Molecular Engineering of Electrolyte Solvents for Lithium Metal Batteries: Strategies, Challenges, and Prospects

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Lithium metal batteries hold the promise of transformative advancements in energy storage due to their ultrahigh theoretical energy density, yet their commercialization remains hindered by critical challenges, including uncontrolled lithium dendrite growth and unstable solid electrolyte interphases. Central to overcoming these barriers is the electrolyte engineering, particularly the molecular design of the solvents, which critically governs Li^+ solvation behavior, interfacial stability, and electrochemical performance. Although numerous new solvent molecules have been successively developed, very few can simultaneously achieve high reductive and oxidative stability in order to satisfy the compatibility requirements of lithium metal anodes and the tolerance demands of high-voltage cathodes, while also ensuring safety and environmental friendliness. This concept aims to systematically summarize the advantages and limitations of mainstream molecular modification strategies developed in recent years, and to offer insights for guiding the future design of advanced solvents. Herein, the dominant strategies, including fluorination, nonfluorinated structural adjustment, and heteroatoms incorporation, are comprehensively examined and future directions are proposed that emphasize on ecofriendly solvent synthesis and multifunctional integration. In this article, inspiration is provided for advancing lithium metal batteries via rational solvent design, tackling challenges in both fundamental science and practical applications.

1. Introduction

The relentless pursuit of higher energy density in energy storage systems has positioned lithium metal batteries (LMBs) at the forefront of technological innovation.[1,2] With a theoretical capacity of 3860 mAh g^{-1}, lithium metal anode (LMA) significantly outperforms conventional carbon-based anodes, like graphite (372 mAh g^{-1}), enabling LMBs to theoretically achieve energy densities exceeding 500 Wh kg^{-1} when paired with high-voltage cathodes like LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811).[3,4] However, the highly reactive nature of lithium metal poses formidable challenges that impede practical deployment (**Figure 1**). Uncontrolled lithium deposition can lead to dendritic growth, which may penetrate separators, potentially causing internal short circuits and catastrophic thermal runaway.[5,6] Concurrently, the high reactivity of LMA with electrolyte triggers persistent side reactions, resulting in the formation of a fragile and heterogeneous solid electrolyte interphase (SEI), which is typically enriched in organic components and lacks sufficient mechanical robustness to accommodate the volume changes during cycling, thereby leading to the accumulation of "dead Li" and accelerated capacity fade.[7,8] Therefore, LMBs typically exhibit inferior cycling stability and pose potential safety hazards.[9,10]

Central to surmounting these obstacles is the electrolyte engineering, especially the molecular design of the solvents, which plays a critical role in governing Li^+ solvation behavior, interfacial stability, and electrochemical performance.[11] Nevertheless, traditional solvents in commercial electrolytes for lithium-ion batteries (LIBs) prove inadequate for LMBs. As the cornerstone solvents in LIBs, carbonates, such as ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC), exhibit strong Li^+ solvation capability but suffer from severe reduction on the LMA, leading to the formation of unstable SEI.[12] Ethers, such as 1,2-dimethoxyethane (DME), although exhibiting higher reductive stability, are prone to oxidation at voltages above 4 V, limiting the compatibility with high-voltage cathodes.[13] These limitations underscore the pressing necessity for solvent designs tailored to meet the distinct requirements of LMBs. In general, effective solvent engineering must reconcile multiple criteria: sufficient reductive and oxidative stability to ensure the compatibility with both electrodes, appropriately controlled solvation strength for regulating SEI composition, and thermal resilience to guarantee reliable operation across extreme temperatures.

