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Recent progress in ether-based electrolytes for high-voltage lithium metal batteries

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Abstract: Ether-based solvents generally show better affinity for lithium metal, and thus ether-based electrolytes (EBEs) are more inclined to form a uniform and thin solid electrolyte interface (SEI), ensuring the long cycle stability of the lithium metal batteries (LMBs). Nonetheless, EBEs still face the challenge of oxidative decomposition under high voltage, which will corrode the structure of cathodes, destroy the stability of the electrode−electrolyte interface, and even cause safety risks. Herein, the types and challenges of EBEs are reviewed, the strategies for improving the high voltage stability of EBEs and constructing stable electrode−electrolyte interfaces are discussed in detail. Finally, the future perspectives and potential directions for composition optimization of EBEs and electrolyte−electrode interface regulation of high-voltage LMBs are explored.

Key words: ether-based electrolyte; lithium metal batteries; high voltage; solvation structure; electrode−electrolyte interfaces

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1 Introduction

Due to the escalating demand for high energy density storage devices, lithium-ion batteries (LIBs) employing carbon/silicon based materials as anodes and high-voltage layered materials as cathodes (>4.2 V vs Li/Li^+) are no longer adequate for certain applications owing to their relatively limited energy density [1−3]. Recently, lithium metal anode (LMA), with a higher theoretical specific capacity of 3862 mA·h/g and lower electrochemical potential (−3.040 V compared to standard hydrogen electrodes), have attracted considerable attention and is considered the most promising anode for high energy density LIBs [4−6]. However, compared to carbon/silicon based anodes, LMA with high reactivity places higher demands on the electrolyte composition. Conventional carbonate solvents, including cyclic and linear carbonate blends, exhibit remarkable capability in forming a solid electrolyte interfaces (SEI) layer with exceptional stability on the surface of carbon/silicon based anodes. Usually, this stable SEI can not only serve as both an electron insulator and a conduit for lithium ion transport, but also effectively impede the further reactions between the anode and electrolyte and prevent the co-intercalation of solvent molecules into the anodes, thereby significantly enhancing the cycle life of LIBs [7,8]. The carbonate-based electrolyte, however, exhibits enhanced reactivity towards the LMA in comparison to the other anodes, resulting in diminished coulombic efficiency (CE), severe capacity attenuation, and safety hazards [9−11]. Typically, carbonate electrolytes are prone to form unstable SEI rich in organic species on the LMA surface, which will continuously dissolve and

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reconstruct during cycling, ultimately presenting an uneven and porous morphology. In addition, the non-uniform and porous SEIs will induce uneven deposition/exfoliation of lithium and ultimately promotes dendrite growth and "dead lithium" formation on the anode surface, posing a significant threat to both safety performance and lifespan of lithium metal batteries. In this regard, electrolyte chemistry is one of the main strategies for achieving efficient application of lithium metal batteries. Among various potential electrolyte systems for LMBs (including carbonate-based electrolytes [12−14], ether-based electrolytes (EBEs) [15−18], ionic liquids [19−21], inorganic and polymer solid electrolytes [22−25] etc.), ether-based electrolytes with better reduction stability exhibit stronger affinity for LMA, and display more prominent advantages in enhancing the interface stability and inhibiting lithium dendrite growth, thereby ensuring that LMBs show sustained high CE and cycling stability [26,27].

Numerous previous works have demonstrated the mechanism of action of electrolytes (including EBEs), that is, the EBEs will exert a direct influence on electrochemical performance through their inherent physicochemical properties and participation in electrochemical reactions, as well as an indirect impact through their participation in the formation of SEI and cathode electrolyte interface (CEI) [8].

Specifically, first, the ion conductivity of the electrolyte determines the ion transport capacity and kinetic performance within the batteries, while electrochemical stability limits the operating voltage window and energy density of the batteries. Second, the molecular spatial configuration of solvent molecules, the concentration of lithium salts, and the solvation structure will determine the operating voltage range of the electrolyte and the reversibility of lithium ions. In addition, the composition and solvation structure of the electrolytes directly affect the composition and chemical stability of CEI/SEI, and the interfacial reaction activity of the cells, thereby indirectly determining the electrochemical performance of the batteries.

