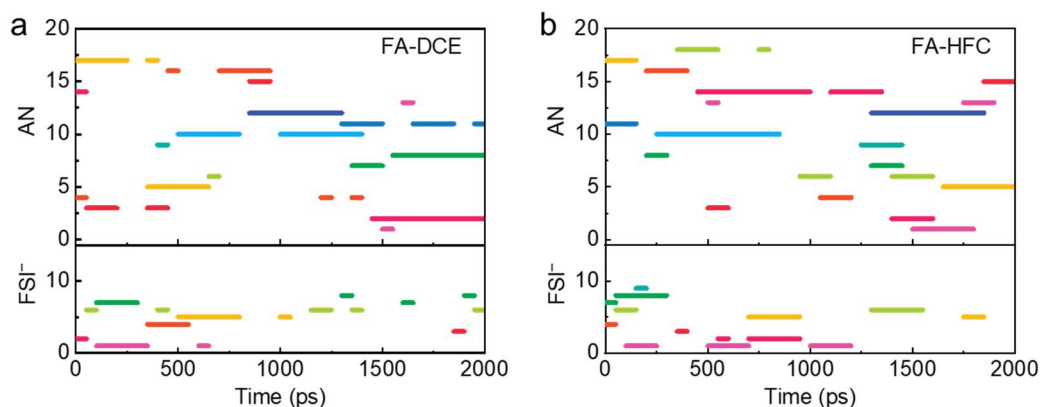


Fig. R42 | Evolution of Li^+ solvation environment in FA-DCE (a) and FA-HFC electrolyte (b) from MD simulations at 298 K. The vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li^+ in the simulation time of 2,000 ps.

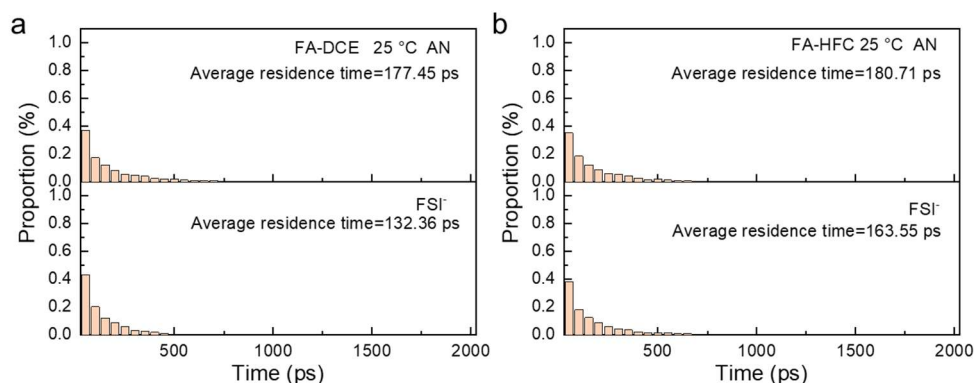


Fig. R43 | Residence time distribution of AN and FSI^- in FA-DCE (a) and FA-HFC electrolyte (b) at 298 K.

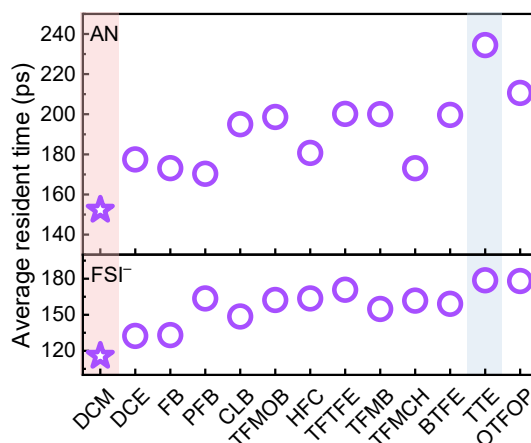


Fig. R44 | The average residence time of Li^+ in LiFSI/AN-based electrolytes with different moderators.

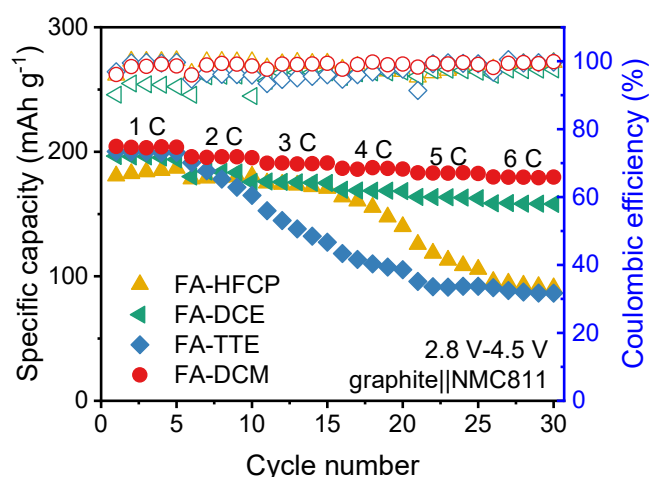


Fig. R45 | Rate performance of graphite||NMC811 cells with different electrolytes in the range of 2.8-4.5 V at 25 °C.

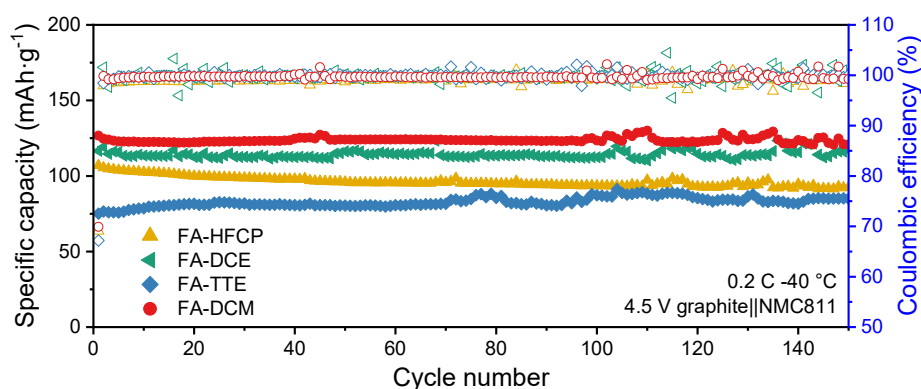


Fig. R46 | Cycling performance with different electrolytes in the range 2.8-4.5 V at 0.2 C under -40 °C.

In the revised manuscript, we added the following sentences and highlighted them, we also added Fig. R40 and Fig. R44 as Fig. 1c and Fig. 3e, respectively.

(Page 9)

Notably, the FA-DCM electrolyte exhibits the highest proportion of CIPs among the **thirteen** analyzed moderator-based electrolytes (Supplementary Fig. 4c-n and Fig. 6).

(Page 12)

Owing to its relatively high *D* value of dichloroethane (DCE), the 1.5 M LiFSI in an

AN-DCE mixture (1:4, vol) (denoted as FA-DCE electrolyte) demonstrates a residence time close to that of FA-DCM (177.45 ps for AN and 132.26 ps for FSI) (Supplementary Fig.14a and Fig. 15f). In contrast, the 1.5 M LiFSI in an AN-1,1,2,2,3,3,4-heptafluorocyclopentane (HFC) mixture (1:4, vol) (denoted as FA-HFC electrolyte), with an intermediate D value, exhibits a significantly longer residence time (180.71 ps for AN and 163.55 ps for FSI) (Supplementary Fig.14b and Fig. 15g).

(Page 16)

The graphite||NMC811 full cell with FA-DCM electrolyte delivers a high capacity of 179.8 mAh g⁻¹ at a demanding rate of 6 C—higher than that of FA-DCE (158.3 mAh g⁻¹) and FA-HFC (99.3 mAh g⁻¹) (Supplementary Fig. 29), more than double the capacity of the FA-TTE cell (83.2 mAh g⁻¹), and substantially outperforming cells using BE

(Page 19)

The graphite||NMC811 full cells based on FA-DCE (large D value), FA-HFC (moderate D value), and FA-TTE (small D value) electrolytes reached 113.3 mAh g⁻¹, 102.4 mAh g⁻¹, and 78.6 mAh g⁻¹, respectively, providing experimental evidence for the universality of adopting the D value as a screening metric.

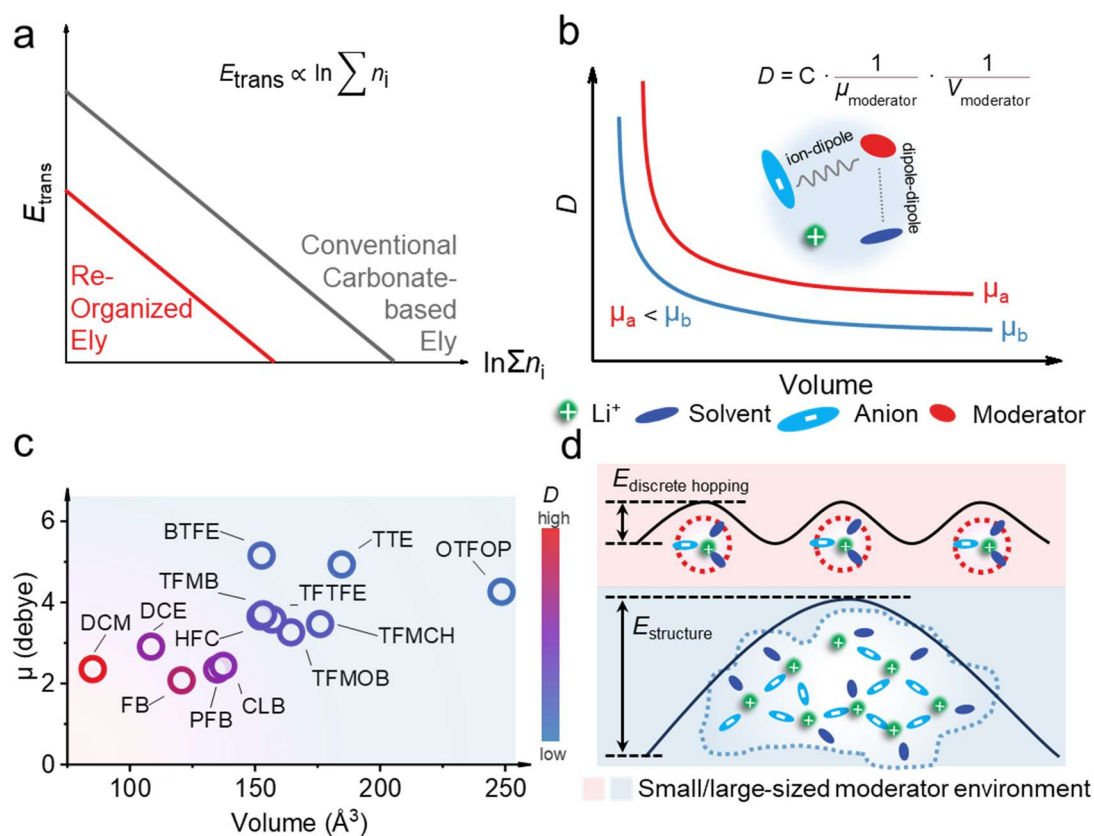


Fig. 1 | Moderator screening strategy. **a**, Variation of Li^+ transfer energy (E_{trans}) as a function of the natural logarithm of the total effective charge carriers ($\sum n_i$) **b**, Functional relationship between the disintegration of solvation structures (D) and moderator properties [dipole moment ($\mu_{\text{moderator}}$) and molecule volume ($V_{\text{moderator}}$)]. **c**, $\mu_{\text{moderator}}$ and $V_{\text{moderator}}$ for various moderators. **d**, Transfer energy barriers for discrete hopping mechanism and structure mechanism in small-sized and large-sized moderator environment, respectively.