Recent modification approaches in molecular design can be classified into three primary categories: fluorination to enhance oxidative stability and improve interfacial properties, nonfluorination strategies involving the adjustment of structural parameters, such as chain length and steric hindrance, and synergistic effects achieved through the incorporation of heteroatoms (**Figure 2**). However, the existing reviews predominantly emphasize on macroscopic and holistic electrolyte design while paying insufficient attention to the specific design of solvent molecules. Herein, this concept summarizes recent advancements, providing a comprehensive overview of solvent design principles and their mechanisms of action in LMBs. By bridging molecular innovation with

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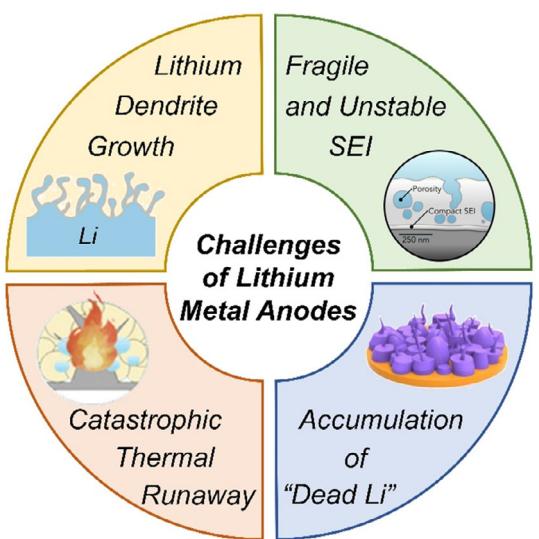
Figure 1. Challenges of LMAs: lithium dendrite growth. Reproduced with permission.[5] Copyright 2017, Springer Nature, catastrophic thermal runaway. Reproduced with permission.[6] Copyright 2025, Wiley, fragile and unstable SEI. Reproduced with permission.[7] Copyright 2023, Elsevier, and accumulation of "dead Li". Reproduced with permission.[8] Copyright 2023, Wiley.

Figure 2. Primary molecular design strategies: fluorination strategy, non-fluorinated structural adjustment, and heteroatoms incorporation.

the practical requirements of LMBs, this concept seeks to provide inspiration for novel electrolyte engineering.

2. Fluorination Strategies for Carbonates and Ethers

The incorporation of fluorine atoms into solvent molecules has emerged as a transformative and innovative approach to enhance the stability of electrolytes and improve interfacial compatibility in LMBs.[14] Fluorination functions via multiple mechanisms: it facilitates preferential defluorination on the LMA to form a LiF-rich SEI, while concurrently reducing the electron density on oxygen atoms through the electron-withdrawing effect to improve oxidative stability. LiF, which is characterized by its high interfacial energy and excellent mechanical strength, plays a crucial role in suppressing dendrite growth and stabilizing the electrode–electrolyte interface in LMBs, thus ensuring long-term cycling stability.[15] Additionally, the reduced molecular forces in fluorinated solvents, stemming from the diminished polarization capability of fluorine, lead to decreased desolvation barrier of Li$^+$, ultimately promoting uniform lithium distribution during the electrodeposition process.[16]

In carbonate solvents, fluoroethylene carbonate (FEC), as a representative fluorinated molecule, is widely adopted owing to its superior film-forming capability. Compared to its nonfluorinated counterpart EC, FEC undergoes earlier reduction due to its lower unoccupied molecular orbital (LUMO) energy level, forming a compact SEI enriched with LiF, which not only improves lithium plating/stripping Coulombic efficiency but also enhances stability under high current densities.[17] Through further fluorination of FEC, the LUMO energy level of difluoroethylene carbonate (DFEC) is further decreased, promoting easier defluorination while simultaneously improving oxidative stability.[18] However, fluorinated cyclic carbonates are intrinsically prone to ring-opening reactions, rendering them inherently unstable as the primary solvent and thereby limiting their application to additive levels (<30%) in the electrolytes.[19] Conversely, fluorinated linear carbonates demonstrate superior stability, rendering them more appropriate as the dominant solvent. For instance, bis(2,2,2-trifluoroethyl) carbonate (BTC) exhibits exceptional thermal stability (−30 to 70 °C) and high-voltage tolerance (4.8 V), as well as a weakly solvating ability attributed to its perfluorinated

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structure.[20] Despite these advantages, the nonpolar nature of BTC leads to its relatively low ionic conductivity (1.67 mS cm^{-1}). To balance solvation capacity and stability, asymmetric fluorination strategies have been developed. Ethyl (2,2,2-trifluoroethyl) carbonate (ETFEC), which features partial fluorination of only one terminal group, achieves an impressive equilibrium: it dissolves 5 M lithium bis(fluorosulfonyl)imide (LiFSI) while maintaining high ionic conductivity and enables stable cycling in Li∥NCM811 cells for over 200 cycles (**Figure 3**).[21]