In this review, we first outline the basic classification, chemical composition, and action mechanism of EBEs, as well as the key challenges they have faced so far. In summary, the stability of the CEI and SEI formed during the electrochemical reaction process largely determines the electrochemical performance of the batteries. Therefore, regulating the electrolyte composition and solvation structure to regulate interface stability is one of the important strategies to achieve high-performance LMBs. Subsequently, we delved into and proposed the most reliable electrolyte component optimization and solvation structure regulation strategies studied to date, and thus to maximize the cycle life and coulombic efficiency of LMBs. Finally, this review reveals and emphasizes the compatibility mechanism of the electrode−electrolyte interface reactions, summarizes and outlines potential optimization solutions, which should be of extensive interest to a broad audience working on rechargeable batteries.

2 Categorization of ether electrolytes

2.1 Typical ether electrolytes

Ether-based electrolytes typically consist of linear and cyclic ethers. Cyclic ethers, such as 1,3-dioxlane (DOL), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MeTHF), show higher chemical stability and better film-forming ability due to the cyclic molecular structure. In LMBs, the cyclic ether can form a dense and stable SEI on the surface of lithium metal. This SEI can not only effectively prevent the growth of lithium dendrites, but also improve the cycle life and safety of the batteries. However, the use of cyclic ethers in LIBs is limited due to their high chemical reactivity with LMA. Linear ethers, such as dimethoxyethane (DME), diethylene glycol dimethyl ether (DEGDME), triethylene glycol monomethyl ether (TrEGDME), tetraethylene glycol dimethyl ether (TEGDME) and 1,2-diethoxyethane (DEE), exhibit lower viscosity and higher ionic conductivity, and can effectively facilitate the transport of lithium ions. However, TrEGDME exhibits poor battery performance and is therefore utilized sparingly [8]. However, most of linear ethers can react with lithium metal to form a stable SEI, thus preventing the direct contact between lithium metal and electrolyte, thereby reducing the occurrence of side reactions. However, the use of linear ethers in LIBs is limited due to their poor chemical stability under high voltage. In conclusion, linear ethers and cyclic ethers mixed electrolyte are extensively employed in traditional ether-based electrolytes. In terms of lithium salts, common options for ether-based electrolytes include lithium hexafluorophosphate ($LiPF_6$), lithium difluoro(oxalato)borate (LiDFOB), lithium bis(fluorosulfonyl)imide (LiFSI), etc. with standard salt concentration of 1 mol/L [28]. Nevertheless, this dilute concentration (1 mol/L) ether-based solvents demonstrate relatively low oxidative electrochemical stability (<4.0 V), posing challenges in matching high-voltage cathodes with various anode materials and hindering the achievement of high energy density batteries [29].

2.2 High concentration electrolytes or local high concentration ether-based electrolytes

The solvation structure of electrolytes can be divided into three distinct categories: solvent-separated ion pair (SSIP), contact ion pair (CIP), and aggregated ions (AGG), which are typically significantly influenced by the solvent molecular and salt concentration [30,31]. During the process of lithium deposition, the Li^+ ions along with coordination solvent molecules and anions aggregate on the surface of LMA. Subsequently, they will be reduced and decomposed to form a SEI layer. The formation of CIP and AGG solvation structure reduces the LUMO level of anion, and therefore the anion decomposites preferentially than the solvent and forms anion-derived inorganic SEI [32,33]. Therefore, one of the effective and intuitive strategies for regulating a stable electrode−electrolyte interface is to increase the concentration of CIPs and AGGs in the electrolyte, that is, to maximize the salt-to-solvent ratio, thereby accelerating the formation of anion-derived inorganic SEI to promote ion migration and improve CE [34].

High concentration electrolytes (HCEs) exhibit exceptional compatibility with the high-voltage cathodes and LMAs due to their distinctive salt-encapsulated-solvent structure. In this system, anions dominate in the solvated sheath of Li^+ ions, and the reduction between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy induced by solvent molecule coordination promotes the selective decomposition of anions at lower potentials, facilitating the formation of inorganic SEIs derived from anions to enhance charge efficiency [34,35]. Additionally, the formation of a robust CEI layer on the cathode can effectively mitigate the oxidative degradation of electrolyte components. However, despite its advantageous properties, such as superior compatibility and enhanced CEI formation capabilities, HCE faces challenges associated with its high cost as well as elevated viscosity and limited ion mobility number that lead to increased overpotential and compromised rate performance during cell cycling.

