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Perspective

Lithium Bond in High-Concentration Electrolytes

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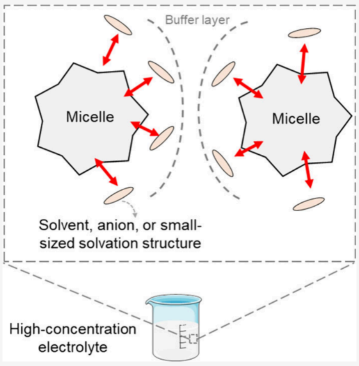
ABSTRACT: High-concentration electrolytes (HCEs) are promising for rechargeable batteries, but the stabilization mechanism of their large-sized solvation structures is not fully understood. This Perspective highlights the crucial role of lithium bonds as secondary interactions analogous to hydrogen bonds in stabilizing HCEs. By analyzing bond parameters, experimental criteria, and coordination behavior, we demonstrate that lithium bonds form between lithium in aggregate micelles and diluents, solvents, and anions in outer solvation shells. The surrounding molecules attracted through lithium bonds act as the buffer layer to mitigate micelle collision and phase separation, thereby maintaining the colloidal integrity of HCEs. Finally, we outline future research directions for lithium bond chemistry to guide the advanced electrolyte design.



Lithium batteries are indispensable to modern society, where the electrolyte plays a pivotal role in ion conduction and critically affects the electrode interfaces and overall battery performances.[1−4] Among various electrolyte systems, high-concentration electrolytes (HCEs) have attracted considerable attention for their exceptional ability to stabilize anodic and cathodic interphases, particularly in high-energy-density, long-cycling-life, and fast-charging batteries.[5−8] The unique solvation structure of HCEs, featuring anionic participation and the formation of large-sized aggregates (AGGs) and contact ion pairs (CIPs), is central to their superior functionality at the molecular level.[9−11] However, a fundamental question remains for how these expansive solvation structures with micellar scales (>1 nm) can exist stably in HCEs without phase separation.[12−14] The underlying physicochemical stabilization mechanism is still poorly understood, posing a significant barrier to the rational design of next-generation HCEs.

The concept of the lithium bond, a secondary interaction analogous to the well-established hydrogen bond, offers a promising perspective to decipher this puzzle. First proposed in the 1950s and experimentally confirmed in the 1970s, lithium bonds have recently regained interest in battery research.[15−17] For instance, Song *et al.* followed the lithium bond theory to construct a deep eutectic electrolyte, and the lithium-ion interaction behavior with anions is significantly altered to promote the lithium mobility and stable interphase formation.[18] Similar to other secondary interactions such as the halogen bond and $\pi-\pi$ stacking, lithium bonds are weaker than primary interactions including ionic and covalent bonds, but stronger than the van der Waals force in bond energy.[19] The secondary interactions play a significant role in stabilizing the nanostructures, such as the hydrogen bonds in maintaining the double-helix structure of DNA molecules and the halogen bonds in participating in the supramolecule self-assembly.[20,21] Similarly, lithium bonds are anticipated to play a crucial role in stabilizing the nanoscale architecture of battery electrolytes, especially in HCEs with non-negligible lithium bond percentages.

In this Perspective, we systematically analyze the lithium bond properties and reveal a mechanism of HCE stabilization through lithium bond formation between lithium in AGG micelles and species in the outer solvation shells. The discussion begins with an examination of the distinctive colloidal nature and solvation scales of HCEs, highlighting their contrast with routine dilute solutions. Subsequent analysis focuses on the properties of lithium bonds, integrating computational and experimental evidence such as nuclear magnetic resonance (NMR) based criteria and coordination number (CN) analyses to demonstrate their significant presence in HCEs. Building on the shift from chelation to

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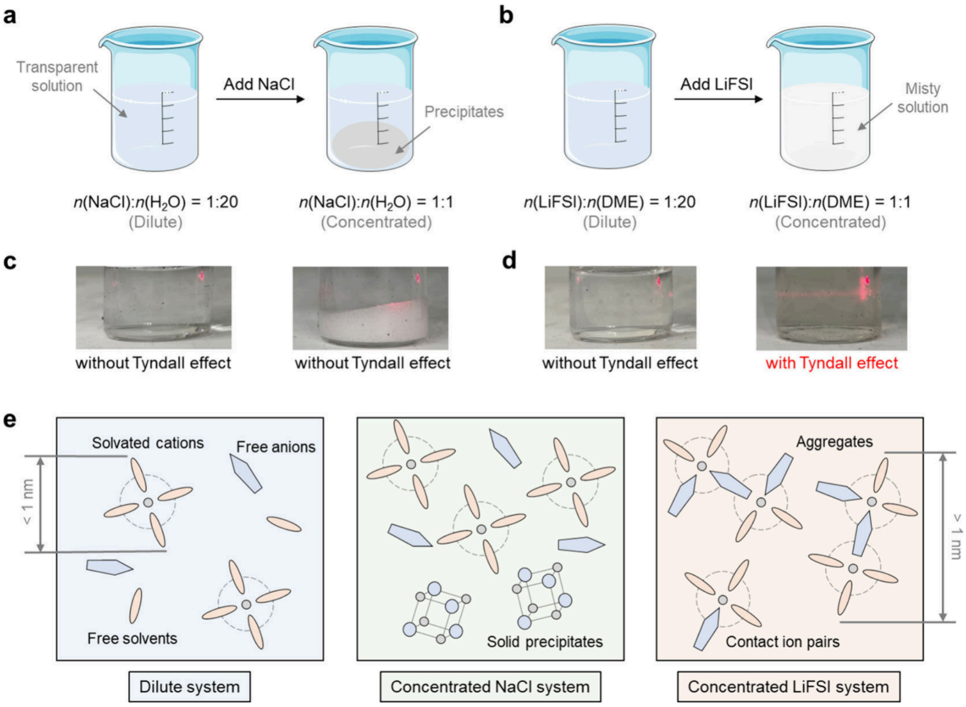