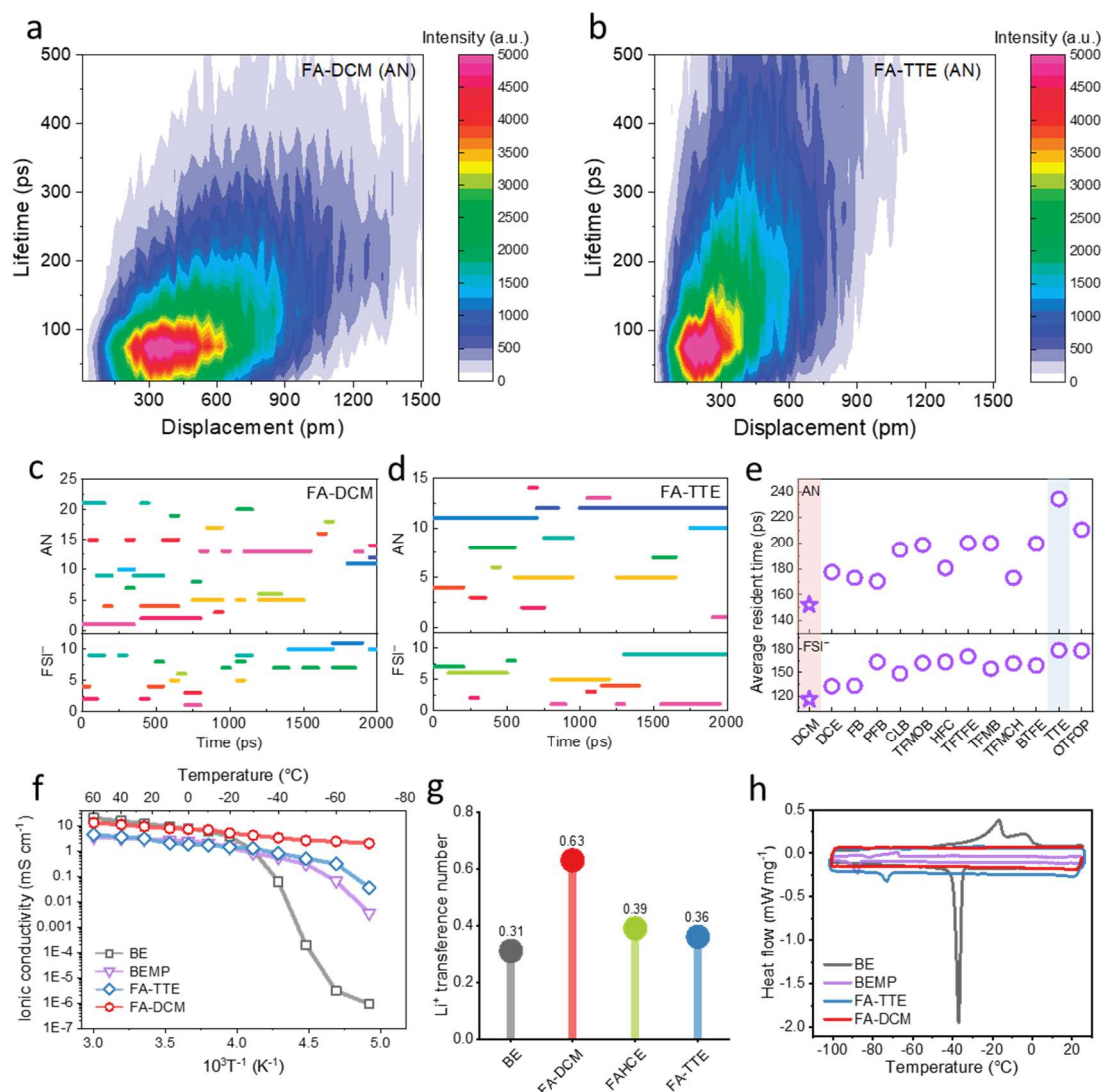
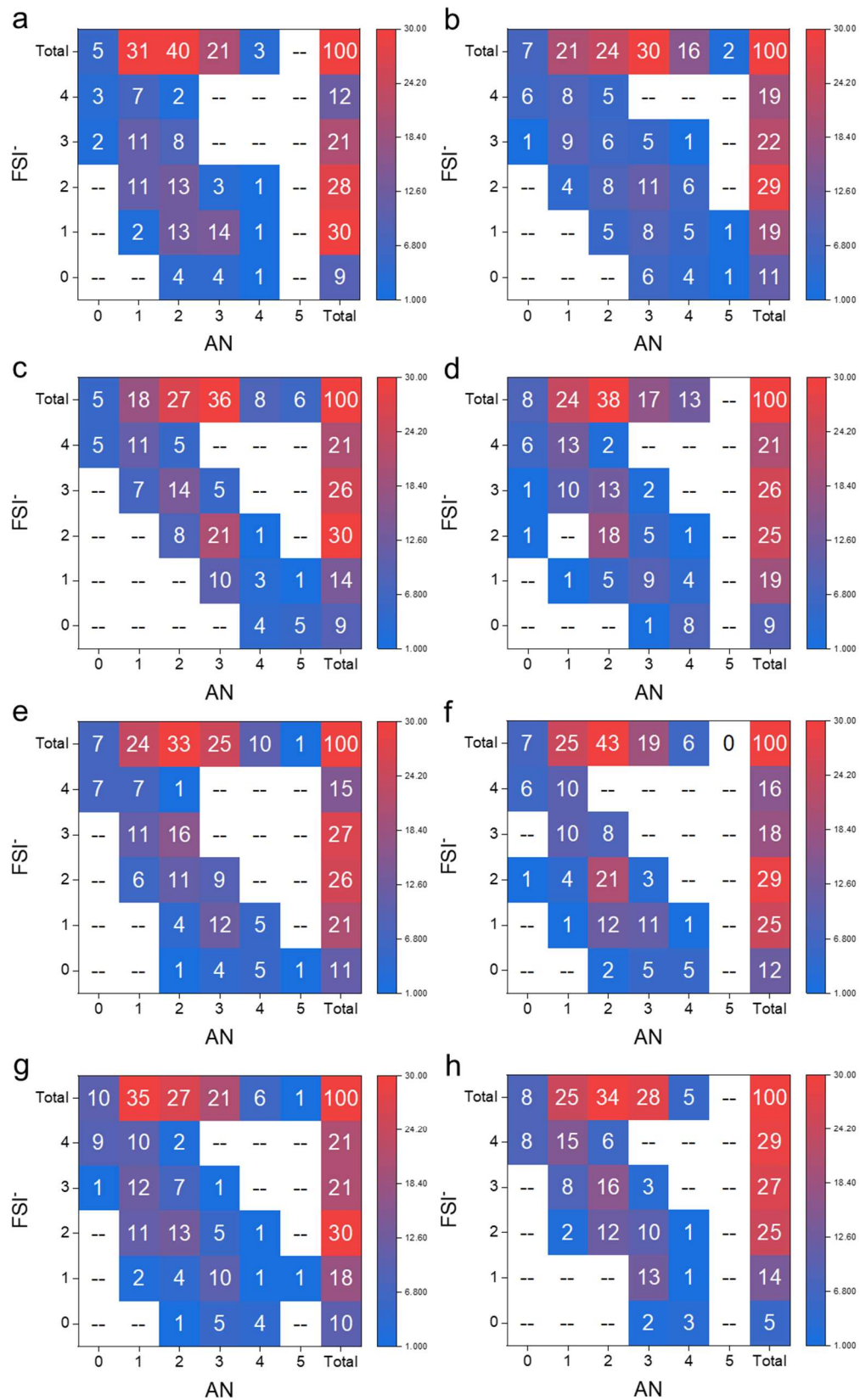
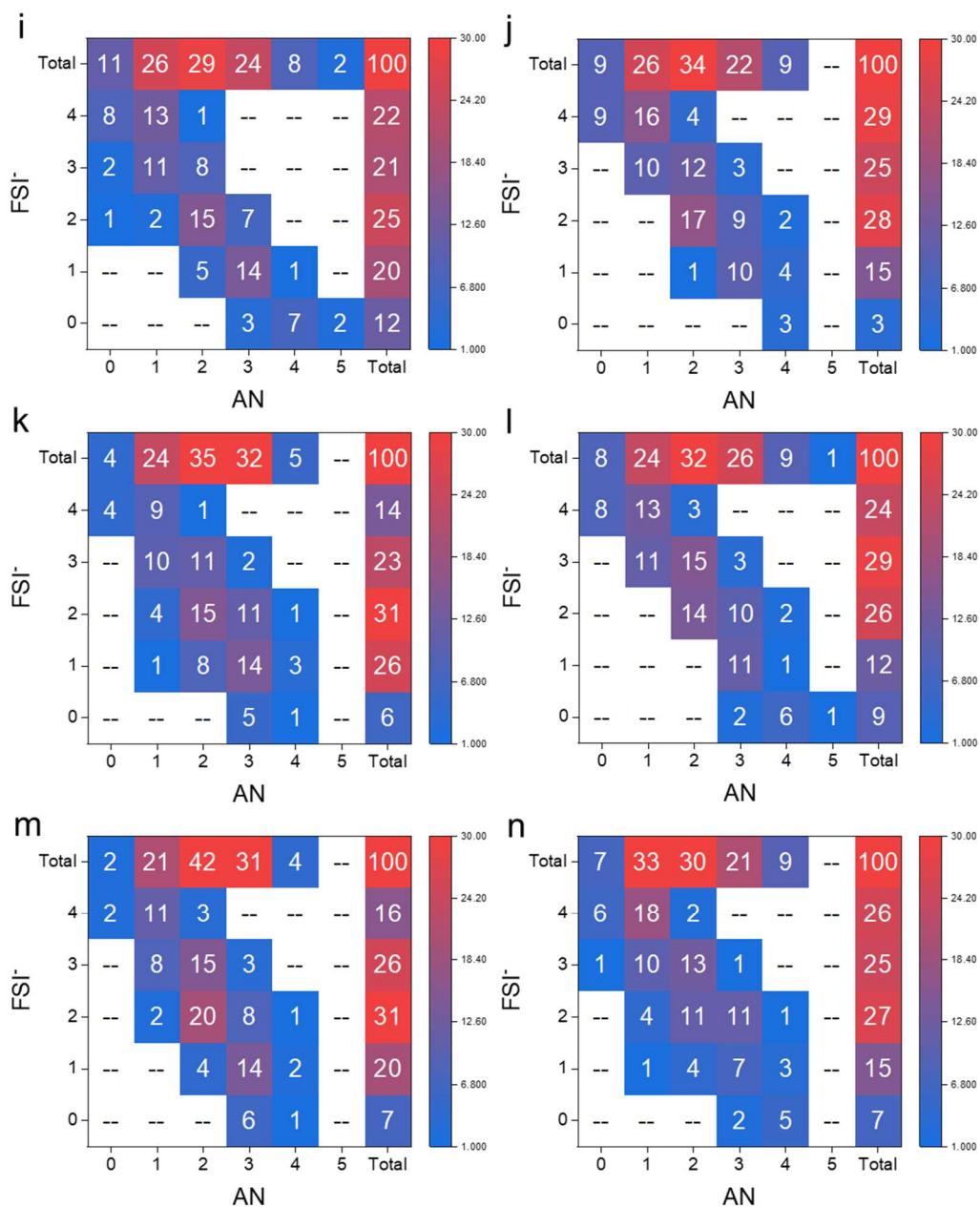


Fig. 3 | Physical properties of the electrolytes. **a,b**, Lifetime/displacement function of AN in FA-DCM electrolyte (**a**) and FA-TTE electrolyte (**b**). **c,d**, Evolution of Li⁺ solvation environment in FA-DCM electrolyte (**c**) and FA-TTE electrolyte (**d**) from MD simulations at 298 K (the vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li⁺ in the simulation time of 2,000 ps). **e**, The average residence time of Li⁺ in LiFSI/AN-based electrolytes with different moderators. **f**, Temperature dependence of the ionic conductivity of different electrolytes. **g**, Li⁺ transference numbers of different electrolytes at 25 °C. **h**, Differential scanning calorimetry cooling and heating curves of different electrolytes.

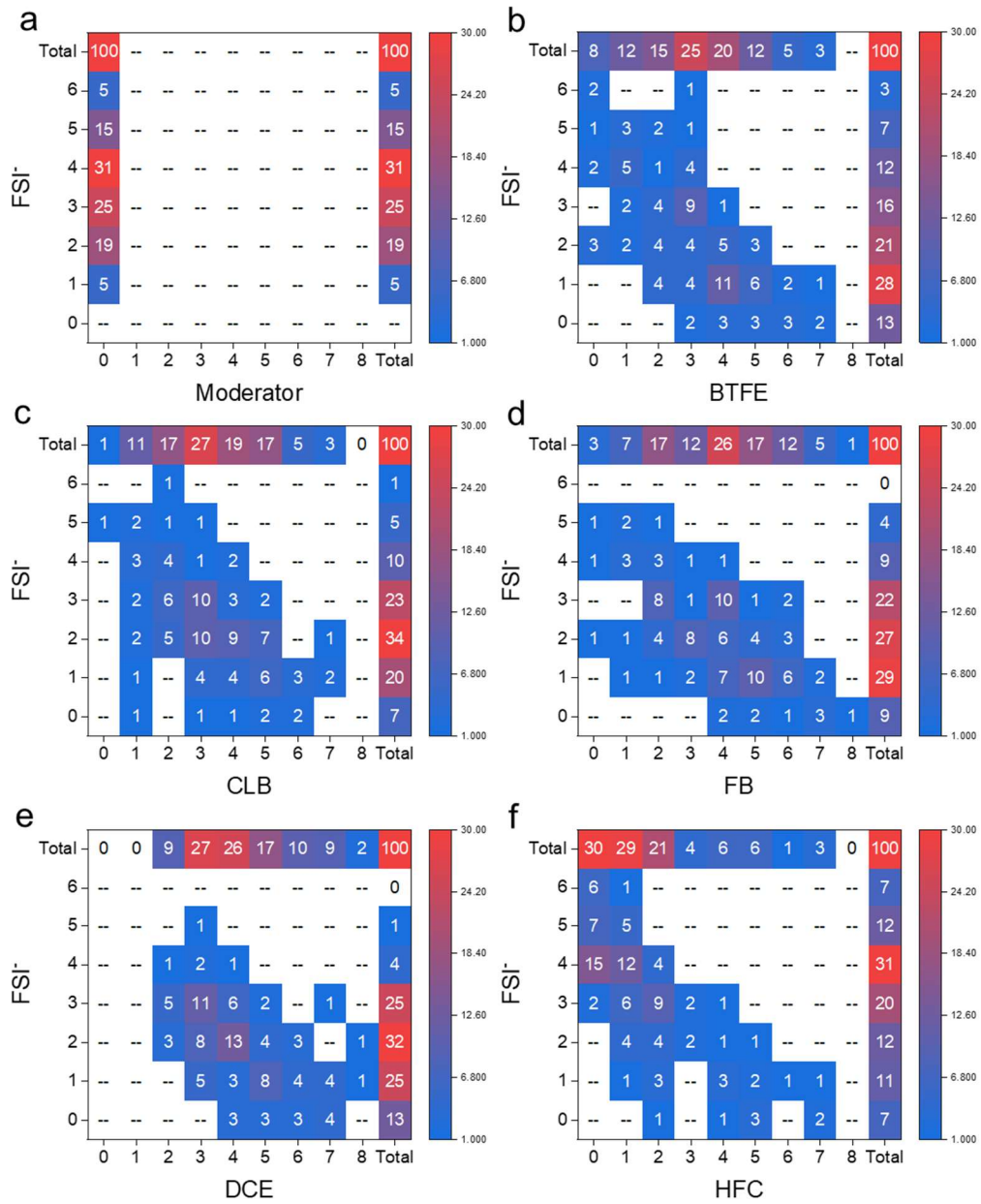
In the revised supporting information, we added Fig. R41a, c, 42, 43, 45 and 46 as Supplementary Fig. 4g, 6e, 14, 15g, 31 and 40.