Furthermore, the recent studies propose that local high concentration electrolytes (LHCEs), consisting of non-coordinating diluents and strongly coordinating solvents, can address the aforementioned limitations of HCEs by facilitating electrolytes with elevated concentrations of CIPs and AGGs clusters while maintaining low salt concentrations [36]. In this context, LHCEs have been further investigated through the incorporation of various highly fluorinated hydrofluoric ethers (HFEs) and fluoride benzenes (such as benzotrifluoride and 1,2-difluorobenzene) as the inert diluents [37−40]. These LHCEs demonstrate excellent anode stability and retain a solvation structure akin to that observed in HCEs at reduced salt concentrations as well as effectiveness in stabilizing SEI.

2.3 Fluorinated ether-based electrolytes

Reports on the utilization of fluorinated ethers as solvents and their advantageous effectiveness in solvating Li^+ ions are extremely scarce [41,42]. The high-voltage fluorinated ethers were designed to effectively combine the exceptional redox stability of fluoroethers with the Li^+ solvation ability of ether-based electrolytes and superior ionic conductivity, while simultaneously preserving the salt solvation cluster in the solvent at typical salt concentrations. A direct approach involves covalently linking the fluorinated and ether segments to integrate all desirable properties of the electrolyte into a single molecule. The spatial arrangement of these functional groups and availability of Li^+ binding sites play crucial roles in governing ionic conductivity, solvation ability, and redox stability [43]. Although fluorinated ether solvents enhance the oxidative stability of electrolytes, they compromise Li^+ solvation ability to some extent. Therefore, rational molecular design of solvents is imperative for achieving both high redox stability and excellent ionic conductivity.

2.4 Weakly solvated ether-based electrolytes

Extensive research has been conducted on weakly coordinating solvents (WCSs) as potential alternatives to HCEs and LHCEs. The introduction of WCSs can regulate the solvation structure of electrolytes and form CIPs and AGGs within electrolytes, leading to the formation of stable SEI layers enriched with inorganic components [44−47]. The solvation capacity of solvent molecules can be roughly estimated based on its dipole moment and dielectric constant, which are typically correlated. These electrostatic factors also serve as representative indicators of the ability for a solvent to stabilize charged ions [48,49]. Lower values of these parameters indicate weaker solvation forces that drive the formation of solvation structures enriched with additional CIP and AGG species in electrolytes. In this context, various low-dielectric-constant solvents have been proposed and demonstrated their effectiveness in lithium metal batteries [50].

Table 1 lists the reaction mechanism, electrochemical window, solvation behavior and SEI formation characteristics of four ether electrolytes.

3 Challenges encountered in ether-based electrolyte systems

3.1 Oxidation stability

Electrolyte systems with low salt-to-solvent ratios (SSRs, <1:2, molar ratios), which contain a substantial number of non-coordinated solvent molecules, usually present significant challenges in achieving elevated oxidative stability and optimal electrode interfacial compatibility, particularly in LMBs. To ensure enduring cycling performance in LMBs, it is imperative to construct an electrochemically robust interfacial layer between the electrolyte and electrode [51,52]. The lower the energy level of HOMO, the greater the difficulty in electron loss, resulting in higher oxidative stability for the molecule. Conversely, a higher energy level of LUMO leads to increased difficulty in electron gain and thus enhances the reduction stability [53]. As shown in Fig. 1, compared to carbonate-based electrolytes, ether-based electrolytes exhibit higher LUMO energy levels, resulting in improved reduction stability [8]. Additionally, ether-based electrolytes demonstrate excellent compatibility with LMAs, easily forming a more robust SEI layer on the surface of LMAs to promote uniform deposition/stripping of Li^+ and maintain sustained high coulombic efficiency [54,55]. However, due to safety concerns and limitations imposed by the oxidative decomposition of ether solvent molecules under high-voltage, the operating voltage window of electrolytes composed of them is usually restricted (<4.0 V) and their practical application in high-voltage LMBs is limited [56,57].