Figure 1. The physicochemical properties of the high-concentration electrolytes. (a) The physical states of the dilute and concentrated NaCl aqueous systems. In a concentrated NaCl system, transparent solution forms with the NaCl precipitation. (b) The physical states of the dilute and concentrated LiFSI-based DME systems. In the concentrated LiFSI system, misty solution forms without the solid LiFSI precipitation. The Tyndall effect evaluations in (c) dilute and concentrated NaCl systems and (d) dilute and concentrated LiFSI systems. The Tyndall effect illustrates that the concentrated LiFSI solution is in a colloidal state. (e) The molecular-level solvation schematics of the dilute solution, concentrated NaCl solution, and concentrated LiFSI solution. The solvation structure sizes between dilute solution and concentrated NaCl solution are analogous and less than 1 nm, while the solvation structure size in concentrated LiFSI solution is over 1 nm.

bridging coordination modes at high concentrations, we find that lithium bonds form between Li^+ in micelles constituted by one or several AGGs and surrounding diluents, solvents, or anions. The above surrounding species acting as surfactants are with both polar and nonpolar regions, thereby forming a buffer layer to prevent micellar collision and phase separation. This insight leads to the interpretation of HCEs as colloidal systems primarily stabilized by lithium bonds. Finally, we outline future research directions for lithium bond chemistry, highlighting its potential to guide advanced electrolyte design.

The Physicochemical Properties of HCEs

To address the fundamental question of how expansive solvation structures remain stable, it is first necessary to define the unique physical state of HCEs that distinguishes them from conventional dilute solutions. In solution chemistry, not all of the solvents and salts can constitute the HCE system. For instance, sodium chloride (NaCl) aqueous solution serves as a basic electrolyte for the chlor-alkali industry, while it cannot form the typical single-phase HCE (Figure 1a). The dilute NaCl solution (such as $n(NaCl):n(H_2O) = 1:20$) is transparent, and the concentrated system (such as $n(NaCl):n(H_2O) = 1:1$) constitutes the two separated phases (transparent NaCl saturated solution with $n(NaCl):n(H_2O) = 1:9.02$ and NaCl precipitate). However, lithium bisfluorosulfonimide (LiFSI)-based 1,2-dimethoxyethane (DME) solutions behave differently and can form single-phase HCE (Figure 1b). The dilute LiFSI solution (such as $n(LiFSI):n(DME) = 1:20$) is transparent, while the concentrated system (such as $n(LiFSI):n(DME) = 1:1$) is misty without any precipitate. Through the Tyndall effect evaluations, the laser directly passes through the dilute and concentrated NaCl solutions as well as the dilute LiFSI solution without a trace, while the laser pathway trace is apparent in the concentrated LiFSI solutions (Figure 1c,d). The above distinct phenomena illustrate that the dilute NaCl or LiFSI and concentrated NaCl systems are composed of small-sized dispersion (<1 nm) with the solution state, while the concentrated LiFSI system is composed of large-sized dispersion (1−100 nm) with the colloidal state.[22]

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From the aspect of solvation structure, there are abundant solvent-separated ion pairs (SSIPs) in the dilute solutions, where cations are solvated by solvents, and anions are relatively far away from the solvation shell[23] (Figure 1e). In the concentrated NaCl system, the solution constitutes only SSIPs with small size, and the NaCl nanoparticles cannot be dispersed in the solution but as the precipitates.[24] From the viewpoint of classic inorganic chemistry, the high dielectric constant of water leads to complete salt dissociation in the $NaCl/H_2O$ system. As the salt concentration increases, the lack of secondary interactions to stabilize large clusters causes Na^+ and Cl^- ions to directly aggregate into a 3D lattice driven by the thermodynamic preference for macroscopic crystallization. Additionally, neither water nor Cl^- ions can act as surfactants to prevent the coalescence of these aggregates. In contrast, there are AGGs and CIPs in the concentrated LiFSI system, where anions directly coordinate with cations to form the large-sized solvation shell especially the AGGs involving two or more cation centers.[25] One or several AGGs constitute a micelle with over 1 nm scale, and several micelles stably existing without collision constitute the HCE in the colloidal state. The distinct behaviors between concentrated NaCl and LiFSI systems are so inspiring that large-sized micelles can stably exist in certain systems, depending on the properties of solvents and anions such as polarity and steric. However, the underlying chemical mechanism of the phenomena described above remains unclarified.

Lithium Bond Interactions in HCEs

The identification of the colloidal nature in HCEs at the macroscale suggests the presence of specific stabilizing forces. As primary interactions alone cannot fully account for this stability, the role of secondary interactions is examined. Hydrogen bonds have been demonstrated to stabilize nanostructures in many structural biology and supramolecular systems. Due to the similarity between lithium and hydrogen, the lithium bond is deemed to be analogous to the hydrogen bond as a typical secondary interaction,[26] and the lithium bond theory can be applicable to clarify the micelle stabilization mechanism in HCEs.