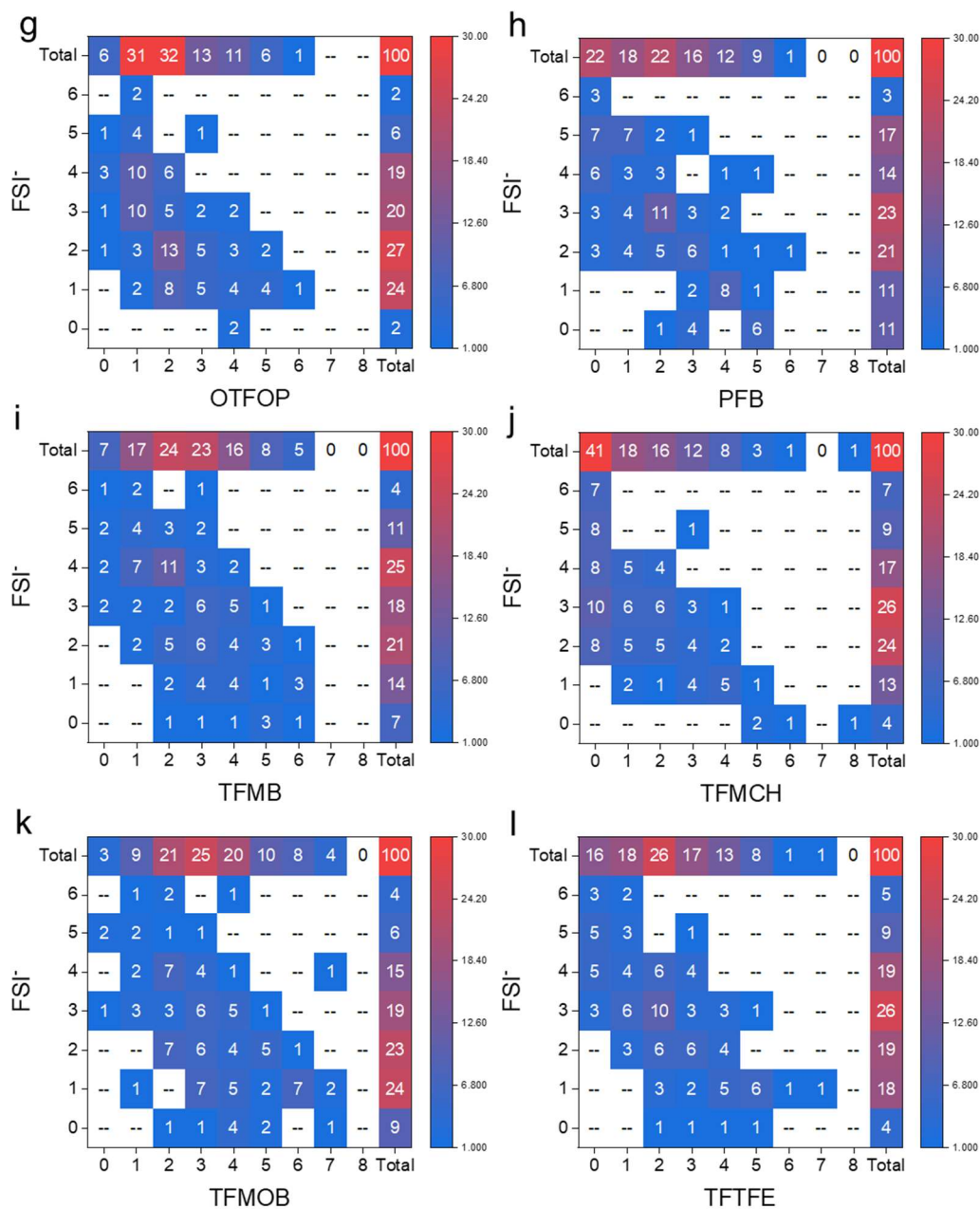




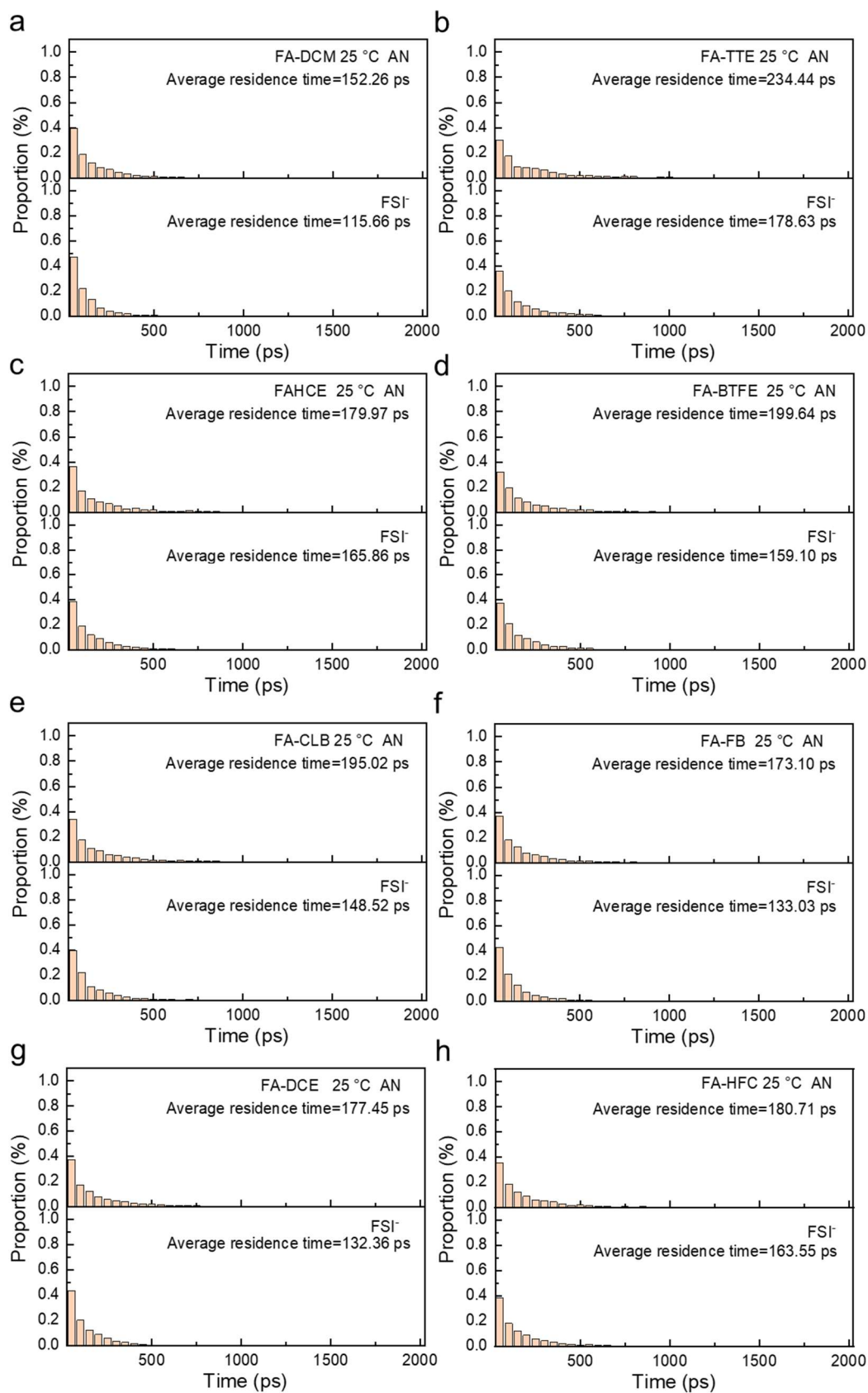
Supplementary Fig. 4 | Heatmaps of Li⁺ solvation sheath in different electrolytes.

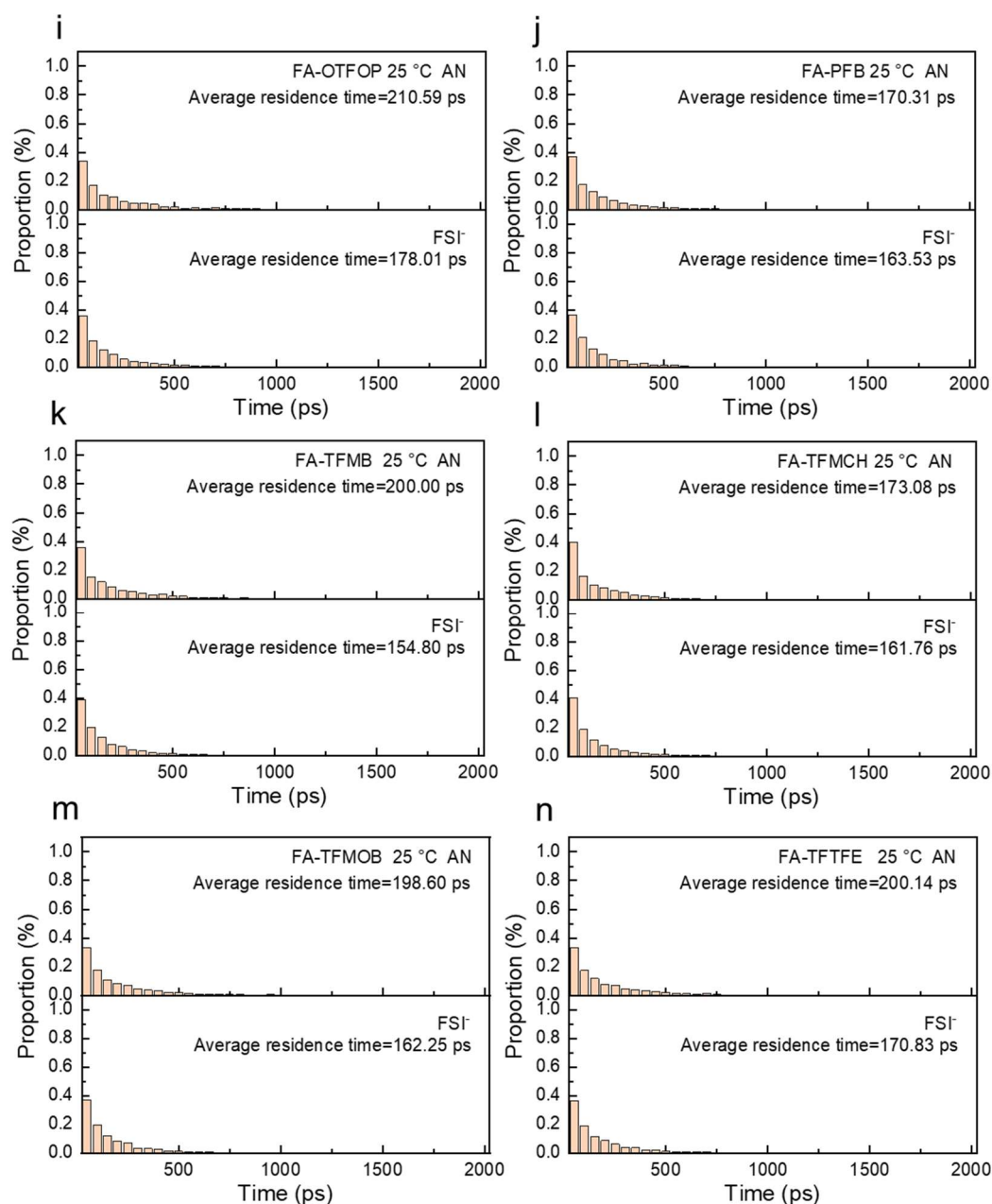
FA-DCM electrolyte (a), FA-TTE electrolyte (b), FAHCE electrolyte (c), FA-BTFE electrolyte (d), FA-CLB electrolyte (e), FA-FB electrolyte (f), **FA-DCE electrolyte (g)**, FA-HFC electrolyte (h), FA-OTFOP electrolyte (i), FA-PFB electrolyte (j), FA-TFMB electrolyte (k), FA-TFMCH electrolyte (l), FA-TFMOB electrolyte (m) and FA-TFTFE electrolyte (n).





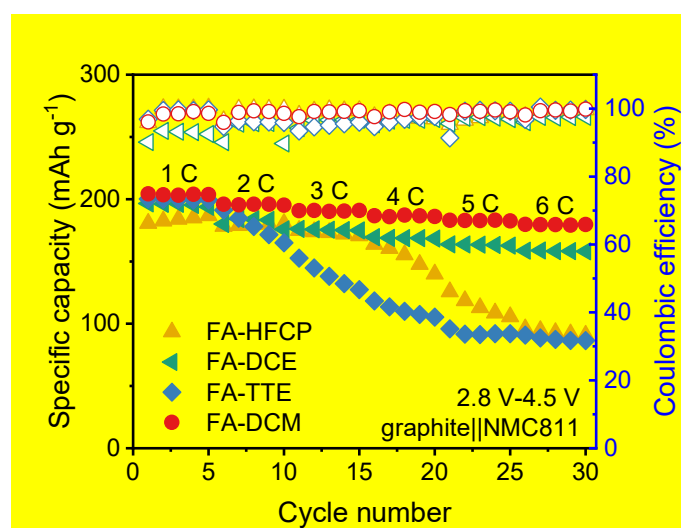
Supplementary Fig. 6 | Heatmaps of Li^+ solvating environment (3 Å to 5 Å) in different electrolytes. FAHCE electrolyte (a), FA-BTFE electrolyte (b), FA-CLB electrolyte (c), FA-FB electrolyte (d), **FA-DCE electrolyte (e)**, FA-HFC electrolyte (f), FA-OTFOP electrolyte (g), FA-PFB electrolyte (h), FA-TFMB electrolyte (i), FA-TFMCH electrolyte (j), FA-TFMOB electrolyte (k) and FA-TFTFE electrolyte (l).





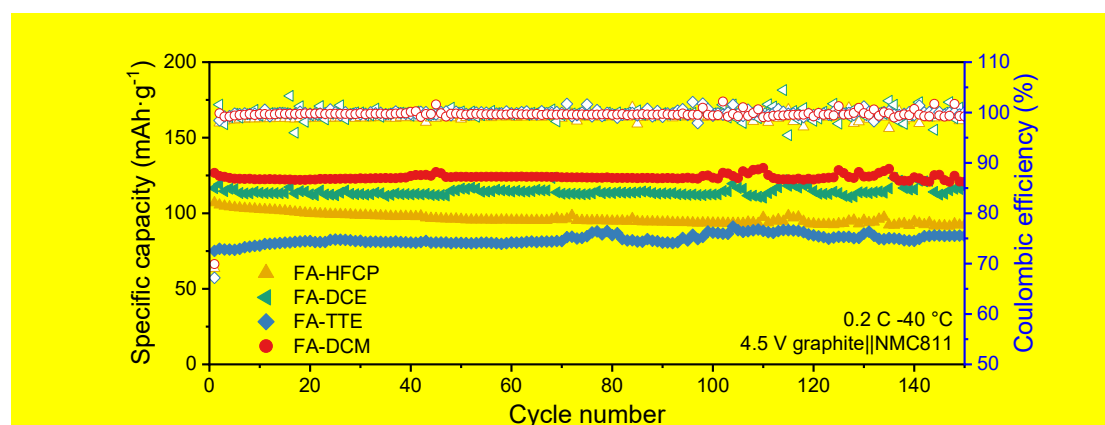
Supplementary Fig. 15 | Residence time distribution of AN and FSI⁻ in different electrolytes. FA-DCM electrolyte (a), FA-TTE electrolyte (b), FAHCE electrolyte (c), FA-BTFE electrolyte (d), FA-CLB electrolyte (e), FA-FB electrolyte (f), **FA-DCE electrolyte (g)**, FA-HFC electrolyte (h), FA-OTFOP electrolyte (i), FA-PFB electrolyte (j), FA-TFMB electrolyte (k), FA-TFMCH electrolyte (l), FA-TFMOB electrolyte (m) and FA-TFTFE electrolyte (n).