Ethers, which are inherently reductive-stable but oxidatively vulnerable, benefit from fluorination through reduced electron density on oxygen atoms. The targeted fluorination of ether molecules allows fine-tuning of their solvation properties, thereby enabling tailored design of distinct solvation structures.[22] Strategic incorporation of fluorine atoms within the central part of the main chain in 2,2,3,3-tetrafluoro-1,4-dimethoxybutane (FDMB) broadens its oxidative window while concurrently improving compatibility with LMAs. FDMB-based electrolyte can form an ultrathin SEI (≈6 nm), and the fluorinated backbone additionally suppresses the corrosion at high voltages by forming protective AlF$_3$ layers.[12] Terminal group fluorination, unlike central fluorination, suppresses molecular solvation ability while maintaining the Li$^+$-coordinated chelation framework intact, thereby not compromising the ionic conductivity. Therefore, the terminal fluorinated FnDEE series (n = 3–6) strikes an optimal equilibrium between electrochemical stability and high ionic mobility, sustaining stable polarization during operation and achieving >140 cycles in anode-free pouch cells.[23] By further introducing asymmetric fluorinated structures, the fluorinated 1-ethoxy-2-methoxyethane (FxEME, × = 1–3) effectively resolves the issues of inadequate reversibility at high-rate and sluggish redox kinetics observed in the aforementioned fully-fluorinated ethers, which is achieved by introducing directional dipole moments that significantly enhance charge transfer kinetics and facilitate Li$^+$ desolvation (Figure 3).[24] Despite performance gains in fluorinated linear ethers for LMBs, nonpolar -CF$_3$/-CHF$_2$ groups compromise ionic conductivity, whereas monofluoro (-CH$_2$F) substitutions with localized polarity enhance Li$^+$ solvation and conductivity without sacrificing stability. Hence, a series of

monofluorinated linear ethers exhibit enhanced fast-charging performance.[25–27] Additionally, some fluorinated cyclic ethers have also been designed by introducing exocyclic -CF$_3$ groups, demonstrating weakly solvated ability.[28–30]

Despite its numerous advantages in enhancing solvent properties, fluorination is not without its drawbacks. Fluorination not only elevates the LUMO energy level of the solvents but also concurrently increases the highest occupied molecular orbital (HOMO) energy level, which consequently weakens the reductive stability of the solvents. Upon interaction with LMA, the fluorinated solvents become susceptible to defluorination reactions, leading to their irreversible loss. Besides, the environmental unfriendliness of fluorinated substances has raised significant concerns, particularly with respect to bioaccumulation and toxicity. Furthermore, the complex synthesis of fluorinated solvents escalates production costs, thereby hindering scalability. Therefore, it is of vital importance to develop environmentally friendly fluorine-free solvents with equivalent excellent performance.

3. Nonfluorinated Structural Adjustments

The environmental and economic challenges posed by fluorination have stimulated considerable interest in alternative molecular designs that achieve comparable performance without relying on fluorine. These nonfluorinated strategies often focus on modulating the molecular structure, including intramolecular hybridization, chain length adjustment, modification of weakly solvating characteristics, as well as adoption of glyme structure (**Figure 4**).