The lithium bond chemistry has been explored for over 60 years since the proposal in 1959 by Shigorin.[15] In the early studies, four types of lithium bond complexes, (including LiY dimers, X−LiY σ-type Li-bonded complexes, X−LiY π-type Li-bonded complexes, and LiY oligomers, where X = NH_3, Me_3N, H_2O, MeOH, Me_2O, and Y = H, F, Cl, Br) are mainly considered in the organometallic chemistry field.[27,28] The bond energies of the four types of lithium bonds described above are evaluated. Most lithium bond energies are around 50 kJ mol^{-1}, which is much lower than the over 250 kJ mol^{-1} of the primary interactions including covalent and ionic bonds (*e.g.*, 341 kJ mol^{-1} of the Li−O bond in Li_2O crystal)[29−31] (Figure 2a). With the rapid development of lithium battery technology in recent 30 years, the significance of the lithium bond chemistry has been re-evaluated, and the applicable properties of lithium bond are considered to explain physicochemical phenomena.[18,32,33]

The lithium bond is employed to probe the HCE electrolyte through experimental and theoretical methods. Taking the typical lithium salt LiFSI and typical solvent DME as examples, the NMR chemical shift of the ^{7}Li nuclei ($\delta(^7Li)$) exhibits a volcano plot versus the LiFSI to DME molar ratio[34,35] (Figure 2b). In detail, as the LiFSI concentration increases, the value of $\delta(^7Li)$ first reduces due to the anion coordination rendering the rise of electron density and then counterintuitively increases due to the electron localized effect induced by the lithium bond formation. You *et al.* demonstrated that, as the LiFSI concentration increases, the percentage of AGG and CIP species also exhibits a volcano plot,[34] where lithium bonds can replace part of the primary interactions to dominate the solvation structure in HCEs.

To quantify the lithium bond percentage in HCE, Zhang and co-workers proposed the lithium coordination number (CN) as an indicator to distinguish the lithium bond and primary interactions based on the electron properties, which serves as a basis for direct lithium bond quantification.[35] In detail, $\delta(^7Li)$ exhibits a volcano plot versus the CN, and the transition point corresponds to the CN of 4. Therein, the lithium bond and primary interaction tend to dominate the bond properties under the low and high CN conditions, respectively. In the lithium bond region, the electron localization function (ELF) demonstrates a significant localization effect characterized by a rising deformation factor φ that reflects an increased electron cloud asymmetry and reduced nuclear shielding. In contrast, within the primary interaction region, φ decreases back toward unity as the spatial distribution of the electron cloud becomes more symmetric, leading to enhanced magnetic shielding of the lithium nucleus. Typical solvents including DME, dimethyl carbonate (DMC), 1,3-dioxolane (DOL), and ethylene carbonate (EC), and typical anions including FSI^-, bis(fluorosulfonyl)imide ($TFSI^-$), hexafluorophosphate (PF_6^-), and nitrate (NO_3^-) are considered in lithium bond percentage quantification with low and high concentrations, and the lithium bond formation is judged from the CN value of no more than 4 obtained from MD simulations[36] (Figure 2c). As a result, as the average value of every combination in the above anions and solvents, the lithium bond percentage in HCEs is around 15%, higher than the one of around 2% in low-concentration electrolytes (LCEs). The increment of lithium bond percentage in HCEs suggests that the formation and stabilization of the large-sized solvation shell with the micelle state are largely dependent on the abundantly emerged lithium bond.

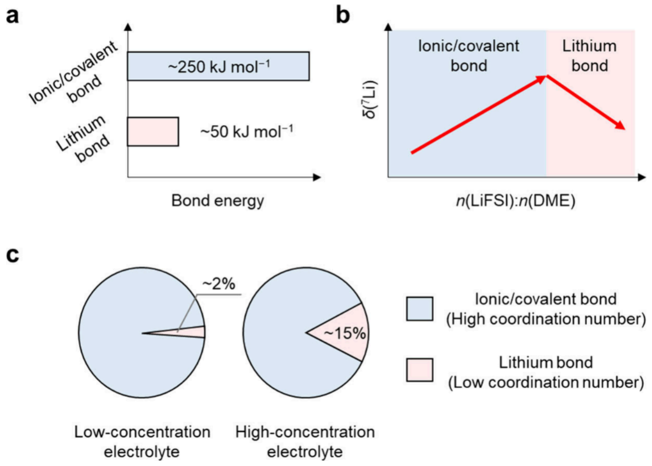

Figure 2. Lithium bond formation in high-concentration electrolytes. (a) The bond energies of lithium bond as a secondary interaction and ionic/covalent bonds as primary interactions. Energy statistics are obtained from refs 28−30. (b) ^{7}Li-nuclear magnetic resonance (NMR) shift variations versus the molar ratios of LiFSI and DME. The volcano-type NMR shift variation manifests the lithium bond formation in high-concentration electrolytes. Reproduced from ref 34 with permission from American Chemical Society copyright 2024 and from ref 35 with permission from Elsevier Ltd. copyright 2025. (c) Lithium bond percentage in low- and high-concentration electrolytes distinguished by the lithium coordination number. Reproduced from ref 36 with permission from Wiley-VCH, copyright 2025.