(Page 52)



Supplementary Fig. 31 | Rate performance of graphite||NMC811 cells with different electrolytes in the range of 2.8-4.5 V at 25 °C.

(Page 61)



Supplementary Fig. 40 | Cycling performance with different electrolytes in the range 2.8-4.5 V at 0.2 C under -40 °C.

10) TEM images show SEI thickness but do not report spatial uniformity or standard deviation. More statistical analysis across particles would improve reliability of conclusions.

Reply: We thank the reviewer for this insightful comment. In response, we have added more representative TEM images of SEI layers formed on graphite electrodes after

cycling in BE and FA-DCM electrolytes (Fig. R47a-h). Furthermore, we performed statistical analysis of SEI thickness across the particles and present the distribution histograms in Fig. R47i. The average SEI thickness for the BE electrolyte was 17.52 nm with a standard deviation of 7.71 nm, indicating a relatively thick and non-uniform interphase. In contrast, the FA-DCM electrolyte yielded a significantly thinner and more uniform SEI, with an average thickness of 3.20 nm and a narrower standard deviation of 0.48 nm. The results clearly show that the SEI formed in FA-DCM electrolyte is thinner and more spatially uniform, with a narrower standard deviation, compared to the thicker and more heterogeneous SEI observed in the BE electrolyte.

This quantitative analysis confirms that FA-DCM promotes the formation of a thinner and spatially homogeneous SEI compared to BE, thereby establishing a stronger correlation between interphase structure and the observed electrochemical improvements.

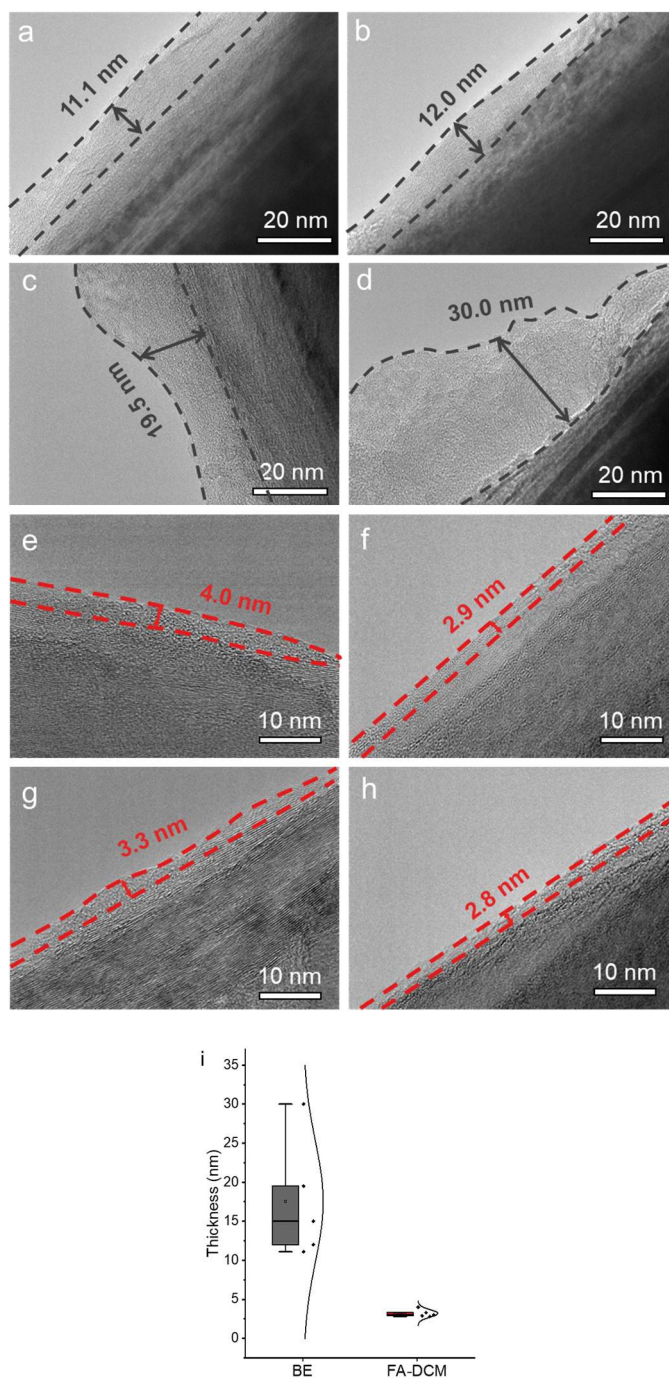
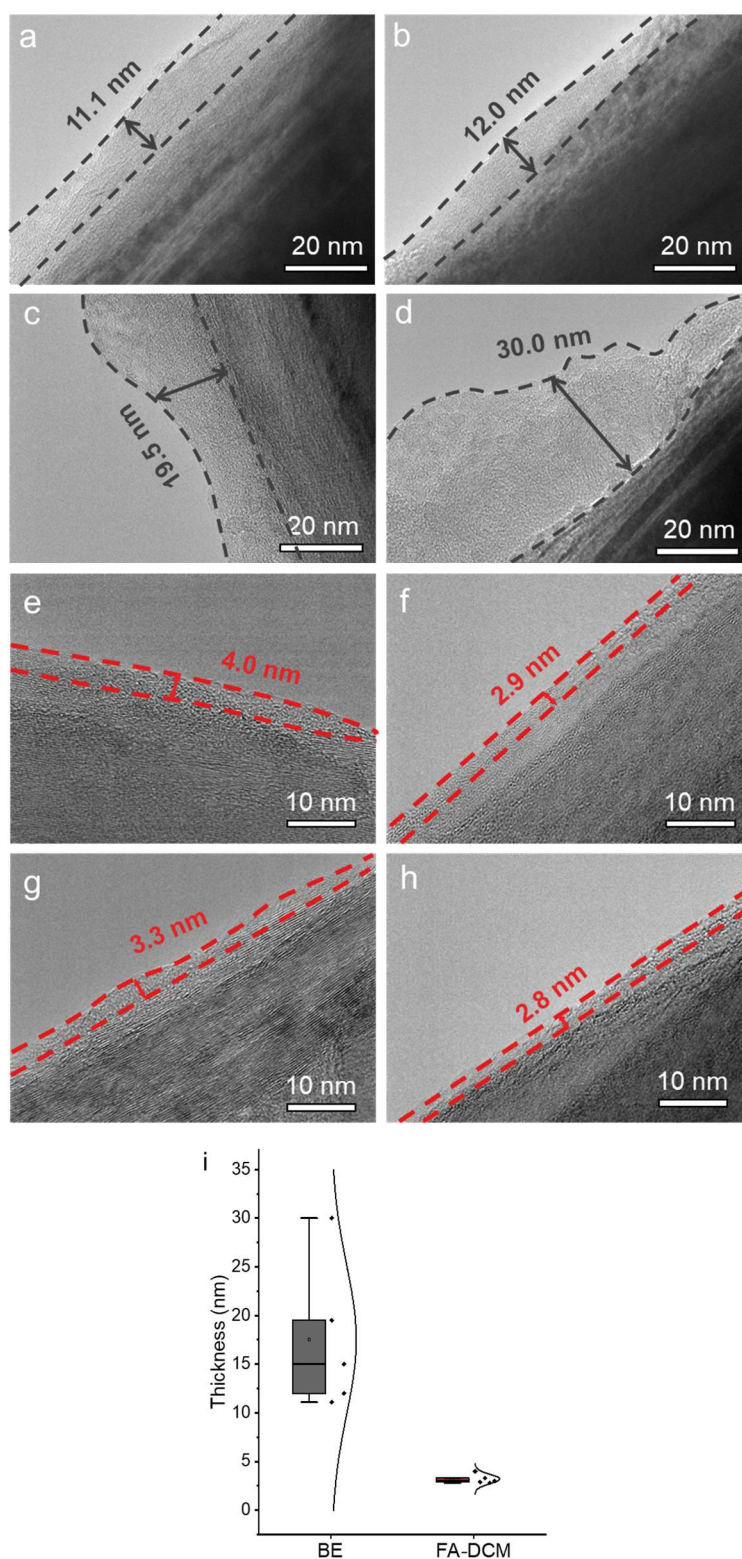


Fig. R47 | TEM characterizations. TEM images of multiple graphite particles recovered from graphite||NMC811 cells using BE electrolyte (a-d) and FA-DCM electrolyte (e-h) after 50 cycles and the thickness distribution of SEI using different electrolytes (i).

In the revised supporting information (Pages 71 and 72), we added Fig. R47 as Supplementary Fig. 50.



Supplementary Fig. 50 | TEM characterizations. TEM images of multiple graphite particles recovered from graphite||NMC811 cells using BE electrolyte (a-d) and FA-DCM electrolyte (e-h) after 50 cycles and the thickness distribution of SEI using different electrolytes (i). Scale bars, 10 nm.

Statistical analysis of TEM images reveals that the BE electrolyte forms a thick, non-uniform SEI (17.52 ± 7.71 nm) on graphite, significantly thicker than the uniform SEI (3.20 ± 0.48 nm) formed by the FA-DCM electrolyte.

11) Operando Raman or FTIR spectroscopy could provide real-time insights into DCM-FSI-Li⁺ interactions and validate the simulated solvation structures experimentally.

Reply: We thank the Reviewer #4 for this valuable suggestion. To experimentally validate the simulated solvation structures, we performed Electrical *in-situ* Fourier-transform infrared spectroscopy on Li||graphite cells assembled with FA-DCM electrolyte. During discharging/charging, we observed a progressive decrease in the intensity of the coordinated FSI⁻ vibrational band (I: 746 cm^{-1})²¹, accompanied by a simultaneous increase in the intensity of two characteristic bands associated with uncoordinated FSI⁻ (II: S-F stretch, 830 cm^{-1} ; III: SO₂ stretch, 1180 cm^{-1})²¹. This evolution directly indicates a gradual dissociation of FSI⁻ from Li⁺, consistent with the breakdown of large clusters (Fig. R48). This is attributed to the DCM-FSI⁻ interactions, which weaken the FSI⁻-Li⁺ binding, thereby reducing the number of coordinated FSI⁻; otherwise, the peak intensity of FSI⁻ would remain essentially unchanged even in the presence of an electric field¹⁹.

These spectroscopic observations corroborate the MD simulation results, which showed weakened Li⁺-FSI⁻ coordination and increased Li⁺ mobility in the FA-DCM electrolyte. Taken together, the operando FTIR evidence strongly supports our mechanistic conclusion that the inclusion of DCM disrupts excessive Li⁺-anion association and facilitates discrete Li⁺ hopping.

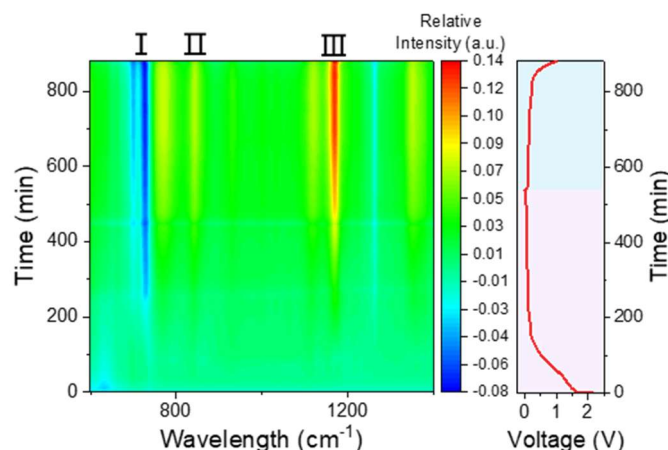


Fig. R48 | Electrical *in-situ* Fourier-transform infrared spectroscopy of FA-DCM electrolyte during discharging/charging.

In the revised manuscript, we added the following text and highlighted it in yellow (Page 10) and added Fig. R48 as Fig. 2f (Page 11):

To further substantiate our position, we have cited *Adv. Funct. Mater.* 2025, e11694 and *Angew. Chem. Int. Ed.* 2025, 64, e202412896 as Ref. 44 and 45 in the revised manuscript, respectively.

To experimentally validate the simulated solvation structures, we performed electrical *in-situ* Fourier-transform infrared spectroscopy (FTIR) on Li||graphite cells assembled with FA-DCM electrolyte. During discharging/charging, we observed a progressive decrease in the intensity of the coordinated FSI⁻ vibrational band (I: 746 cm⁻¹)⁴⁴, accompanied by a simultaneous increase in the intensity of two characteristic bands associated with uncoordinated FSI⁻ (II: S-F stretch, 830 cm⁻¹; III: SO₂ stretch, 1180 cm⁻¹)⁴⁴. This evolution directly indicates a gradual dissociation of FSI⁻ from Li⁺, consistent with the breakdown of large clusters. This is attributed to the DCM-FSI⁻ interactions, which weaken the FSI⁻-Li⁺ binding, thereby reducing the number of coordinated FSI⁻; otherwise, the peak intensity of FSI⁻ would remain essentially unchanged even in the presence of an electric field⁴⁵.