By integrating the functional groups of both ethers and carbonates, intramolecular hybridization has emerged as a powerful strategy to combine the reductive stability of ethers with the oxidative resilience of carbonates. Bis(2-methoxyethyl) carbonate (BMC), a linear carbonate containing ether-like alkoxy groups, serves as an illustrative example of this strategy. The electron-donating alkoxy groups decrease the electrophilicity of the carbonyl carbon, thereby improving its reductive stability. BMC-based electrolytes enable Li∥NCM811 cells to achieve a high
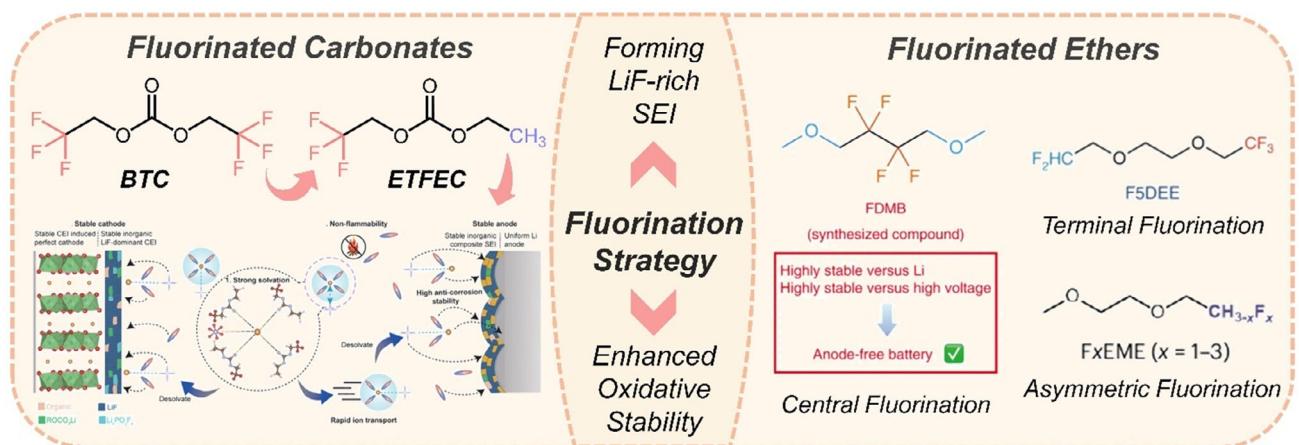

Figure 3. Fluorinated carbonates and ethers. Reproduced with permission.[12,21,23,24] Copyright 2024, Wiley; Copyright 2020, Springer Nature; Copyright 2022, Springer Nature; Copyright 2025, Springer Nature.
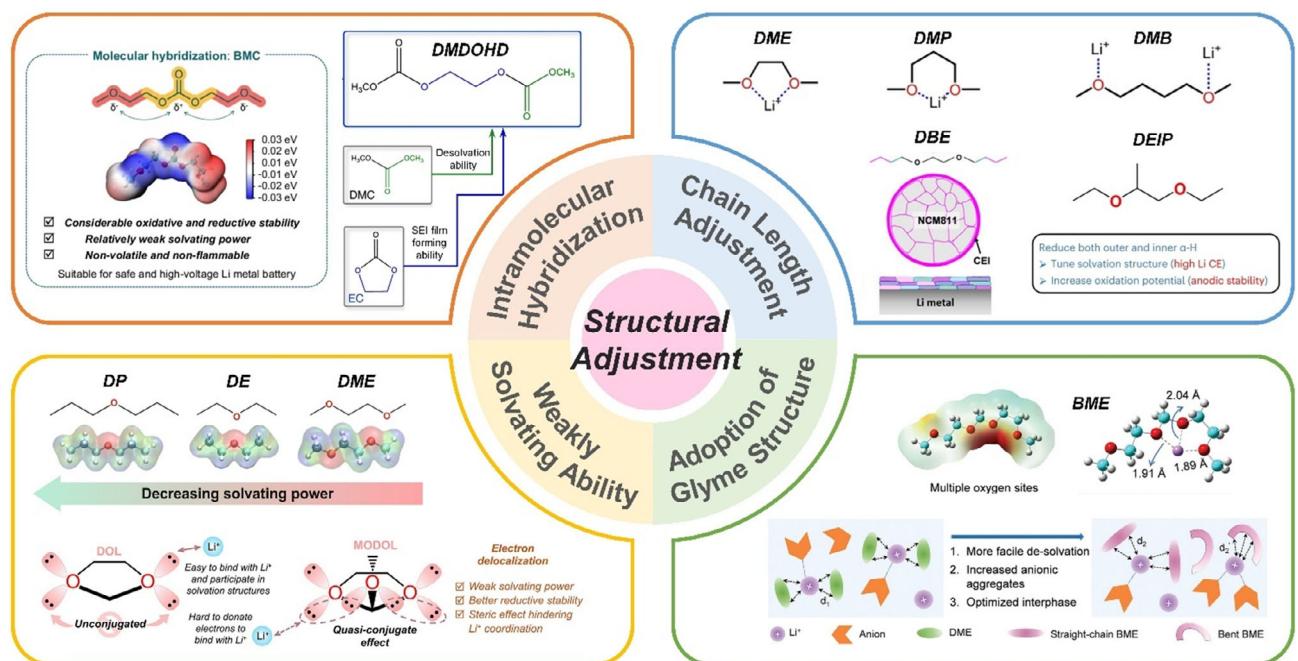
Figure 4. Nonfluorinated structural adjustment strategy. Reproduced with permission.[31–33,36,37,39–41] Copyright 2024, Springer Nature; Copyright 2024, Springer Nature; Copyright 2023, Wiley; Copyright 2023, Wiley; Copyright 2024, Springer Nature; Copyright 2023, Springer Nature; Copyright 2025, Wiley; Copyright 2023, Wiley.