Lithium Bond in Stabilizing the Micelles of HCEs

Following the quantitative identification of pervasive lithium bonds in HCEs, the focus is transitioned toward the underlying geometric and structural principles that govern the stabilization

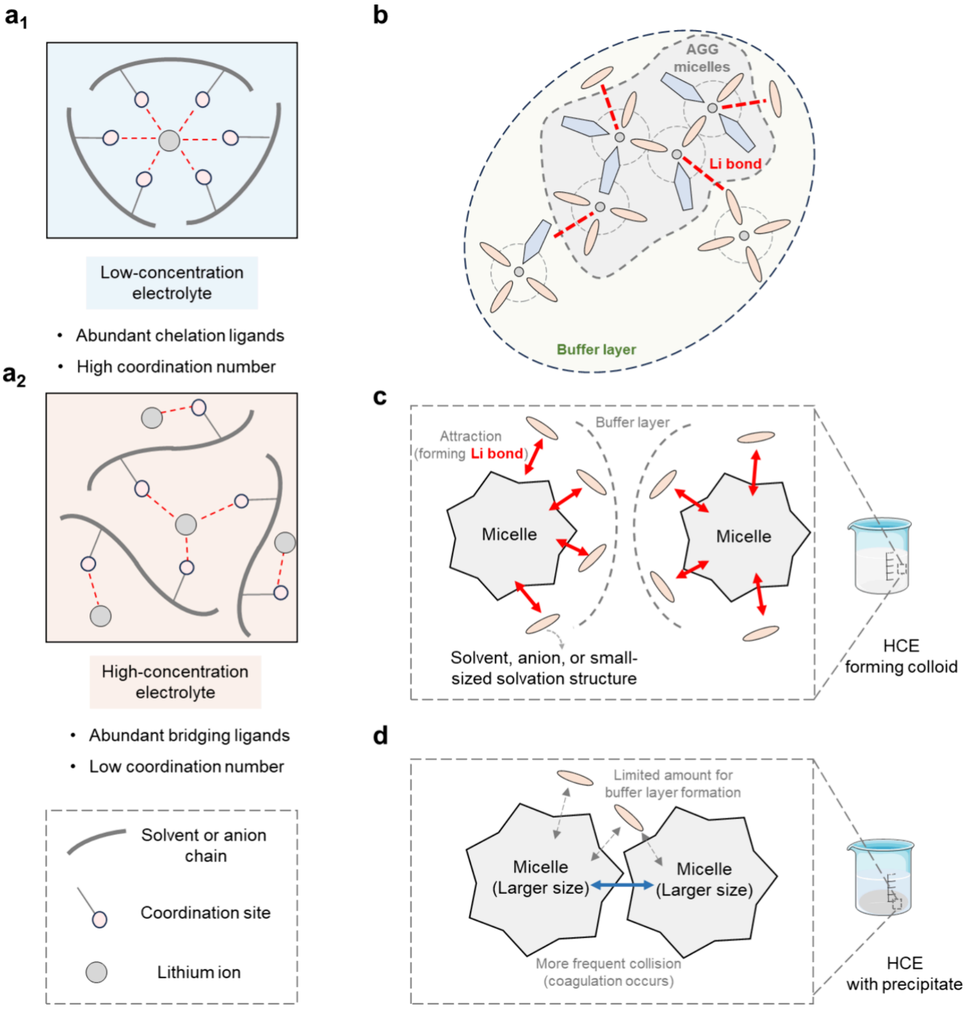

Figure 3. Lithium bond-induced stabilization mechanism of the high-concentration electrolytes. (a) The schematics of the lithium solvation environments in (a_1) low-concentration and (a_2) high-concentration electrolytes. Solvents and anions mostly serve as the bridging ligands in high-concentration electrolytes, rendering a relatively low coordination number and unsatisfactory charge shielding of the lithium ions. (b) The nanostructure of the micelles and surrounding species acting as the buffer layer. Therein, the blue and orange bars represent the anions and solvents, respectively; the gray and green regions represent the boundary of the micelle and buffer layer, respectively; and the red line represents the lithium bond formation between Li^+ and surrounding solvents or anions without direct coordination. The microscopic schematics in the high-concentration electrolytes (c) forming colloid and (d) with precipitate. In the former system, due to the unsatisfactory charge shielding of the lithium ions, micelles constituted by one or several AGGs are surrounded by small-sized solvation structures through lithium bonds, which serves as an effective buffer layer and avoids the coagulation between micelles. In the latter system, when the lithium salt concentration further increases, the micelle numbers as well as sizes increase and the distance between micelles decreases, resulting in more frequent collision and micelle coagulation.

of micellar architectures against aggregation. In the $Fe(OH)_3$ colloid, the formation of hydrogen bonds between OH^- anions and H_2O solvents is capable of stabilizing the large-sized micelles.[37] The stabilization mechanism through secondary interactions between the $Fe(OH)_3$ colloid and HCE is analogous. Consequently, the lithium bond can account for the stabilization of large-sized AGG micelles.