3.2 Electrode−electrolyte compatibility

The interfacial chemistry between electrode and electrolyte is primarily determined by the solvation structure of the electrolyte, which relies on competitive coordination among solvent molecules, anionic ligands, and Li^+ ions through the ion−dipole or ion−ion interactions [58,59]. Although dipole interactions are negligible at room temperature, they cannot be disregarded at lower temperatures. Nowadays, in mainstream ether electrolytes (with typical lithium salt concentration of 1 mol/L), solvation structure of Li^+ is typically coordinated with several solvent molecules while

Table 1 Reaction mechanism, electrochemical window, solvation behavior and SEI formation characteristics of four ether electrolytes

Classification of ether electrolytes	Reaction mechanism	Electrochemical window	Solvation behavior	SEI formation characteristics
Typical ether electrolyte	Good reduction stability and poor oxidation stability	Low	More free solvents	Solvent dominant
HCEs or LHCEs ether-based electrolyte	More CIPs and AGGs meanwhile reduced free solvents	High	Less free solvents, more CIPs and AGGs	Anion dominant
Fluorinated ether-based electrolyte	Preferentially reduced to form LiF-rich SEI	High	More fluorinated ether	Fluorinated solvent dominant
Weakly solvated ether-based electrolyte	Weak coordination of Li^+ with solvents	Better	More CIPs and AGGs	Anion dominant

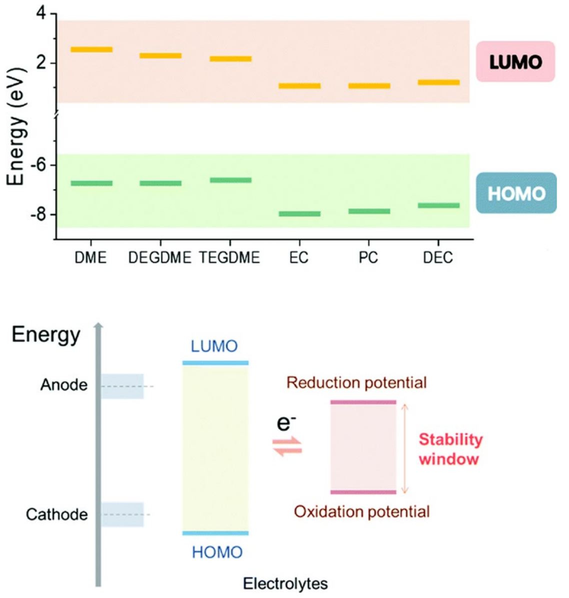

Fig. 1 Ether-based electrolyte exhibiting higher LUMO energy level and greater anode stability for LMA in comparison to carbonate-based electrolyte and higher HOMO energy level and lower stability against high-voltage oxidation (Reproduced with permission [8], Copyright 2022, Royal Society of Chemistry)

the anion remains uncoordinated [60,61]. The solvation structure mentioned above would result in chemically unstable and mechanically weak SEIs. In general, an SEI rich in inorganic substances promotes lithium ion migration, effectively suppresses side reactions between electrodes and electrolyte, and exhibits favorable mechanical properties. To achieve a dense and uniform SEI that is abundant in inorganic substances, one approach is to increase the SSRs, such as by employing HCEs or LHCEs [62−64]. Another approach involves identifying a solvent with weak solvation ability, where the anion demonstrates stronger coordination than the solvent molecule and thus becomes incorporated into the Li^+ solvation structure [65,66]. Therefore, it is crucial to design advanced ether-based electrolyte systems rationally that can strike a balance between LMA compatibility and high-voltage cathodes compatibility.

4 Solution strategy for high-voltage ether-based electrolyte system

4.1 Modified solvent molecular structure

Although there exists a certain research foundation for various electrolytes, it remains crucial to minimize the amount of lithium salt while ensuring high energy density and ionic conductivity, as well as achieving compatibility between electrolyte and high-voltage cathode. The incorporation of electron-withdrawing groups onto solvent molecules holds significant practical implications in advancing electrolyte systems. By introducing electron-withdrawing or spatial groups on solvent molecules, the coordination sites for Li^+ solvation can be reduced, thereby facilitating effective coordination between Li^+ and anions within the solvation structure to form an anion-derived electrode−electrolyte interface layer and enhance the electrochemical stability [67,68].