capacity retention of 92% after 150 cycles, outperforming the conventional approach of physically mixing carbonates and ethers.[31] Similarly, dimethyl 2,5-dioxahexanedioate (DMDOHD), integrating EC and DMC features, elongates the molecular chain to enhance steric hindrance, which reduces solvent decomposition and enables Li||LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO) cells to retain 94% capacity after 200 cycles.[32] These hybrid architectures exemplify how structural innovation can effectively circumvent the limitations of traditional solvents.

Systematic modification of ether solvents through backbone engineering substantially affects the Li$^+$ solvation structure and electrochemical stability. Carbon chain elongation modulates the size of the chelate ring and the coordination strength. For instance, 1,3-dimethoxypropane (DMP) forms a six-membered Li$^+$ chelate ring with enhanced solvation stability compared to the five-membered ring formed in DME, effectively enhancing the high-voltage stability while promoting LiF-rich interphase formation on cathode through preferred hydrogen transfer reaction.[33] However, excessive chain extension (1,4-dimethoxybutane, DMB) reduces coordination stability, inducing a monodentate binding mode and lower oxidative resistance. Notably, strong Li$^+$-solvent binding in DMP compromises the interfacial stability, necessitating high-concentration electrolytes to improve SEI quality. Central chain shortening and terminal group extending can weaken the solvation capability by disrupting the chelate coordination structure and increasing steric hindrance, respectively. Dimethoxymethane (DMM) adopts a [gauche, gauche] conformation as a result of hyperconjugation effects, enabling monodentate coordination with Li$^+$ and reducing the desolvation energy.[34] Extending terminal alkyl chains enhances steric hindrance, forming contact ion pairs/aggregates-dominated solvation structures at standard salt

concentrations. Thus, 1,2-diethoxyethane (DEE) and 1,2-dibutoxyethan (DBE) can form inorganic-rich SEI, along with enhanced low-temperature performance.[35] Moreover, DBE exhibits elevated boiling point (203.3 °C) and enhanced thermal stability, while mitigating the catalytic reactivity between NCM811 and the electrolyte at high voltages through diminished solvation strength.[36] Excepting from chain length adjustment, introducing branched chains through selective methylation of DME's α-H atoms reduces solvation power and precisely modulates ionic transport.[37]

Apart from the regulation of chain length, reducing the number of oxygen atoms in ether molecules can also weaken the coordination ability of solvent molecules by disrupting the chelate coordination, thereby optimizing the solvation structure. As a representative monoxy ether, diethyl ether (DE) exhibits exceptionally low solvation strength, enabling efficient Li$^+$ desolvation kinetics even at ultralow temperatures (−60 °C).[38] Structural extension of DE's terminal alkyl groups (dipropyl ether, DP) further diminishes solvation capacity while concurrently improving oxidative stability. Molecular dynamics analyzes indicate that DP reduces ether molecule density within the electrochemical double layer, thereby limiting direct solvent oxidation at the cathode interface while simultaneously retaining ion aggregation tendencies. Therefore, this synergistic modulation of electrochemical double layer structure enhances the high-voltage compatibility of DP-based electrolyte.[39] Aside from reducing oxygen atoms, taking advantages of unique molecular spatial configuration can also achieve weakly solvating ability of the solvent. Through a distinguished quasi-conjugated effect between the nonbonding hybrid orbitals of the exocyclic and the endocyclic oxygen, 2-methoxy-1,3-dioxolane (MODOL) is endowed with limited solvating power, facilitating the formation of optimized