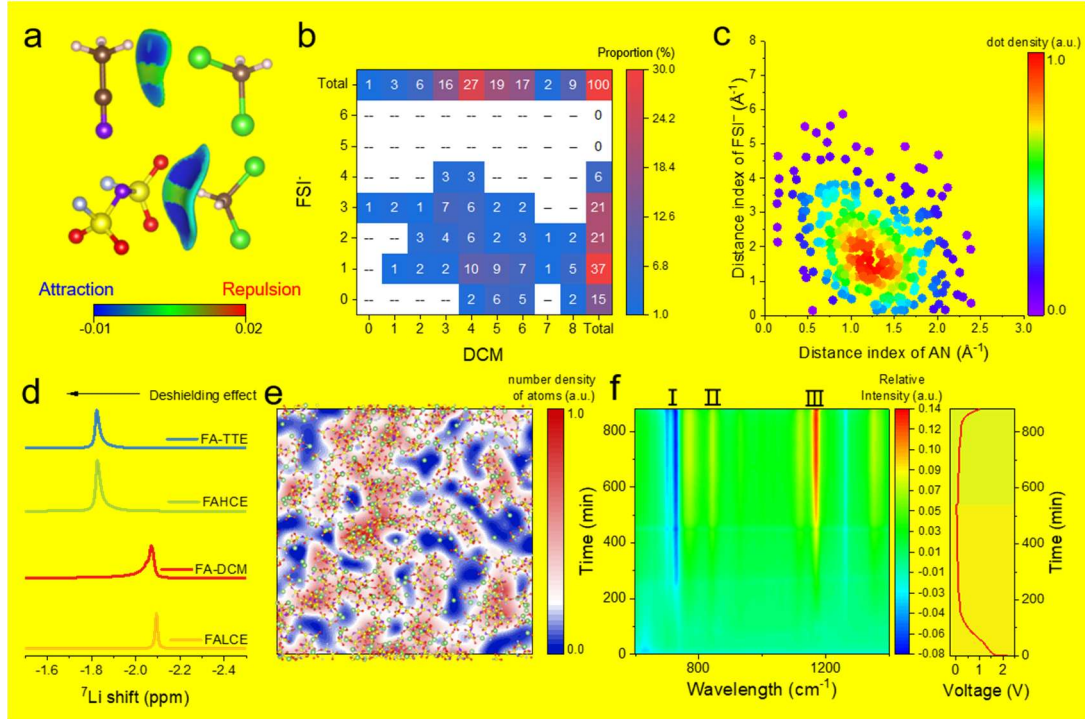


Fig. 2 | Solvation structures of different electrolytes. **a**, $\text{Sign}(\lambda_2)\rho$ colored isosurfaces of $\delta g^{\text{inter}} = 0.005$ a.u. corresponding to independent gradient model based on Hirshfeld partition analysis for DCM-AN, DCM-FSI⁻ complexes. The blue, green and red on isosurfaces represent the attractive interaction, van der Waals interaction and repulsive interaction between molecules, respectively. **b**, Heatmaps of Li⁺ solvating environment (3 Å to 5 Å around Li⁺) in FA-DCM electrolyte, the color bar represents the proportion of the number of this species to the total number of clusters. **c**, Distance index of FSI⁻ and AN in FA-DCM electrolyte. Distance index = $\sum 1/x_n$, where x_n represents the distance between Li⁺ and N (AN)/O (FSI⁻), the color bar represents the density of Li⁺. **d**, Coaxial ⁷Li nuclear magnetic resonance spectra of different electrolytes. **e**, MD simulation snapshots of FA-DCM electrolyte. (lime green, Cl atom; red, O atom; yellow, S atom; purple, N atom; silver, F atom; tan, C atom; white, H atom). **f**, Electrical *in-situ* Fourier-transform infrared spectroscopy of FA-DCM electrolyte during discharging/charging.

In the revised method (Page 33), we added the following text and highlighted it in yellow:

The solvation structures of different electrolytes were measured by ⁷Li coaxial nuclear magnetic resonance spectroscopy (NMR) (Bruker 600MHz), Raman spectrum (Horiba LabRAM HR Evolution) and electrical *in-situ* Fourier-transform infrared spectroscopy (FTIR) (Thermo IS50).

12) The full-cell performance at low temperature is excellent, but long-term cycling at

room temperature is not included. This data would be important for assessing general electrolyte viability.

Reply: We thank the reviewer for this valuable comment. We would like to emphasize that the data in Fig. 4a, b, f, g and Supplementary Fig. 24 of this study were carried out at room temperature. These measurements inherently involve prolonged cycling at various current densities, thereby providing direct evidence of room-temperature stability. At 25 °C, Li||graphite cells incorporating with FA-DCM electrolyte retain 94% of their initial capacity after 1000 cycles at 10 C (Fig. 4a, b and Supplementary Fig. 24). Even at 6 C, graphite||NMC811 cells with FA-DCM electrolyte exhibit high capacity of 179.8 mAh g⁻¹ and maintain a stable cycling without significant fading over 470 cycles (Fig. 4f, g). These results confirm that the FA-DCM electrolyte not only ensures outstanding low-temperature performance but also demonstrates robust long-term cycling stability under ambient conditions, underscoring its broad applicability for practical lithium-ion batteries.

13) While full cells are tested, a Li||Li symmetric cell cycling test would help evaluate long-term interfacial stability and dendrite suppression behavior.

Reply: Thanks for reviewer's comments. We agree that Li||Li symmetric cell tests are valuable for probing dendrite growth and interfacial stability in Li-metal batteries. In this manuscript, we focus on the Li ion battery, not on Li metal battery. Li ions are only required to shuttle back and forth between cathode and anode.

The superior electrochemical performances observed in graphite||NMC811 full-cells with FA-DCM electrolyte can be attributed to the formation of a uniform, LiF-LiCl-rich SEI, as revealed by XPS/TOF-SIMS analyses (Fig. 6e, g-j and Supplementary Fig. 54-57), confirms the favorable interfacial stability of the FA-DCM electrolyte. These results demonstrate that our electrolyte formulation robustly suppresses interfacial side reactions, ensuring long-term stability under demanding low temperature and high-rate cycling conditions.

14) Important physical parameters such as density and viscosity of the FA-DCM electrolyte are not reported, yet they directly affect Li⁺ ion mobility and solvation dynamics.

Reply: We thank the reviewer for this constructive comment. The density of the FA-DCM electrolyte has been measured (Table R11). In addition, the viscosity of the FA-DCM electrolyte at different temperatures (from -40 °C to 25 °C) has already been reported in the original submission (Supplementary Fig. 13; the revised version, Supplementary Fig. 21).

These data provide a comprehensive characterization of the key physical parameters that directly influence Li⁺ mobility and solvation dynamics. We believe these additions strengthen the manuscript and directly address the reviewer's concern.

Table R11. Density of different electrolytes.

Electrolyte	Density (g mL ⁻¹)
BE	1.317
BEMP	1.227
FA-DCM	1.426
FA-TTE	1.776
FALCE	0.992
FAHCE	1.353

In the revised manuscript (Page 14), we added the following text and highlighted it in yellow:

At room temperature, the FA-DCM electrolyte, which has relatively low viscosity (4.66 mPa s, Supplementary Fig. 21) and moderate density (1.426 g mL⁻¹, Supplementary Table 6), exhibits moderate ionic conductivity (9.15 mS cm⁻¹),

In the revised supporting information (Page 11), we now added Table R11 as Supplementary Table 6.

Supplementary Table 6. Density of different electrolytes.

Electrolyte	Density (g mL ⁻¹)
BE	1.317
BEMP	1.227
FA-DCM	1.426
FA-TTE	1.776
FALCE	0.992
FAHCE	1.353

15) The link between electrolyte composition and SEI chemistry (e.g., Cl-containing species) is hypothesized but not strongly confirmed. More targeted XPS or TOF-SIMS depth profiles could help.

Reply: We appreciate the reviewer’s constructive suggestion. In addition to the XPS depth profiling already presented, we have conducted TOF-SIMS measurements on graphite electrodes cycled in BE and FA-DCM electrolytes to further resolve the SEI composition. The TOF-SIMS results clearly reveal enriched Cl-containing fragments in the SEI formed in FA-DCM, in agreement with the XPS identification of LiCl species. By contrast, such Cl-related signals are negligible in the SEI formed with BE.

These complementary depth-resolved analyses provide direct evidence for Cl-containing inorganic species in the SEI. This finding corroborates that FA-DCM promotes a thinner, more uniform LiF-LiCl-rich interphase, which leads to the observed improvements in interfacial stability and electrochemical performance.

We also cited the key references (*Adv. Energy Mater.* 2024, 14, 2400067; *ACS*

Energy Lett. 2024, 9, 2545–2553) as ref. 54, 55 in revised manuscript to support our claim.

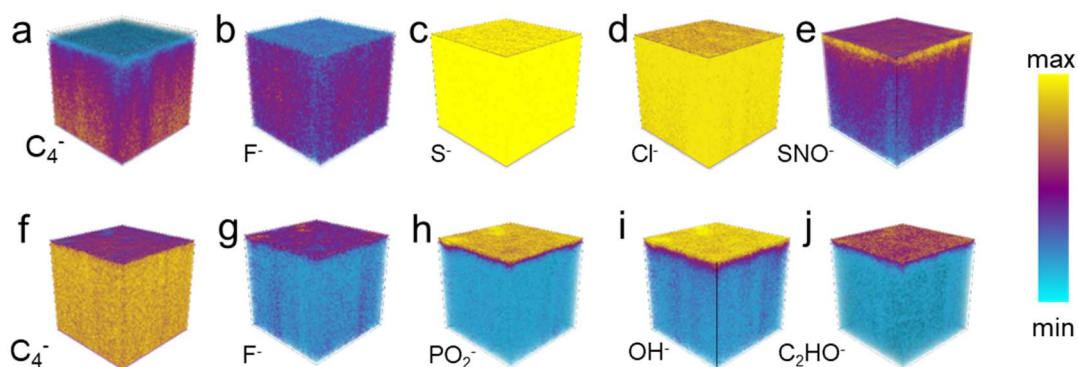


Fig. R49 | 3D-rendering images of C_4^- (a), F^- (b), S^- (c), Cl^- (d) and SNO^- (e) species on the graphite anode surface cycled in FA-DCM electrolyte and C_4^- (f), F^- (g), PO_2^- (h), OH^- (i) and C_2HO^- (j) species on the graphite anode surface cycled in BE electrolytes.

In the revised manuscript, we modified the following sentences and highlighted them in yellow (Page 22), we added Fig. R49b-e, g-j as Fig. 6g-n (Page 23).

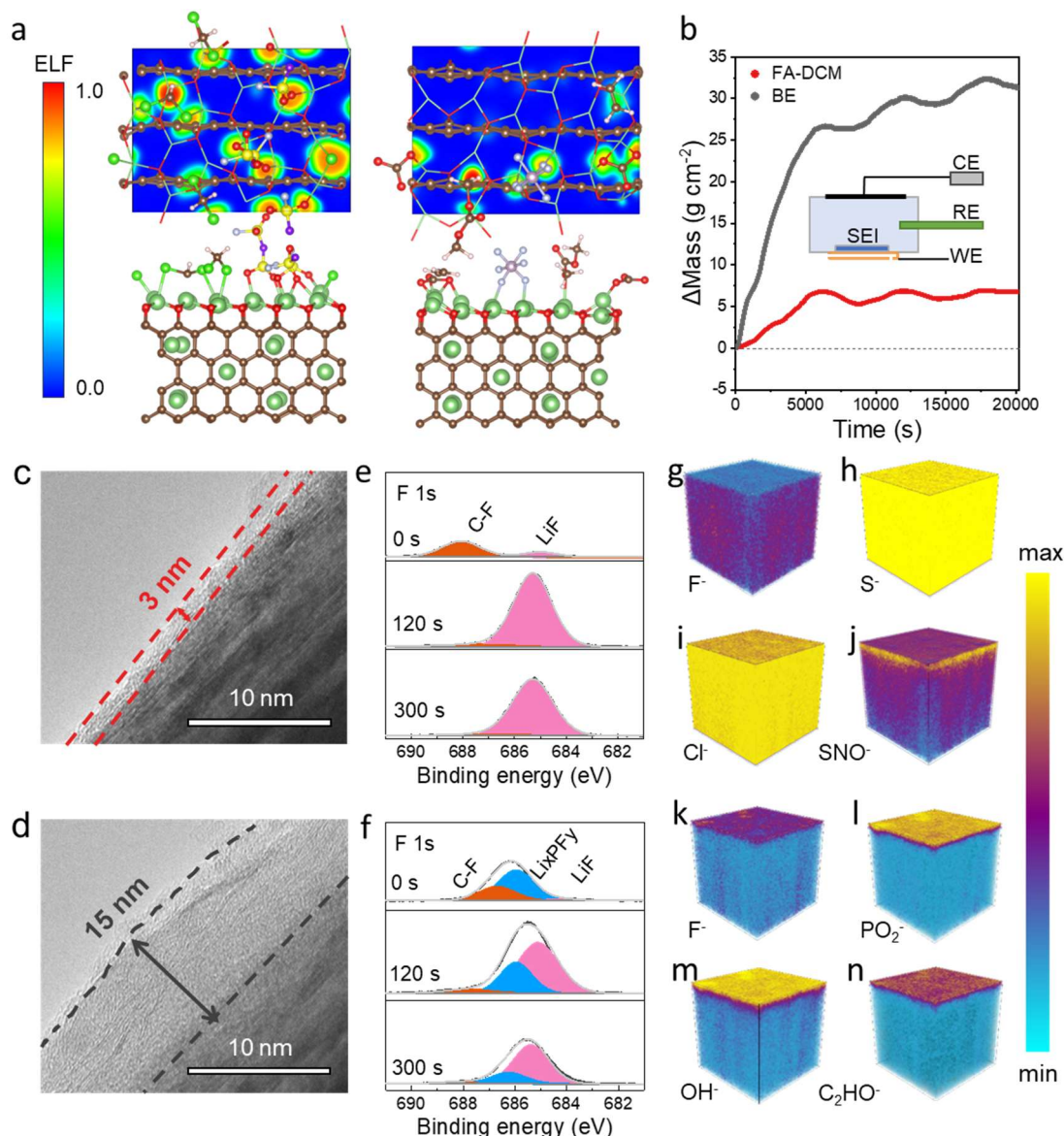


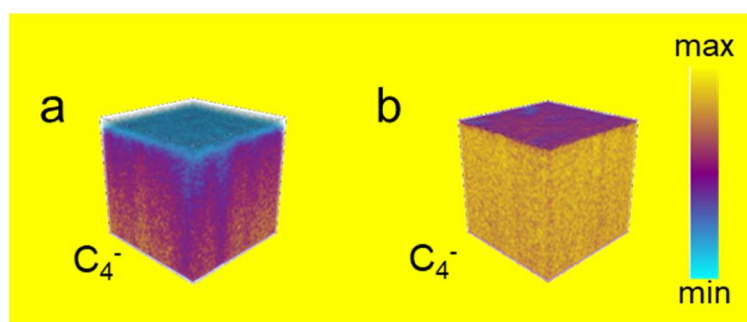
Fig. 6 | Electrolyte/electrode interphase analysis. **a**, The initial decomposition reaction of FA-DCM electrolyte (left) and BE electrolyte (right) on the graphite interphase calculated by *ab initio* molecular dynamics (AIMD). **b**, Electrochemical quartz crystal microbalance with dissipation monitoring (EQCM-D) profiles of mass change ($\Delta Mass$) versus time. (Graphite-sputtered Cu chip resonator is used as the working electrode (WE) and Li metal is used as the counter electrode (CE) and reference electrode (RE). Cells are scanned at a potential window from the 1.50 V to 0.01 V at a scan rate of $5\ mV\ s^{-1}$. Frequency is taken at the 3rd overtone ($n = 3$). **c,d**, Transmission electron microscopy (TEM) images of graphite anodes recovered from Li||graphite cells using FA-DCM (**c**) and BE (**d**) electrolyte after 50 cycles, respectively. Scale bars, 10 nm. **e,f**, X-ray photoelectron spectroscopy (XPS) results of the SEI on cycled graphite in FA-DCM electrolyte (**e**) and BE electrolyte (**f**). **g-n**, 3D-rendering images of F⁻ (**g**), S⁻ (**h**), Cl⁻ (**i**) and SNO⁻ (**j**) species on the graphite anode surface cycled in FA-DCM electrolyte and F⁻ (**k**), PO₂⁻ (**l**), OH⁻ (**m**) and C₂HO⁻ (**n**) species on the graphite anode surface cycled in BE electrolytes.