As shown in Fig. 2, ZHOU et al [69] investigated a unique integrated cyclic chain approach that utilizes commercial ether triethyl orthoformate (TOF) as a single solvent to combine with 2-ethoxy-4-(trifluoromethyl)-1,3-dioxolane (cFTOF) as an electrolyte for advanced high-voltage LMBs through low-cost molecular engineering. This molecular combination exhibits favorable anode stability and the ability to regulate Li^+ solvation. In the low salt concentration electrolyte system, the introduction of the electron-withdrawing group —CF_3 asymmetrically reduces electron density on the —O—, facilitating Li^+ coordination with FSI^-. Consequently, the Li^+ transfer number is increased and uniform and dense

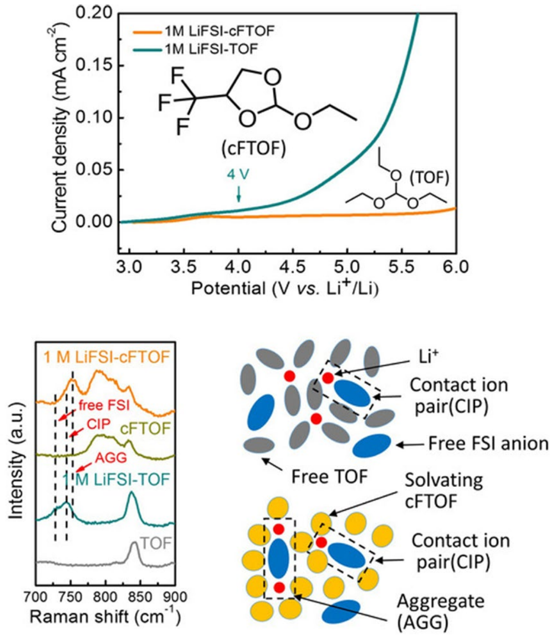

Fig. 2 LSV curves and solvation structures of various electrolyte systems (Reproduced with permission [69], Copyright 2022, Wiley)

LiF-rich SEI is formed. And the full cell assembled using 1 mol/L LiFSI-cFTOF demonstrates a capacity retention of 94% after 100 cycles.

In addition to the unique integrated chain method described above, as shown in Fig. 3, ZHAO et al [43] discovered that the combination of cyclic fluorinated ethers with linear ether segments led to the synthesis of a novel fluorinated ether, namely 2,2-dimethoxy-4-(trifluoromethyl)-1,3-dioxolane ether (DTDL). The incorporation of an electron-withdrawing group ($—CF_3$) significantly enhanced the oxidative stability at high voltages for this compound. However, in order to maintain Li^+ solvation ability, adjustments were made to the spatial arrangement of $—CF_3$ to prevent direct attachment of fluorinated carbon atoms to —O— atoms as observed in other fluorinated ethers like bis(2,2,2-trifluoroethyl) ether (BTFE), 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE). This distinctive solvation structure effectively enhances the oxidation stability of electrolyte up to 5.5 V, and achieves stable SEIs rich in inorganic species and high lithium ion migration numbers (0.75). As a result, the Li||Cu half-cell using 1 mol/L LiFSI-DTDL electrolyte demonstrates an impressive average CE of 99.2% after 500 cycles. And the full cell assembly employing 2 mol/L LiFSI-DTDL electrolyte with $Li||LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811) configuration exhibits a capacity retention rate of 84% after 200 cycles at 0.5*C*.