SEI.[40] In addition to these weakly solvating ethers, a series of glyme ethers containing more glycol units can significantly suppress pernicious side reactions through reducing the lifetime of labile molecules owing to their stronger Li$^+$ solvating capability, demonstrating exceptional electro-oxidation resistance and thermal stability.[41–43]

4. Incorporation of Heteroatoms

Although many new types of carbonate and ether solvents with excellent properties can be obtained through molecular structure design, they still have unavoidable shortcomings, which requires the employment of additional strategies, such as introducing additives and increasing the salt concentration, to achieve the construction of high-performance electrolytes. Beyond carbonates and ethers, solvents incorporating heteroatoms have garnered significant attention due to their unique physicochemical properties arising from distinct functional groups, which offer innovative solutions to long-standing challenges in LMBs (**Figure 5**). The advantages and limitations of various solvent molecules are summarized in **Table 1**.

Nitrogenous molecules, including nitriles, amides, and carbamates, have demonstrated favorable compatibility in LMBs. In nitrile solvents, the cyano group possesses high bond energy, which facilitate the restriction of unbonded electrons and endows the solvent with outstanding oxidative stability.[44] By leveraging its electron-withdrawing effect, introducing cyano groups in place of fluorine atoms can achieve similar effects of enhancing the high-voltage tolerance in ether molecules without significantly reducing the solvating power due to the relatively high dielectric constant.[45] Besides, the cyano group and ether oxygen synergistically establish a chelating coordination with Li$^+$, promoting lithium salt dissociation efficiency, and the reduction of cyano group concurrently yields nitrogen-rich SEI, facilitating rapid Li$^+$ transport.[46,47] Amide and carbamate solvents demonstrate advantages in nonflammability owing to the generation of NCO· radicals at high temperatures, which can terminate the chain propagation reactions and thereby inhibit combustion.[48] Simultaneously, the nitrogen atoms enables electrochemical reduction of amides/carbamates into Li–N species with elevated Li$^+$ conductivity, effectively curbing interfacial resistance buildup during cycling.[49] However, due to the inferior reductive stability, amides and carbamates are difficult to be adopted as single solvents.[50,51]