Time of flight secondary ion mass spectrometry (TOF-SIMS) and in-depth X-ray photoelectron spectroscopy (XPS) analysis were conducted to comprehensively explore the chemical composition of electrode-electrolyte interphase (Fig. e-n, Supplementary Fig. 54-58). In the C 1s spectra (Supplementary Fig. 54a), the FA-DCM electrolyte initially forms carbonyl-containing organic compounds (C=O), which diminish with sputtering depth, whereas the LiF signal (Fig. 6f) and N- and S-containing derivatives (Supplementary Fig. 54d, e) increase, indicating preferential decomposition of FSI⁻ anions at graphite interphase. In addition, Cl 2p spectra further reveal the incorporation of LiCl species (Supplementary Fig. 54f), implying the formation of a dual-layer SEI architecture consisting of an inner LiF-LiCl-rich inorganic layer and an outer organic matrix⁵³⁻⁵⁵. 3D-rendering images obtained from TOF-SIMS further confirm the formation of this bilayer structure (Fig. g-j and Supplementary Fig. 57a), which facilitates efficient charge-transfer kinetics and mechanical robustness.

In the revised method (Page 34), we added the following text and highlighted it in yellow:

X-ray photoelectron spectroscopy (XPS) (Thermo Scientific ESCALAB 250Xi) and time of flight secondary ion mass spectrometry (TOF-SIMS) (ToF.SIMS 5-100 instrument IONTOF GmbH).

In the revised supporting information (Page 79), we added the following text and highlighted it in yellow, we added Fig. R49a, f as Supplementary Fig. 57.



Supplementary Fig. 57 | TOF-SIMS. 3D-rendering images of C₄⁻ species on the graphite anode surface cycled in FA-DCM electrolyte (a) and BE electrolyte (b).

On the graphite surface cycled in the FA-DCM electrolyte, a dense SEI layer is formed, and with increasing depth, partial derivatives are also detected between the graphite layers; in contrast, graphite cycled in the BE electrolyte predominantly exhibits a strong C signal.

16) At elevated temperatures, DCM may evaporate or leak. Mass loss over time or pressure buildup should be tested and reported.

Reply: We thank the reviewer for raising this important point regarding the long-term stability of the DCM-containing electrolyte. To directly address this concern, we performed storage and post-aging electrochemical tests on pouch cells assembled with BE, BEMP, FA-TTE, and FA-DCM electrolytes. The pouch cells were stored at 45 °C for 7 days, after which we obtained the volume change of the gas bag through the water displacement method. Moreover, we also evaluated the capacity retention by comparing the discharge capacity before and after storage.

As shown in Fig. R38 (referred to Question 8), the swelling of graphite||NMC811 pouch cells assembled with the FA-DCM electrolyte was minimal and highly acceptable. Importantly, the capacity retention of FA-DCM is acceptable among the four electrolytes (FA-DCM, 90.7%; FA-TTE, 86.5%; BE, 96.9%; BEMP, 97.2%, Fig. R39, referred to Question 8). These results confirm that the volatility of DCM, while contributing to slight swelling, remains within safe limits without inducing catastrophic failure.

These findings demonstrate that the effect of DCM is not only reversible but also reasonably stable under extended storage at elevated temperature. The pouch cells assembled with FA-DCM electrolyte maintain capacity retention comparable to conventional systems, indicating that the molecular-level benefits of solvation sheath reorganization are preserved over time and cycling.

17) Although DCM affects SEI, its influence on oxidative stability at high voltage (e.g., with NMC811 at >4.3 V) is not evaluated.

Reply: We thank the reviewer for raising this important point. We would like to emphasize that all full-cell electrochemical tests in this study were conducted up to 4.5 V with NMC811 cathodes, thereby directly demonstrating the compatibility of the FA-DCM electrolyte under high-voltage operation (Fig. 4a, b, f, g; Fig. 5b-f; Supplementary Fig. 24, 31, 32, 39, 40 and 41). In addition, linear sweep voltammetry (LSV) measurements further confirm that the FA-DCM electrolyte exhibits a wide electrochemical stability window (exceeding 4.7 V vs. Li^+/Li , Fig. 4e), consistent with the excellent cycling stability observed experimentally. These results together indicate that the inclusion of DCM does not compromise the oxidative stability of the electrolyte under the high-voltage conditions relevant for practical applications.

18) The claim of interface stabilization would be stronger if demonstrated in anode-free or Li-metal full cells, where Coulombic efficiency is highly sensitive to SEI quality.

Reply: We thank the reviewer for this valuable suggestion. While we agree that anode-free or Li-metal full cells are indeed highly sensitive to SEI quality, our study is focused on lithium-ion batteries with graphite anodes, as our electrolyte is specifically designed for fast-charging and low-temperature operation in commercially relevant LIBs. Importantly, the FA-DCM electrolyte already demonstrates robust interfacial stabilization, as evidenced by stable cycling up to 4.5 V, reduced impedance across different rates, and XPS/TOF-SIMS results revealing a LiF/LiCl -rich SEI. These results confirm the electrolyte's effectiveness in the targeted LIB systems. Extension to Li-metal or anode-free configurations will be an interesting direction for future work.

19) The GITT data shows reduced overpotentials, but the actual diffusion coefficients are not calculated or compared across systems.

Reply: We thank the reviewer for pointing out this important issue. We would like to clarify that the GITT measurements originally shown in Fig. 4d were conducted at relatively high current densities (10 C). Under such conditions, the potential response is strongly influenced by ohmic and concentration polarization, making the extraction

of reliable Li^+ diffusion coefficients challenging. For this reason, we presented the overpotential data as an indicator of kinetic improvements.

To directly address the reviewer's concern, we have additionally performed GITT measurements under sufficiently small current perturbations (0.1 C) on graphite electrodes with both low (0.53 mAh g^{-1}) and high areal loadings (3.40 mAh g^{-1}). The calculated Li^+ diffusion coefficients reveal that the FA-DCM electrolyte ($4.432 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) maintains a diffusivity similar to the baseline carbonate electrolytes (BE, $4.289 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$; BEMP, $4.430 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) and FA-TTE electrolyte ($4.201 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) using graphite electrodes with a low areal loading of 0.53 mAh cm^{-2} (Fig. R30c, d, referred to Question 2). However, under the more demanding high-loading graphite conditions (3.40 mAh cm^{-2}), the FA-DCM electrolyte exhibits a higher diffusion coefficient ($4.579 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) than the other three electrolytes (FA-TTE, $4.069 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$; BE, $2.876 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$; BEMP, $3.225 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$, Fig. R31c, d, referred to Question 2). This enhancement may originate from the superior wettability of the FA-DCM electrolyte toward the porous and tortuous electrode structure, as well as the formation of a LiCl-LiF-rich SEI, which enables faster interfacial Li^+ migration compared to SEI containing only LiF or organic components¹, thereby influencing the apparent diffusion coefficient. These results confirm that the enhanced Li^+ mobility observed with FA-DCM is not limited to the electrolyte phase but also translates into improved solid-state diffusion within the electrodes.

20) The effects of LiFSI salt and DCM moderator are entangled. A control with DCM but no LiFSI, or other salts, would help isolate the role of the moderator.

Reply: We thank the reviewer for pointing out this important issue. To disentangle the respective effects of the LiFSI salt and the DCM moderator, we additionally prepared an electrolyte with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) replacing LiFSI. Graphite||NMC811 full-cell tests with this LiTFSI-based electrolyte ("TA-DCM electrolyte" for short) demonstrate that the incorporation of DCM still significantly enhances low-temperature ($-40 \text{ }^\circ\text{C}$) cycling and enables stable operation under high-

rate 6 C conditions (Fig. R50, 51).

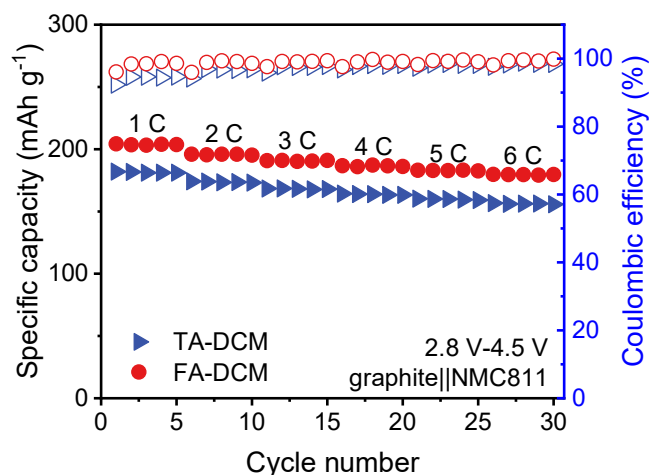


Fig. R50 | Rate performance of graphite||NMC811 cells with different electrolytes in the range of 2.8-4.5 V at 25 °C.

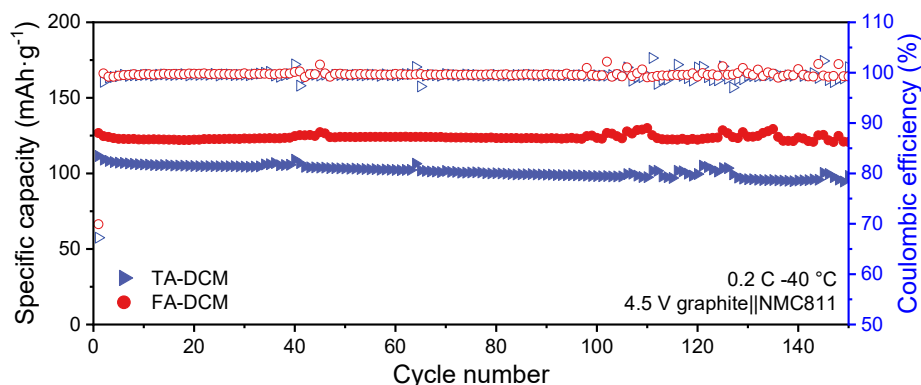


Fig. R51 | Cycling performance with different electrolytes in the range 2.8-4.5 V at 0.2 C under -40 °C.

Furthermore, MD simulations reveal a shortened Li^+ residence time consistent with the disruption of large solvation clusters, in line with our proposed mechanism. These results confirm that the beneficial role of DCM as a moderator is not exclusively dependent on the choice of LiFSI salt, but represents a generalizable strategy for tailoring solvation structure and improving ion transport under demanding conditions (Fig. R52, 53).

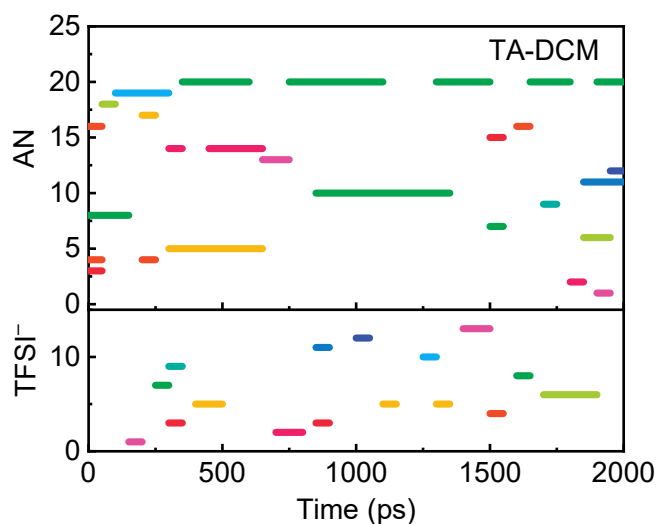


Fig. R52 | Evolution of Li^+ solvation environment in TA-DCM electrolyte from MD simulations at 298 K. The vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li^+ in the simulation time of 2,000 ps.