From the perspective of the solvation structure variation, the anions or solvents serving as electron donors tend to interact with lithium ions serving as electron acceptors through the chelation coordination in LCEs, whereas they interact via bridging coordination in HCEs[38,39] (Figure 3a). In detail, the molar ratio of electron donors to acceptors is continuously reduced when the lithium salt concentration increases, and the limiting condition is the electrolyte becoming an infinitely dilute solution when its concentration approaches zero and becoming nearly pure lithium salt when its concentration approaches infinity. Taking the LiFSI−DME system as an example, lithium ions in the infinitely dilute solution are surrounded by chelation-coordinated DME solvents to form the $Li^+(DME)_3$ structure with a high CN of six, and lithium ions in the LiFSI crystal are bridging-coordinated by the FSI^- anions serving as monodentate ligands to form the $Li^+(FSI^-)_4$ localized structure in the unit cell with the low CN of four.[35] The reduced CN in HCEs than LCEs can also be proved through the molecular dynamic simulations.[6,35]

Due to the reduced CN in HCEs, the positive charge of the lithium ions cannot be fully shielded by the surrounding anions and solvents in the inner solvation shell of HCEs, and anions, solvents, or diluents with negative regions in the outer solvation shells can also interact with lithium ions.[12,34] The above lithium bond interaction between the lithium ions and outer solvation shells is mainly based on the ion−dipole attraction, which is much weaker than the primary interactions formed between the lithium ions and inner solvation shells (Figure 3b). Namely, the surrounding species through lithium bond interactions serves as a buffer layer outside the large-sized micelles constituted by one or several AGGs in case of the collision between micelles. Additionally, the anions and solvents in the outer solvation shell are amphiphilic, where there are both polar segments and nonpolar segments in the molecular structures.[12,40] Attributed to the lithium bond formation, the uneven charge outside the micelle surfaces is well dispersed, the nonpolar segments in buffer layer stabilize the regions between micelles, and the collision possibility between several micelles are lowered (Figure 3c). As a result, the lithium bond induces micelles constituted by large AGGs to stably exist in HCEs and form the colloidal state without coagulation. However, if continuously adding lithium salts to the HCE system, the numbers and the size of micelles increase and the distances between them decrease, rendering the collision frequency between micelles are reinforced (Figure 3d). Moreover, from the aspect of hard and soft acidic theory, the charge distribution outside the large and soft micelles is much more uneven, further deteriorating the coagulation. In this way, the above micelles collide with each other and induce coagulation to form precipitates; therefore, there is also a value of "maximal solubility" in HCE systems. For instance, in the LiFSI/DME system, the maximal solubility reaches a lithium salt to solvent molar ratio of around 1:1, where the micelles remain stable in lower ratio while the lithium salt precipitates in higher ratio.[12] The stabilization mechanism detailed above provides a new theoretical lens to view HCEs, transitioning the focus from a simple solution chemistry perspective to a more complex colloidal perspective.

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Summary and Outlook

In this Perspective, a comprehensive analysis of lithium bond chemistry in HCEs is presented, culminating in a proposed mechanism by which lithium bonds stabilize the electrolyte nanostructure. The discussion begins by elucidating the unique physicochemical properties of HCEs, which exhibit a colloidal state wherein AGG species of micellar dimensions (>1 nm) coexist stably. The nature of lithium bonds is thoroughly examined, including their physicochemical properties, experimental identification criteria, and characteristic coordination behaviors. A significant phenomenon is the transition from chelation to bridging coordination in HCEs, which facilitates the formation of lithium bonds between lithium ions in micelles constituted by one or several AGGs and small-sized species in outer solvation shell. These species attracted by lithium bonds effectively act as a buffer layer, preventing micelle collision and phase separation. Accordingly, HCEs can be regarded as colloidal systems whose integrity is maintained by pervasive lithium bond interactions.

The investigation of lithium bond chemistry in electrolytes is encouraging but remains in its infancy. Several fundamental challenges at the nano-, micro-, and macroscales require urgent attention. To this end, several perspectives are proposed for future lithium bond chemistry research.

First, deepening our mechanistic understanding of lithium bond formation is imperative. Lithium bonds take a non-negligible percentage of the interactions in electrolytes, especially HCEs. However, current studies predominantly focus on the inner solvation shell, often overlooking the critical interactions within the outer shell, where lithium bonds predominantly operate. Elucidating the coordination behavior and fundamental principles governing lithium bonds is essential for the rational design of next-generation electrolytes. Concretely, specific efforts should be directed toward the molecular engineering of the electrolyte components. For instance, by systematically modifying the polarity and steric hindrance of functional groups on solvents or lithium salt anions, researchers can deliberately promote the occurrence of low-coordination structures. Such targeted structural tuning would effectively increase the proportion of lithium bonds, creating ideal model systems for exploring the fundamental competition between secondary and primary interactions. Besides lithium, sodium and potassium salts can also constitute stable HCEs, the underlying chemistry concerning sodium and potassium-based secondary interactions in beyond-lithium batteries should also be paid attention to.[41]

Second, advancing quantitative characterization methodologies represents a major frontier. The current reliance on theoretical calculations for parameters like bond length and energy highlights a significant experimental gap. Beyond basic spectroscopy, more sophisticated NMR techniques such as relaxation time measurements could be employed to quantitatively calibrate the bond energies within lithium bond networks through specifically analyzing the differences between spin−lattice and spin−spin relaxation times. Furthermore, by emulating characterization paradigms from hydrogen bond research, the electrolytes could be anchored within rigid frameworks like molecular sieves or specific solid-phase materials exhibiting lithium-bond attributes. This would facilitate the direct visualization of lithium bond formation and the resulting nanostructures through high-resolution imaging techniques such as atomic force microscopy.[42,43] Developing advanced and accurate spectroscopic techniques, coupled with computational methods, is crucial for moving from indirect evidence to direct quantification of lithium bond properties.[44]

Beyond basic spectroscopy, more sophisticated NMR techniques such as relaxation time measurements could be employed to quantitatively calibrate the bond energies within lithium bond networks through specifically analyzing the differences between spin−lattice and spin−spin relaxation times