Sulfamide solvents, inspired by the molecular architecture of lithium salts, like LiFSI and lithium bis(trifluoromethanesulfonyl)-imide (LiTFSI), feature a unique fluoro sulfamide group, which can enhance the dispersion of negative charges, exhibiting excellent thermostability and ensuring high ionic conductivity.[52]
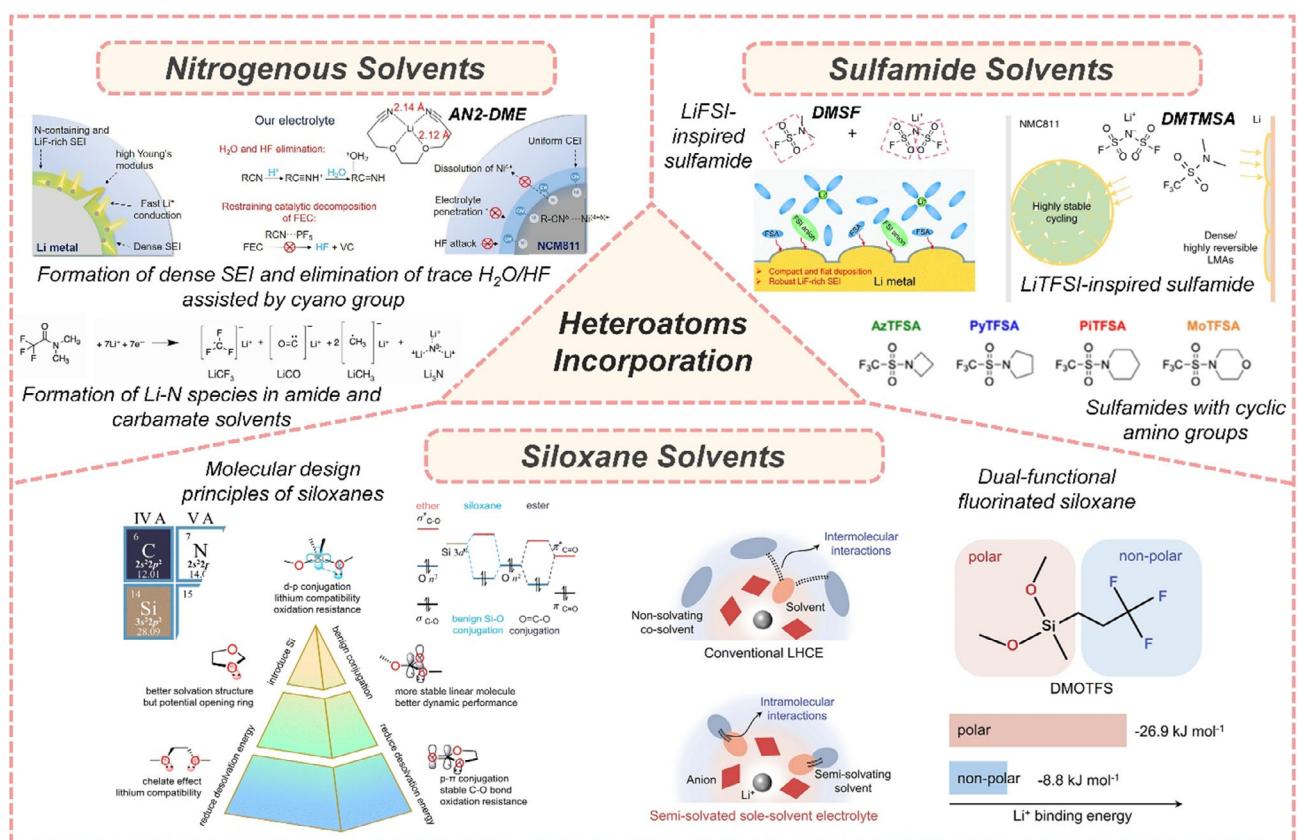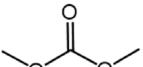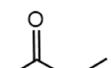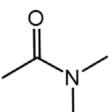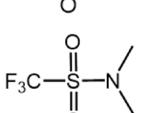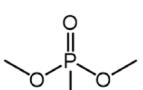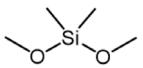

Figure 5. Heteroatoms incorporation strategy. Reproduced with permission.[46,50,53–56,58] Copyright 2024, National Academy of Sciences; Copyright 2020, Springer Nature; Copyright 2020, The Royal Society of Chemistry; Copyright 2021, Springer Nature; Copyright 2025, American Chemical Society; Copyright 2022, The Royal Society of Chemistry; Copyright 2023, American Chemical Society.

Table 1. Characteristics of various solvent molecules.

Solvent type	Functional group	Advantages	Limitations
Ethers	(structure)	Superior compatibility with LMA; Low viscosity; High ionic conductivity	Limited oxidative stability; Strong solvation energy; Low dielectric constants
Carbonates	(structure)	High oxidative stability	Incompatibility with LMA
Carboxylates	(structure)	Lower melting points; Improved electrochemical kinetics	Uneven organic-rich SEI
Nitriles	$-C \equiv N$	High-voltage resistance; High dielectric constants	Poor reductive stability
Amides	(structure)	Nonflammability	Poor reductive stability
Sulfones	(structure)	High oxidative stability; Improved thermal stability	High viscosity; Poor SEI formation
Sulfamides	F_3C (structure)	Excellent film-forming ability	Complex synthetic process
Phosphates	(structure)	Nonflammability	Incompatibility with LMA
Siloxanes	(structure)	High oxidative stability; Excellent compatibility with LMA	Relatively high freezing point