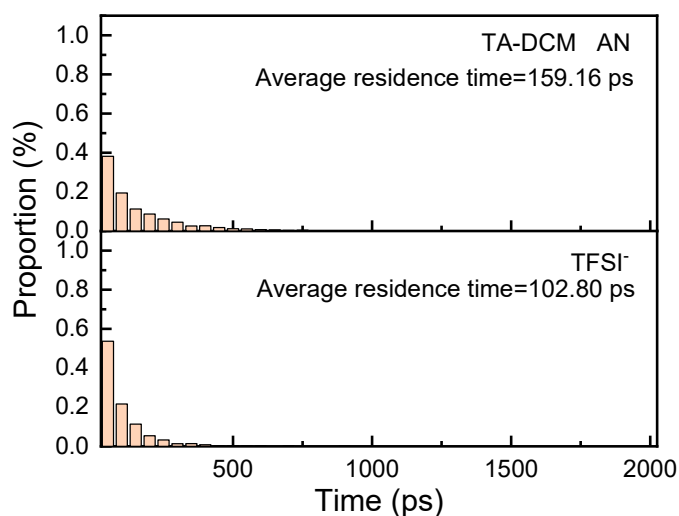
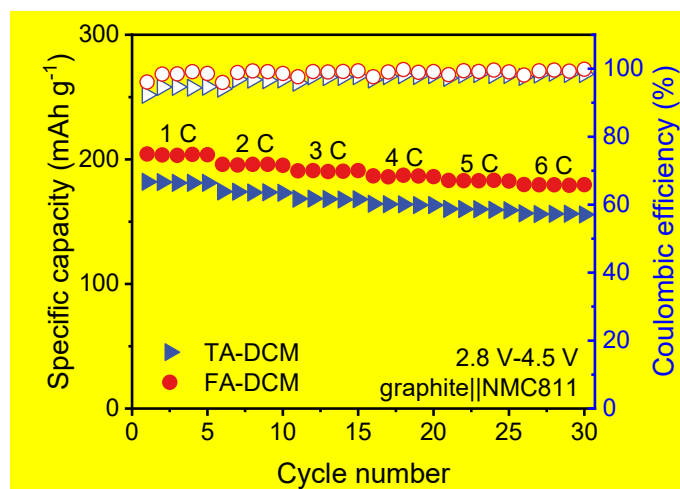


Fig. R53 | Residence time distribution of AN and FSI⁻ in TA-DCM electrolyte at 298K.

In the revised manuscript (Page 19 and 20), we added the following text and highlighted it in yellow:

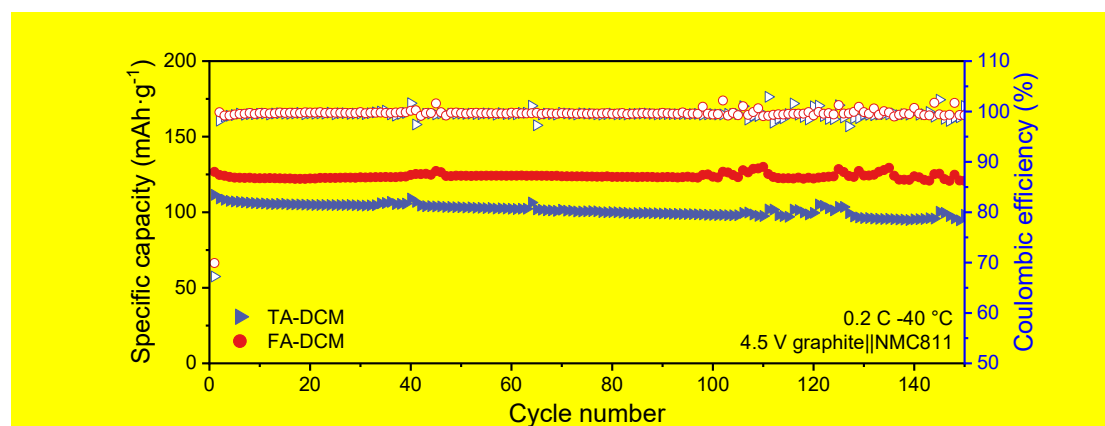
A control with lithium bis(trifluoromethanesulfonyl)imide replacing LiFSI further confirms the effectiveness of DCM (Supplementary Fig. 43-46).

In the revised supporting information (Page 64-67), we added Fig. R50-53 as Supplementary Fig. 43-46, we also added the following text and highlighted it in yellow:



Supplementary Fig. 43 | Rate performance of graphite||NMC811 cells with different electrolytes in the range of 2.8-4.5 V at 25 °C.

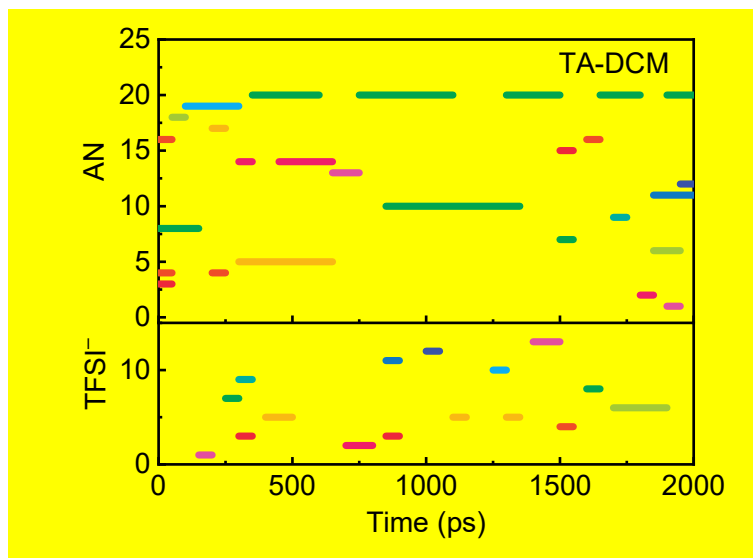
To disentangle the respective effects of the LiFSI salt and the DCM moderator, we additionally prepared an electrolyte with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) replacing LiFSI. Graphite||NMC811 full-cell tests with this LiTFSI-based electrolyte (“TA-DCM electrolyte” for short) demonstrate that the incorporation of DCM still enables stable operation under high-rate 6 C conditions.



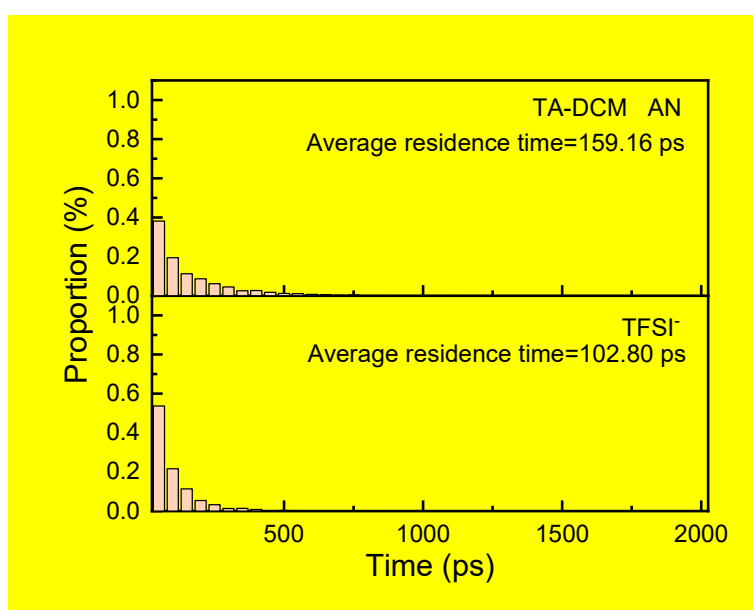
Supplementary Fig. 44 | Cycling performance with different electrolytes in the range of 2.8-4.5 V at 25 °C.

range 2.8-4.5 V at 0.2 C under -40 °C.

Graphite||NMC811 full-cell tests with TA-DCM electrolyte demonstrate that the incorporation of DCM still enhances low-temperature (-40 °C) cycling.



Supplementary Fig. 45 | Evolution of Li^+ solvation environment in TA-DCM electrolyte from MD simulations at 298 K. The vertical axis represents the serial number of different solvents or anions coordinated with the investigated Li^+ in the simulation time of 2,000 ps.



Supplementary Fig. 46 | Residence time distribution of AN and FSI⁻ in TA-DCM electrolyte at 298K.

MD simulations reveal a shortened Li⁺ residence time consistent with the disruption of large solvation clusters, in line with our proposed mechanism. These results confirm that the beneficial role of DCM as a moderator is not exclusively dependent on the choice of LiFSI salt, but represents a generalizable strategy for tailoring solvation structure and improving ion transport under demanding conditions (Supplementary Fig. 45 and 46).

Closing remarks:

We sincerely thank Reviewer #4 for their thoughtful and detailed review of our manuscript. The reviewer's comments have greatly assisted us in improving the rigor and impact of our study. We believe that the revisions made in response to these comments have substantially strengthened the manuscript, and we hope they satisfactorily resolve the reviewer's concerns.

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Detailed responses to the reviewers' comments

Manuscript ID: NCOMMS-25-35862A

Title: **Solvation sheath reorganization enables fast ion transfer kinetics**

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Reviewer #1 (Remarks to the Author):

This manuscript presents an innovative electrolyte design strategy for Li-ion batteries under extreme conditions. The *D*-value descriptor and DCM-based electrolyte demonstrate excellent performance in practical pouch cells. I find the manuscript suitable for publication. However, the following minor issues need to be addressed.

Reply: We sincerely thank the reviewer for the positive evaluation of our work. We are encouraged that the reviewer finds our manuscript suitable for publication. We have carefully addressed all comments provided below to further improve the clarity and completeness of the manuscript. Detailed responses and corresponding revisions are listed point-by-point in the following sections.

Q1. The *D*-value ($D = C \cdot 1/\mu \cdot 1/V$) is a key contribution but its derivation is only in Supplementary Note 4. Please add a brief explanation (3-4 sentences) in the main text on page 6 about: (a) the physical meaning of this relationship, and (b) whether this descriptor can be applied to other solvent systems beyond AN-based electrolytes.

Reply: We thank the reviewer for highlighting this important point.

(a) The *D*-value quantifies the ability of a moderator molecule to regulate the Li⁺-anions-solvent interactions, which originates from the competitive coordination strength, dictated by the ion-dipole/dipole-dipole interaction energy, and steric accessibility, determined by the molecular volume (Supplementary Note 4). Specifically, *D* is inversely proportional to both the $\mu_{\text{moderator}}$ and $V_{\text{moderator}}$. A smaller $V_{\text{moderator}}$ facilitates deeper penetration into the Li⁺ solvation sheath and a low $\mu_{\text{moderator}}$ alters the interaction energy balance in favor of moderator-anion coordination over moderator-solvent coupling. This synergistic effect allows the moderator to effectively compete for coordination sites and disrupt the robust Li⁺-anion clusters.

(b) Since the *D*-value is derived from fundamental molecular properties (μ and V) and does not depend on a specific solvent, it is applicable to a wide range of electrolyte systems beyond those based on AN.

In the revised Manuscript (Page 6), we added the following text and highlighted it in

yellow:

The D -value quantifies the ability of a moderator molecule to regulate the Li^+ -anions-solvent interactions, which originates from the competitive coordination strength, dictated by the ion-dipole/dipole-dipole interaction energy, and steric accessibility, determined by the molecular volume (Supplementary Note 4). Specifically, D is inversely proportional to both the $\mu_{\text{moderator}}$ and $V_{\text{moderator}}$. A smaller $V_{\text{moderator}}$ facilitates deeper penetration into the Li^+ solvation sheath and a low $\mu_{\text{moderator}}$ alters the interaction energy balance in favor of moderator-anion coordination over moderator-solvent coupling. This synergistic effect allows the moderator to effectively compete for coordination sites and disrupt the robust Li^+ -anion clusters.

The D -value is derived from fundamental molecular properties (μ and V), ensuring its generalizability beyond AN-based electrolytes to a wide range of solvent systems.

Q2. The SEI/CEI thickness measurements from TEM (Fig. 6c-d) and XPS depth profiling (Fig. 6e-f) are crucial but lack statistical information. Please specify: (a) how many particles/locations were analyzed for the TEM thickness measurements, (b) the sputtering rate and total depth for XPS profiling, and (c) add a table summarizing the atomic percentages of key elements (F, N, S, Cl for FA-DCM; F, P, C, O for BE) at different depths to quantitatively support the claimed "dual-layer SEI architecture."

Reply: We appreciate the reviewer's constructive suggestion to provide more quantitative details on the SEI/CEI characterization.

(a) For the TEM thickness measurements, as shown in Fig. 6c, d and Supplementary Fig. 50a-h, five individual particles/locations were analyzed to ensure statistical reliability. The average SEI thickness values and corresponding standard deviations (17.52 ± 7.71 nm for BE and 3.20 ± 0.48 nm for FA-DCM) have also been included in Supplementary Fig. 50i.

(b) For XPS depth profiling, the sputtering rate was 0.02 nm s^{-1} , and the sputtering times of 0 s, 120 s, and 300 s correspond to depths of 0.0 nm, 2.4 nm, and 6.0 nm, respectively.

(c) As recommended, we have included Table R1 summarizing the atomic

percentages of the key elements (F, N, S and Cl for the FA-DCM electrolyte; F, P, C and O for the BE electrolyte) at different sputtering depths. The quantitative depth-resolved composition clearly corroborates the formation of a dual-layer SEI architecture, characterized by an inner LiF-LiCl-enriched inorganic layer and an outer organic matrix. In contrast, the SEI formed in BE electrolyte lacks a significant inorganic-rich inner layer, maintaining an organic-dominated composition from the interior to the surface.

Table R1. The atomic percentages of key elements with different electrolytes at different sputtering depths.

Electrolyte	Sputtering depth	0.0 nm	2.4 nm	6.0 nm
	Element	Atomic %	Atomic %	Atomic %
FA-DCM	F 1s	10.21	25.63	25.9
	N 1s	6.67	2.65	3.3
	S 2p	9.84	4.92	4.56
	Cl 2p	4.2	8.89	9.04
BE	F 1s	15.86	23.17	24.84
	P 2p	2.18	2.8	2.8
	C 1s	34.55	11.83	9.93
	O 1s	27.89	21.62	20.3

In the revised manuscript (Pages 23 and 35), we added the following text and highlighted it in yellow:

Time of flight secondary ion mass spectrometry (TOF-SIMS) and in-depth X-ray photoelectron spectroscopy (XPS) analysis were conducted to comprehensively explore the chemical composition of electrode-electrolyte interphase (Fig. e-n, Supplementary Fig. 54-58 and **Supplementary Table 10, 11**).

X-ray photoelectron spectroscopy (XPS) (Thermo Scientific ESCALAB 250Xi) **with a sputtering rate of 0.02 nm s⁻¹**

In the Supporting information (Page 16), we added Table R1 as Supplementary Table

11 and highlighted it in yellow:

Supplementary Table 11. The atomic percentages of key elements with different electrolytes at different sputtering depths.