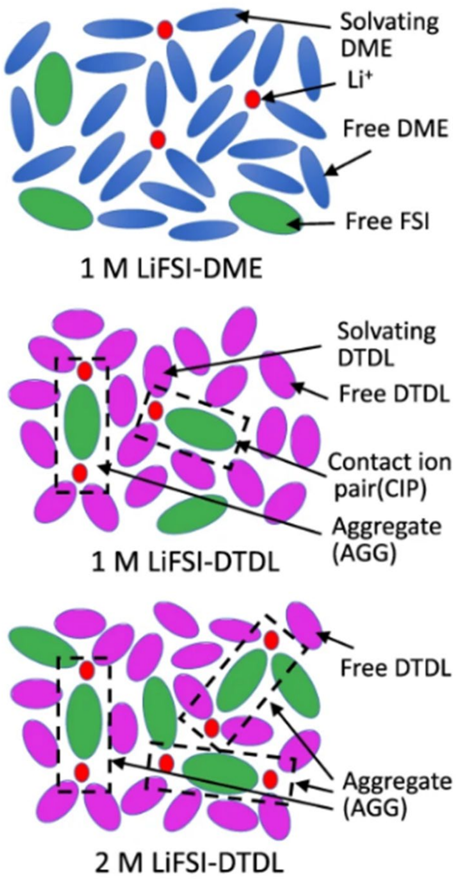

Fig. 3 Schematic diagrams of Li^+ coordination structures in different electrolytes (Reproduced witch permission [43], Copyright 2022, Nature Publishing Group)

As shown in Fig. 4, TAN et al [70] studied a novel chloroether, 1,2-di(2-chloroethoxy)-ethyl ether (Cl-DEE), which replaces the conventional DEE molecule with chlorine. The incorporation of the chlorine functional group significantly elevated the flash point of DEE from 35 to 126 °C, resulting in distinctive flame retardancy properties while maintaining excellent solubility for lithium salts. In response, the LHCE composed of LiFSI/1.6Cl-DEE/3TTE (molar ratio) exhibits homogeneous lithium deposition and stripping behavior. The Li||NMC811 full cell demonstrates an outstanding capacity retention rate exceeding 88% after 200 cycles at 4.6 V, with potential for continued stable cycling even up to 4.7 V.

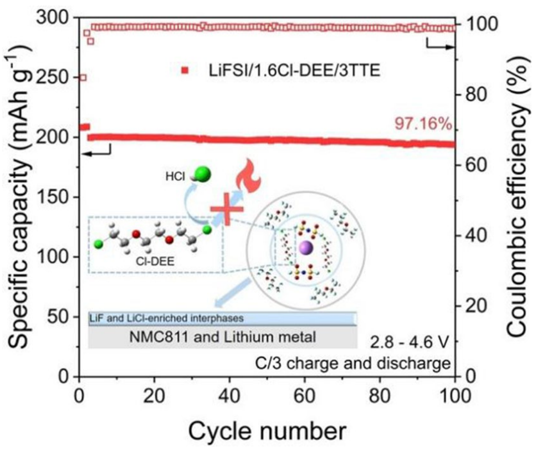

Fig. 4 Electrolyte of LiFSI/1.6Cl-DEE/3TTE with chlorinated-DEE as base solvent (Reproduced with permission [70], Copyright 2022, Wiley)

As shown in Fig. 5, RUAN et al [71] explored a monofluoro solvent, 1,2-bis(2-fluoroethoxy)ethyl ether (FDEE), which demonstrates enhanced oxidative stability while maintaining salt solubility due to the single F substitution. In comparison to conventional anion-dominated solvation systems, the highly polar monofluoro $—CH_2F$ group of FDEE exhibits strong interaction with Li^+ in similar solvents, significantly improving the solvation structure of electrolyte and effectively enhancing its ionic conductivity, interfacial charge migration kinetics, and interfacial stability. The utilization of FDEE as a solvent simultaneously modulates the reaction on both electrode surfaces to form a robust and highly conductive interface layer. Consequently, the FDEE-based LHCE displays substantially improved ionic conductivity (twice that of ClDEE), enabling rapid charging at a rate of 10 mA/cm^2. Furthermore, it demonstrates exceptional cycling stability with a CE of 99.4% after 350 cycles in assembled Li||Cu half-cells, remarkable high-voltage stability up to 4.7 V, and excellent flame retardancy.