N,N-dimethylsulfamoyl fluoride (DMSF), structurally analogous to LiFSI, is more conducive to form LiF-rich SEI compared to FEC, enabling dense lithium deposition.[53] Similarly, N,N-dimethyltrifluoromethane-sulfonamide (DMTMSA), which exhibits structural similarity to LiTFSI, can effectively inhibit transition-metal dissolution and stress-corrosion cracking while ensuring highly reversible lithium plating/stripping.[54] By replacing the dimethylamino group with cyclic amino groups, more sulfamides have been developed, demonstrating optimized solvation structure and SEI through modulating the electronic and steric properties.[55]

Siloxanes, characterized by Si—O bonds with d-p conjugation, demonstrate exceptional oxidative stability surpassing ethers. The conjugation between the 3d orbitals of silicon and the 2p orbitals of oxygen occupied by the lone pair electrons lowers HOMO energy, granting oxidation resistance up to 5 V. The conjugation effect additionally confers Si—O bonds with a higher force constant compared with C—O bonds, indicative of enhanced chemical stability of siloxanes.[56] As a prototypical siloxane, dimethyl dimethoxy silane (DMMS) can form a silicon-rich organic SEI which balances flexibility and mechanical strength and possesses rapid ion transport kinetics, enabling Li||NCM811 cells to operate at extreme temperatures ($-114\,°C$).[57] By further fluorination, the oxidative stability of siloxanes are ulteriorly enhanced, along with modified solvation structure. As a dual-function solvent,

3,3,3-trifluoropropyl methyl dimethoxy silane (DMOTFS) combines solvating and nonsolvating moieties within its molecular structure, mimicking localized high-concentration electrolyte (LHCE) solvation structures at moderate salt concentrations. Additionally, DMOTFS can enhance the decomposition of LiFSI and form a passivation layer on the $LiCoO_2$ (LCO) cathode through sacrificial release of F atoms, thereby enabling outstanding cycling performance of LMBs.[58,59] The unique property of siloxanes that combines both oxidative and reductive stability positions them as frontrunners in the quest for novel solvents for LMBs.

5. Summary and Outlook

This concept provides a comprehensive summary of the mainstream strategies for solvent design in LMBs, including fluorination, nonfluorinated structural adjustment, and incorporation of heteroatoms. The molecular design of electrolyte solvents has significantly advanced the practical viability of LMBs, yet substantial challenges persist. Fluorination, although effective in improving the quality of the SEI and enhancing oxidative stability, encounters significant economic and environmental challenges. Nonfluorinated structural adjustment strategies, including intramolecular hybridization, chain length adjustment, modification of weakly solvating characteristics, and adoption of glyme structure,

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provide sustainable alternatives but often necessitate support of additives or advanced electrolyte formulations, like LHCEs, to achieve optimal performance. Emerging solvents containing heteroatoms, such as sulfonamides and siloxanes, bring about innovative options while still require further optimization for industrial scalability. Consequently, sustained research remains imperative to overcome these limitations, necessitating the deliberate integration of the following molecular design principles. 1) While fluorination enhances oxidative stability and interfacial properties, its high cost and environmental impact necessitate exploring nonfluorinated alternatives leveraging steric effects or multifunctional group synergies. However, most solvents fail to concurrently achieve reductive and oxidative stability. Siloxanes, benefiting from Si—O bond conjugation, uniquely exhibit dual stability and emerges as promising candidates for next-generation solvents, necessitating further exploration for practical application; 2) Molecular modifications enhance cycling stability and wide-temperature performance. However, solvents that can simultaneously ensure safety are still scarce. Extending chain lengths to raise flash points or integrating flame-retardant groups, like phosphate groups, may effectively address this gap; 3) Machine learning enables efficient batch screening via theoretical simulations, accelerating solvent optimization by predicting physicochemical properties, which should be fully utilized for solvent design; 4) Standardized testing protocols and lifecycle assessments are critical to ensure that advancements in solvent design translate into commercially viable, sustainable technologies.

In conclusion, by addressing cost, safety, and performance holistically, advanced solvent designs will unlock the full potential of LMBs. The strategic integration of fluorinated and nonfluorinated approaches, coupled with the exploration of novel heteroatom systems, will define the future of electrolyte engineering.

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Conflict of Interest

The authors declare no conflict of interest.

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