Electrolyte	Sputtering depth	0.0 nm	2.4 nm	6.0 nm
	Element	Atomic %	Atomic %	Atomic %
FA-DCM	F 1s	10.21	25.63	25.9
	N 1s	6.67	2.65	3.3
	S 2p	9.84	4.92	4.56
	Cl 2p	4.2	8.89	9.04
BE	F 1s	15.86	23.17	24.84
	P 2p	2.18	2.8	2.8
	C 1s	34.55	11.83	9.93
	O 1s	27.89	21.62	20.3

Q3. The acknowledgment of DCM toxicity and volatility on page 24 is brief. Please expand this discussion to: (a) explicitly describe the stability results from Supplementary Figs. 59-61 in the main text (specific conditions, duration, and capacity retention values), (b) compare DCM's safety profile with the already-tested DCE moderator, which also shows high D-value and good performance (Fig. 5d), and (c) discuss whether the D-value framework could guide identification of safer alternatives. This would strengthen the practical relevance without requiring new experiments.

Reply: We sincerely thank the reviewer for this insightful comment.

(a) In the revised manuscript, we have explicitly incorporated the stability data from Supplementary Figs. 59-61 into the main text (page 25). The swelling of the pouch cells after cycling under both ambient and low-temperature conditions was minimal, and even after storage at 45 °C for 7 days, the cells retained 90.7% of their initial capacity, indicating the stability of the DCM-based electrolyte under prolonged operation.

(b) In comparison with the DCE-based electrolyte, both systems exhibit similar

pouch cell volume expansion behavior (ΔV after cycling at 25 °C, FA-DCE electrolyte: 18 mL; FA-DCM: 19 mL). However, the DCM-based electrolyte shows superior ionic transport properties and simultaneously forms a more robust and uniform SEI/CEI. This distinction highlights the importance of solvation and interfacial chemistry.

(c) The *D*-value descriptor serves as a theoretical screening tool for identifying suitable moderators that can rationally tune Li^+ -anion-solvent interactions, thereby achieving both efficient ion transport and stable interfacial formation under high-voltage and extreme-temperature conditions. However, the *D*-value does not directly account for physicochemical safety parameters such as boiling point or flash point, which can be easily obtained from the intrinsic molecular properties of candidate solvents.

In the revised Manuscript (Page 25), we added the following text and highlighted it in yellow.

It is worth noting that the toxicity and volatility of DCM limit its broader applicability, but the sealed cells using DCM-based electrolyte still demonstrated decent stability and capacity retention under extended cycling or storage, as the swelling of the pouch cells after cycling at ambient/low temperature is limited and even after being stored at 45 °C for 7 days, the pouch cell retained 90.7% of its initial capacity (Supplementary Fig. 59-61).

Q4. MD simulation results at various temperatures are scattered across multiple supplementary figures (33-38). Please add a supplementary table summarizing Li^+ diffusion coefficients and residence times at 25°C, 0°C, -20°C, and -40°C for FA-DCM and FA-TTE electrolytes to facilitate comparison.

Reply: We appreciate the reviewer's helpful suggestion. To improve clarity and facilitate comparison, we have summarized the relevant transport parameters including Li^+ self-diffusion coefficients and residence times at 25 °C, 0 °C, -20 °C and -40 °C for both FA-DCM and FA-TTE electrolytes in Table R2. These values were extracted from the MD simulations corresponding to Supplementary Figs. 15 and 33-38. The added

table enables a direct comparison of the temperature-dependent Li^+ transport behaviors between the two electrolytes.

Table R2. Transport parameters of different electrolytes at different temperatures extracted from MD simulations in Supplementary Fig. 15 and 33-38.

Electrolyte	Transport parameters	25 °C	0 °C	-20 °C	-40 °C
FA-DCM	Calculated Li^+ diffusion coefficients ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)	5.11	3.19	2.01	0.66
	Residence times for AN (ps)	152.26	193.81	—	—
	Residence times for FSI^- (ps)	115.66	144.28	—	—
	Average migration distance of FSI^- (Å)	49.00	45.86	—	—
	Root mean square displacement of Li^+ over 3000 ps (Å)	32.48	25.99	20.81	11.67
FA-TTE	Calculated Li^+ diffusion coefficients ($\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$)	1.77	0.45	0.14	0.03
	Residence times for AN (ps)	234.44	348.18	—	—
	Residence times for FSI^- (ps)	178.63	249.01	—	—
	Average migration distance of FSI^- (Å)	71.02	226.13	—	—
	Root mean square displacement of Li^+ over 3000 ps (Å)	15.92	9.12	5.00	2.16

In the revised Supporting Information (Page 13), we added Table R2 as Supplementary Table 8 and highlighted it in yellow:

Supplementary Table 8. Transport parameters of different electrolytes at different temperatures extracted from MD simulations in Supplementary Fig. 15 and 33-38.

Electrolyte	Transport parameters	25 °C	0 °C	-20 °C	-40 °C
FA-DCM	Calculated Li ⁺ diffusion coefficients ($\times 10^{-6}$ cm ² s ⁻¹)	5.11	3.19	2.01	0.66
	Residence times for AN (ps)	152.26	193.81	—	—
	Residence times for FSI ⁻ (ps)	115.66	144.28	—	—
	Average migration distance of FSI ⁻ (Å)	49.00	45.86	—	—
	Root mean square displacement of Li ⁺ over 3000 ps (Å)	32.48	25.99	20.81	11.67
FA-TTE	Calculated Li ⁺ diffusion coefficients ($\times 10^{-6}$ cm ² s ⁻¹)	1.77	0.45	0.14	0.03
	Residence times for AN (ps)	234.44	348.18	—	—
	Residence times for FSI ⁻ (ps)	178.63	249.01	—	—
	Average migration distance of FSI ⁻ (Å)	71.02	226.13	—	—
	Root mean square displacement of Li ⁺ over 3000 ps (Å)	15.92	9.12	5.00	2.16

In the revised Manuscript (Page 19), we added the following text and highlighted it in yellow:

MD simulations suggest that while correlated Li⁺-anion motions exist, they are less constraining in FA-DCM electrolyte than in FA-TTE electrolyte regardless of temperatures, leading to reduced residence times for FA-DCM electrolyte at 0 °C (193.8 ps for AN, 144.3 ps for FSI⁻) (Supplementary Fig. 33-36 and **Supplementary Table 8**). Moreover, Li⁺ exhibits a root mean square displacement of 11.67 Å over 3,000 ps in the FA-DCM electrolyte, significantly higher than the 2.16 Å observed in the FA-TTE electrolyte at -40 °C (Fig. 5a, Supplementary Fig. 37 and **Supplementary Table 8**).

Additionally, the calculated diffusion coefficient of Li^+ in the FA-DCM electrolyte reaches $6.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ at -40°C , which is 24.5 times higher than that in the FA-TTE electrolyte, further underscoring the superior capability of the FA-DCM electrolyte in enabling efficient Li^+ transport kinetics at low temperatures (Supplementary Fig. 38 and Supplementary Table 8).

Closing remarks

We sincerely thank the reviewer for the constructive comments and encouraging assessment of our work. All suggestions have been carefully addressed and incorporated into the revised manuscript, which we believe has significantly improved the clarity, rigor and practical relevance of the study. We truly appreciate the reviewer's time and efforts in evaluating our submission.

Reviewer #2 (Remarks to the Author):

This is a well-executed and highly original study.

The authors provide both a new theoretical descriptor and compelling low-temperature pouch-cell data, which together meet the novelty and mechanistic standards of Nature Communications.

The manuscript is scientifically sound, well supported by data, and written clearly.

Reply: We sincerely thank the reviewer for the very positive and encouraging evaluation of our work. We have carefully rechecked the manuscript to ensure that all data and discussions are presented with maximum clarity and precision. We truly appreciate the reviewer's thoughtful assessment and kind support for publication.

Reviewer #3 (Remarks to the Author):

The manuscript titled “Solvation Sheath Reorganization Enables Fast Ion Transfer Kinetics” presents a study on a novel electrolyte design approach for lithium-ion batteries (LIBs), employing dichloromethane (DCM) to reorganize the solvation sheath. The FA-DCM electrolyte demonstrates excellent electrochemical performance in 4.5 V graphite||NMC811 full cells, delivering a remarkable capacity of 179.8 mAh g⁻¹ at 6 C. At an ultra-low temperature of -50 °C, the pouch cell exhibits stable cycling, achieving a high capacity of 0.51 Ah. This study establishes an effective strategy for developing electrolytes tailored for fast-charging and low-temperature LIBs, providing an alternative to conventional carbonate-based electrolytes with improved compatibility for high-voltage cathodes.

The queries raised during the previous review have been adequately addressed by the authors, and I recommend accepting the manuscript as such.

1. The toxicity of DCM has been addressed, and the authors mention excellent sealing of their pouch cells.
2. The cost comparison of different electrolytes has been added in Table R6.
3. The incompatibility issues between acetonitrile and graphite have been explained in the manuscript using graphite||LFP full cells as an example.
4. Revised EIS data have been provided.
5. X-ray photoelectron spectroscopy (XPS) depth profiling, together with time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis, has been included to understand the SEI chemistry.
6. SiC||NMC full cells were tested to demonstrate compatibility with silicon-based anodes.

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.

Reply: We sincerely thank the reviewer and the co-reviewer for the highly positive and

supportive evaluation of our work. We are deeply grateful for the reviewer's recommendation for acceptance and for the valuable time and effort dedicated to evaluating our manuscript.

Reviewer #4 (Remarks to the Author):

The authors have provided a comprehensive and thoughtful revision of the manuscript “Solvation Sheath Reorganization Enables Fast Ion Transfer Kinetics.”

I appreciate the careful and data-driven responses to the earlier review. The revisions have substantially improved the scientific rigor, mechanistic clarity, and overall impact of the work.

Reply: We sincerely thank the reviewer for the thoughtful and positive assessment of our revised manuscript. We greatly appreciate the reviewer’s constructive feedback and insightful comments during the review process, which have helped us refine the scientific rigor and presentation of our work. We are delighted that the revisions meet the reviewer’s expectations.

Reviewer #5 (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.

Reply: We would like to express our sincere gratitude to both the reviewer and the co-reviewer for their valuable time and constructive comments. We appreciate their joint effort under the *Nature Communications* Early Career Researcher co-review initiative.

Detailed responses to the reviewers' comments

Manuscript ID: NCOMMS-25-35862B

Title: **Solvation sheath reorganization enables fast ion transfer kinetics**

Authors: Menglu Li, Di Lu, Jinze Wang, Shuoqing Zhang, Ling Lv, Baochen Ma, Haotian Zhu, Long Li, Sheng Yang, Zirui Li, Yuefei Wu, Jiacheng Qi, Liwu Fan, Ruhong Li, Lixin Chen, Tao Deng, Xiulin Fan

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Reviewer #1 (Remarks to the Author):

The authors have submitted a comprehensive and well-considered revision of the manuscript. I appreciate the detailed, data-driven responses to the previous comments. These modifications have significantly enhanced the scientific rigor, mechanistic clarity, and overall impact of the work.

Reply: We sincerely thank the reviewer for the positive and encouraging evaluation of our revised manuscript. We greatly appreciate the reviewer's recognition of our data-driven revisions and their assessment that these changes have strengthened the scientific rigor, mechanistic clarity and overall impact of the work. Such constructive feedback is highly valuable and motivating, and we are grateful for the time and effort devoted to reviewing our manuscript.

This manuscript presents a well-executed and insightful study on electrolyte design for lithium-ion batteries operating under extreme low temperatures. The authors propose a descriptor-driven strategy using a small, low-dipole moment molecule (DCM) to reorganize the Li^+ solvation sheath and enable fast ion transport via a discrete hopping mechanism. The manuscript demonstrates excellent low-temperature cycling performance, including 1.0 Ah pouch cell operation at $-50\text{ }^{\circ}\text{C}$, which is rare in the field. The study is highly relevant to the development of practical, high-performance batteries for cold environments and fast-charging applications. The experimental design is thorough, and the combination of molecular simulations, spectroscopy, and full-cell validation provides a strong foundation for the claims. However, several aspects require clarification and expansion before publication.

1. The proposed descriptor $D=C/(\mu\cdot V)$ is central to the screening of suitable moderator molecules. However, it remains unclear whether this parameter has been quantitatively correlated with experimentally observed or simulated transport properties. Could the authors provide a quantitative correlation (e.g., regression analysis, R^2 value) between the D value and key ion transport parameters such as ionic conductivity, diffusion coefficient, or Li^+ residence time?
2. The manuscript claims that DCM does not coordinate with Li^+ , thereby contributing to the breakdown of large solvation clusters. However, the RDF analysis (Supplementary Fig. 24b) indicates possible $\text{Li}-\text{Cl}$ interactions in the FA-DCM system. How do the authors reconcile this apparent interaction with their claim that DCM is a non-coordinating solvent? Could weak or transient coordination with Li^+ affect the observed solvation structure or CIP/AGG behavior?
3. The proposed Li^+ transport mechanism involves discrete hopping between locally confined solvation domains. This mechanism is inferred from MD simulations showing reduced residence time and increased RMS displacement. Have the authors conducted, or could they consider, experimental validation of this hopping transport mechanism using techniques such as PFG-NMR, isotopic tracer analysis, or neutron scattering?
4. DCM has a low boiling point and high volatility, which could pose risks for long-term cell performance and safety, especially in pouch-type configurations. Have the authors investigated the volatility-related stability of DCM-based electrolytes in sealed cells over prolonged storage or cycling? Were there any observations of gas evolution, electrolyte loss, or pressure accumulation?
5. XPS depth profiling (Supplementary Fig. 32) indicates a LiF - and LiCl -rich SEI structure, which is proposed to be beneficial for stable cycling. Can the authors provide a more quantitative analysis of the SEI composition? For example, what are the estimated thicknesses or relative volume ratios of the inorganic and organic layers within the SEI?
6. The study mainly focuses on FA-DCM (high performance) and FA-TTE (poor performance), but Supporting Information includes other moderators with intermediate D values (e.g., FB, CLB). Have the authors evaluated the electrochemical performance of these intermediate- D systems? Do their results support the general applicability of the D -based screening model?