Third, the functional role of lithium bonds in electrochemical processes demands clarification. As a pervasive interaction in HCEs, the dual effects of lithium bonds on battery performance must be rigorously evaluated. Future studies could investigate how lithium bonds potentially enhance battery states, such as through facilitating desolvation kinetics. Simultaneously, it is critical to address their potential negative impacts, such as the reduction in ionic conductivity caused by the increased immobilization of anions and solvents within the lithium-bond-mediated networks. Besides in HCE, there are other circumstances with high Li^+ concentration in batteries during operation, where lithium bond chemistry can also function but their roles remain unclarified. For instance, solvents near cathode interfaces are rapidly depleted during fast-charging processes, rendering the occurrence of locally high Li^+ concentration and the deterioration of the electro-osmotic drag polarization.[45] The lithium bond chemistry in regulating lithium interfacial transport and stabilizing the interface under locally high Li^+ concentration conditions deserves much more exploration. Correlating these competing characteristics with specific metrics such as fast-charging capabilities or low-temperature stability will be essential to establish concrete structure−property relationships for advanced electrolyte design.

In summary, the unique insights gleaned from HCE systems have unveiled lithium bond chemistry as a transformative perspective for fundamental electrochemistry. With targeted research guided by these priorities, lithium bond principles are poised to open new avenues to describe lithium-containing systems.

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REFERENCES

(1) Huang, X.-Y.; Zhao, C.-Z.; Kong, W.-J.; Yao, N.; Shuang, Z.-Y.; Xu, P.; Sun, S.; Lu, Y.; Huang, W.-Z.; Li, J.-L.; Shen, L.; Chen, X.; Huang, J.-Q.; Archer, L. A.; Zhang, Q. Tailoring polymer electrolyte solvation for 600 Wh kg^{-1} lithium batteries. *Nature* **2025**, *646* (8084), 343.

(2) Huang, H.; Hu, Y.; Hou, Y.; Wang, X.; Dong, Q.; Zhao, Z.; Ji, M.; Zhang, W.; Li, J.; Xie, J.; Guo, H.; Han, X.; Ouyang, X.; Hu, W. Delocalized electrolyte design enables 600 Wh kg^{-1} lithium metal pouch cells. *Nature* **2025**, *644* (8077), 660.

(3) Li, X.-Y.; Li, B.-Q.; Feng, S.; Li, Z.; Shen, L.; Sun, S.-Y.; Chen, Z.-X.; Jin, T.; Chen, X.; Zhao, M.; Zhang, X.-Q.; Huang, J.-Q.; Zhang, Q. Two-stage solvation of lithium polysulfides in working lithium−sulfur batteries. *J. Am. Chem. Soc.* **2025**, *147* (18), No. 15435.

(4) Li, M.; Wang, C.; Chen, Z.; Xu, K.; Lu, J. New concepts in electrolytes. *Chem. Rev.* **2020**, *120* (14), 6783.

(5) Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu, K. Water-in-salt" electrolyte enables high-voltage aqueous lithium-ion chemistries. *Science* **2015**, *350* (6263), 938.

(6) Pang, Q.; Shyamsunder, A.; Narayanan, B.; Kwok, C. Y.; Curtiss, L. A.; Nazar, L. F. Tuning the electrolyte network structure to invoke quasi-solid state sulfur conversion and suppress lithium dendrite formation in Li−S batteries. *Nat. Energy* **2018**, *3* (9), 783.

(7) Zhang, W.; Koverga, V.; Liu, S.; Zhou, J.; Wang, J.; Bai, P.; Tan, S.; Dandu, N. K.; Wang, Z.; Chen, F.; Xia, J.; Wan, H.; Zhang, X.; Yang, H.; Lucht, B. L.; Li, A.-M.; Yang, X.-Q.; Hu, E.; Raghavan, S. R.; Ngo, A. T.; Wang, C. Single-phase local-high-concentration solid polymer electrolytes for lithium-metal batteries. *Nat. Energy* **2024**, *9* (4), 386.

(8) Yao, N.; Chen, X.; Fu, Z.-H.; Zhang, Q. Applying classical, *ab initio*, and machine-learning molecular dynamics simulations to the liquid electrolyte for rechargeable batteries. *Chem. Rev.* **2022**, *122* (12), No. 10970.

(9) Li, R.; Zhang, H.; Zhang, S.; Li, Y.; Guo, R.; Pei, H.; Yang, M.; Zhang, J.; Chen, L.; Xiao, X.; Chen, L.; Shen, Y.; Deng, T.; Fan, X. Unified affinity paradigm for the rational design of high-efficiency lithium metal electrolytes. *Nat. Energy* **2025**, *10* (9), 1155.

(10) Yamada, Y.; Wang, J.; Ko, S.; Watanabe, E.; Yamada, A. Advances and issues in developing salt-concentrated battery electrolytes. *Nat. Energy* **2019**, *4* (4), 269.

(11) Gao, Y.-C.; Chen, X.; Yuan, Y.-H.; Chen, Y.-P.; Niu, Y.-L.; Yao, N.; Gao, Y.-B.; Li, W.-L.; Zhang, Q. Accelerating battery innovation: AI-powered molecular discovery. *Chem. Soc. Rev.* **2025**, *54* (21), 9630.

(12) Efaw, C. M.; Wu, Q.; Gao, N.; Zhang, Y.; Zhu, H.; Gering, K.; Hurley, M. F.; Xiong, H.; Hu, E.; Cao, X.; Xu, W.; Zhang, J.-G.; Dufek, E. J.; Xiao, J.; Yang, X.-Q.; Liu, J.; Qi, Y.; Li, B. Localized high-concentration electrolytes get more localized through micelle-like structures. *Nat. Mater.* **2023**, *22* (12), 1531.

(13) Ma, B.; Zhang, H.; Li, R.; Zhang, S.; Chen, L.; Zhou, T.; Wang, J.; Zhang, R.; Ding, S.; Xiao, X.; Deng, T.; Chen, L.; Fan, X. Molecular-docking electrolytes enable high-voltage lithium battery chemistries. *Nat. Chem.* **2024**, *16* (9), 1427.

(14) Zhao, C.-X.; Li, Z.; Chen, B.; Chen, F.; Wang, C. Self-adaptive electrolytes for fast-charging batteries. *Nat. Energy* **2025**, *10* (7), 904.

(15) Shigorin, D. N. Infra-red absorption spectra study of H-bonding and of metal-element bonding. *Spectrochim. Acta* **1959**, *14*, 198.

(16) Kollman, P. A.; Liebman, J. F.; Allen, L. C. Lithium bond. *J. Am. Chem. Soc.* **1970**, *92* (5), 1142.

(17) Chen, X.; Bai, Y.-K.; Zhao, C.-Z.; Shen, X.; Zhang, Q. Lithium bonds in lithium batteries. *Angew. Chem., Int. Ed.* **2020**, *59* (28), No. 11192.

(18) Song, X.; Zhang, Y.; Guo, Z.; Wu, S.; Zhao, Y.; Liang, X.; Kim, M.-C.; Kim, H.; Sun, Y.-K. Lithium-bond-based deep eutectic electrolyte solutions for high-temperature lithium metal batteries. *Angew. Chem., Int. Ed.* **2025**, *64*, No. e202511772.

(19) Pizzi, A.; Terraneo, G.; Lo Iacono, C.; Beccaria, R.; Dhaka, A.; Resnati, G. Taxonomy of chemical bondings: Opportunities and challenges. *Angew. Chem., Int. Ed.* **2025**, *64* (27), No. e202506525.

(20) Ou, Y.; Li, C.; Zhou, H.; Zhou, P.; Yan, S.; Hou, W.; Lu, Y.; Ma, X.; Wu, Y.; Wu, S.; Liu, Z.; Chen, X.; Xia, Y.; Zhang, W.; Cao, Q.; Liu, H.; Liu, F.; Song, X.; Zhou, H.; Peng, X.; Feng, J.; Li, K.; Wei, L.; Sun, C.; Zhang, J.; Chen, J.; Liu, K. Supramolecular chemistry for high-performance lithium metal batteries. *CCS Chem.* **2025**, *7* (10), 2864.

(21) Krieg, E.; Bastings, M. M. C.; Besenius, P.; Rybtchinski, B. Supramolecular polymers in aqueous media. *Chem. Rev.* **2016**, *116* (4), 2414.

(22) Ji, H.; Xiang, J.; Li, Y.; Zheng, M.; Yuan, L.; Liao, Y.; Du, L.; Li, Z.; Xie, Z.; Huang, K.; Lin, X.; Xie, Z.; Shen, Y.; Chen, M.; Li, T.; Feng, G.; Sun, Y.; Qie, L.; Li, H.; Zhang, F.; Guo, R.; Feng, X.; Chen, W.; Ai, X.; Lu, J.; Huang, Y. Liquid−liquid interfacial tension stabilized Li-metal batteries. *Nature* **2025**, *643* (8074), 1255.

(23) Peng, J.; Cao, D.; He, Z.; Guo, J.; Hapala, P.; Ma, R.; Cheng, B.; Chen, J.; Xie, W. J.; Li, X.-Z.; Jelínek, P.; Xu, L.-M.; Gao, Y. Q.; Wang, E.-G.; Jiang, Y. The effect of hydration number on the interfacial transport of sodium ions. *Nature* **2018**, *557* (7707), 701.

(24) Gu, B.; Zhang, F. S.; Wang, Z. P.; Zhou, H. Y. The solvation of NaCl in model water with different hydrogen bond strength. *J. Chem. Phys.* **2008**, *129* (18), No. 184505.

(25) Zhang, S.; Li, R.; Deng, T.; Ma, Q.; Hong, X.; Zhang, H.; Zhang, R.; Ding, S.; Wu, Y.; Zhu, H.; Li, M.; Zhang, H.; Lu, D.; Ma, B.; Lv, L.; Li, Y.; Chen, L.; Shen, Y.; Guo, R.; Fan, X. Oscillatory solvation chemistry for a 500 Wh kg^{-1} Li-metal pouch cell. *Nat. Energy* **2024**, *9*, 1285.

(26) Latajka, Z.; Scheiner, S. Ab initio comparison of H bonds and Li bonds. Complexes of LiF, LiCl, HF, and HCl with NH_3. *J. Chem. Phys.* **1984**, *81* (9), 4014.

(27) Sannigrahi, A. B.; Kar, T.; Niyogi, B. G.; Hobza, P.; Schleyer, P. v. R. The lithium bond reexamined. *Chem. Rev.* **1990**, *90* (6), 1061.

(28) Liu, Y.; Peng, B.; Wang, X.; Xie, Y.; Schaefer, H. F., III. The nature of lithium bonding in $C_2H_2Li_2$, C_6Li_6, and lithium halide dimers. *Organometallics.* **2019**, *38* (24), 4708.

(29) Sannigrahi, A. B. The lithium bond. *J. Chem. Educ.* **1986**, *63* (10), 843.

(30) Hou, T.-Z.; Xu, W.-T.; Chen, X.; Peng, H.-J.; Huang, J.-Q.; Zhang, Q. Lithium bond chemistry in lithium−sulfur batteries. *Angew. Chem., Int. Ed.* **2017**, *56* (28), 8178.

(31) Vila, A.; Vila, E.; Mosquera, R. A. Topological characterisation of intermolecular lithium bonding. *Chem. Phys.* **2006**, *326* (2), 401.

(32) Tian, Z.; Hou, L.; Feng, D.; Jiao, Y.; Wu, P. Modulating the coordination environment of lithium bonds for high performance polymer electrolyte batteries. *ACS Nano* **2023**, *17* (4), 3786.

(33) Park, K.; Cho, J. H.; Jang, J.-H.; Yu, B.-C.; De La Hoz, A. T.; Miller, K. M.; Ellison, C. J.; Goodenough, J. B. Trapping lithium polysulfides of a Li−S battery by forming lithium bonds in a polymer matrix. *Energy Environ. Sci.* **2015**, *8* (8), 2389.

(34) You, Q.; Sun, Y.; Wang, F.; Cheng, J.; Tang, F. Decoding the competing effects of dynamic solvation structures on nuclear magnetic resonance chemical shifts of battery electrolytes via machine learning. *J. Am. Chem. Soc.* **2025**, *147* (17), No. 14667.

(35) Yao, N.; Chen, X.; Sun, S.-Y.; Gao, Y.-C.; Yu, L.; Gao, Y.-B.; Li, W.-L.; Zhang, Q. Identifying the lithium bond and lithium ionic bond in electrolytes. *Chem.* **2025**, *11* (1), No. 102254.

(36) Gao, Y.-B.; Li, W.-L.; Chen, X.; Yao, N.; Li, X.-Y.; Gao, Y.-C.; Chen, Y.-P.; Zhang, Q. A universal principle of lithium bond characteristics in lithium battery electrolytes. *Angew. Chem., Int. Ed.* **2026**, *65*, No. e17523.

(37) Licsko, I. Coagulation mechanisms - nano- and microprocesses. *Water Sci. Technol.* **2004**, *50* (12), 193.

(38) Giffin, G. A.; Moretti, A.; Jeong, S.; Passerini, S. Complex nature of ionic coordination in magnesium ionic liquid-based electrolytes: Solvates with mobile Mg^{2+} cations. *J. Phys. Chem. C* **2014**, *118* (19), 9966.

(39) Sawayama, S.; Kondou, S.; Ueno, K.; Fujii, K. Conformational flexibility of solvent molecules enables Li-ion hopping in highly concentrated electrolytes. *J. Phys. Chem. B* **2025**, *129* (31), 7995.

(40) Zhao, Y.; Fang, C.; Zhang, G.; Hubble, D.; Nallapaneni, A.; Zhu, C.; Zhao, Z.; Liu, Z.; Lau, J.; Fu, Y.; Liu, G. A micelle electrolyte enabled by fluorinated ether additives for polysulfide suppression and Li metal stabilization in Li−S battery. *Front. Chem.* **2020**, *8*, 484.

(41) Chen, X.; Bai, Y.-K.; Shen, X.; Peng, H.-J.; Zhang, Q. Sodiophilicity/potassiophilicity chemistry in sodium/potassium metal anodes. *J. Energy Chem.* **2020**, *51*, 1.

(42) Zhang, J.; Chen, P.; Yuan, B.; Ji, W.; Cheng, Z.; Qiu, X. Real-Space Identification of Intermolecular Bonding with Atomic Force Microscopy. *Science* **2013**, *342* (6158), 611.

(43) Mönig, H.; Amirjalayer, S.; Timmer, A.; Hu, Z.; Liu, L.; Díaz Arado, O.; Cnudde, M.; Strassert, C. A.; Ji, W.; Rohlfing, M.; Fuchs, H. Quantitative assessment of intermolecular interactions by atomic force microscopy imaging using copper oxide tips. *Nat. Nanotechnol.* **2018**, *13* (5), 371.

(44) Yang, J.; Dettori, R.; Nunes, J. P. F.; List, N. H.; Biasin, E.; Centurion, M.; Chen, Z.; Cordones, A. A.; Deponte, D. P.; Heinz, T.

F.; Kozina, M. E.; Ledbetter, K.; Lin, M.-F.; Lindenberg, A. M.; Mo, M.; Nilsson, A.; Shen, X.; Wolf, T. J. A.; Donadio, D.; Gaffney, K. J.; Martinez, T. J.; Wang, X. Direct observation of ultrafast hydrogen bond strengthening in liquid water. *Nature* **2021**, *596* (7873), 531.

(45) Zhao, C.-X.; Wang, Z.; Jacobson, D.; Li, Y.; Khaykovich, B.; Fayfar, S.; Zheng, L.; LaManna, J.; Chen, X.; Hussey, D. S.; Chen, F.; Veith, G. M.; Wang, C. Electrolytes that reduce electro-osmotic drag improve fast charging of lithium-ion batteries. *Science* **2025**, *390* (6774), 745.