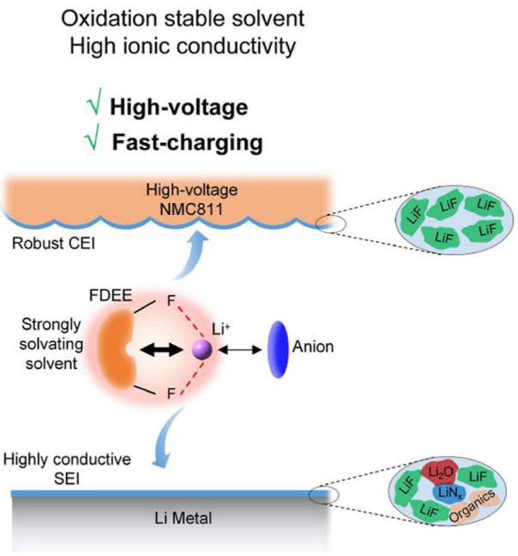

Fig. 5 Solvent chemistry in tailoring electrochemical interphases for high-voltage and fast-charging LMBs (Reproduced with permission [71], Copyright 2023, American Chemical Society)

4.2 Synergy of multiple lithium salt systems

As previously mentioned, the regulation of both CEIs and SEIs is one of the factors that determine the performance of batteries. The quality of the CEI layer heavily relies on the participation of anions; therefore, the selection of lithium salts is crucial for its composition and structure. However, there are still some drawbacks when using a single lithium salt-based ether electrolyte. When used alone, LiTFSI can cause corrosion of the aluminum current collector at high voltage due to the low solubility of the reaction product $Al(TFSI)_3$ [72]. When used alone, $LiPF_6$ can decompose to produce the byproduct HF at high temperature, which destroys the CEI and corrodes the cathode. Therefore, from the perspective of price and performance, synergy of multiple lithium salt systems is highly feasible.

As shown in Fig. 6, JIAO et al [73] discovered that the incorporation of 2 mol/L LiTFSI and 2 mol/L LiDFOB in DME significantly enhances the oxidation stability of ether molecules, resulting in the formation of a stable interface layer on both high-voltage $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ cathode and LMA. The capacity retention remains above 90% after 300 cycles at 4.3 V and approximately 80% after 500 cycles.

As shown in Fig. 7, LI et al [74] discovered that the diluent TTE can decelerate the formation rate of SEI layers derived from lithium salts by reducing solvent concentration. The authors developed a dual-salt ether-based LHCE, LHCE-LiTD55, using LiTFSI and LiDFOB, which resulted

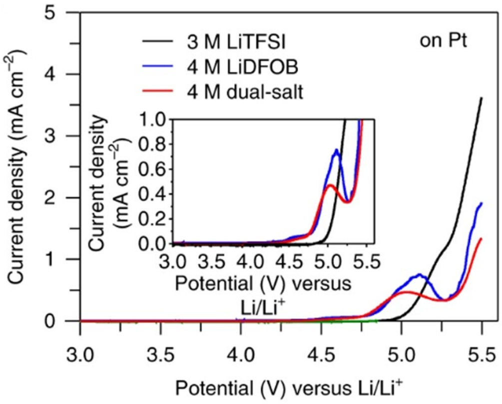

Fig. 6 LSV curves of three high concentration ether-based electrolytes at Pt electrode with scan rate of 0.1 mV/s (enlarged curves are shown in the inset) (Reproduced with permission [73], Copyright 2018, Nature Publishing Group)

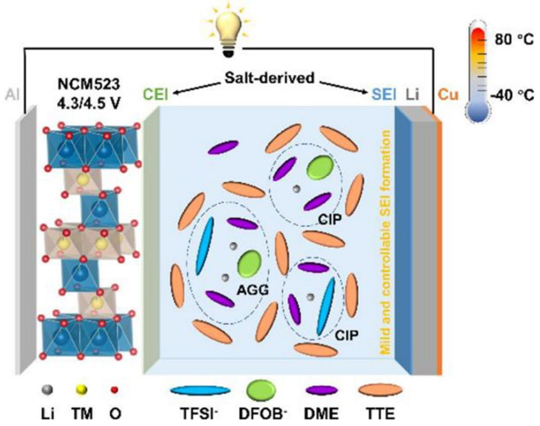

Fig. 7 Dual-salt ether-based localized high-concentration electrolyte (LHCE-LiTD55) (Reproduced with permission [74], Copyright 2023, Elsevier)

in the formation of a mild and controllable SEI. This work confirmed that LHCE-LiTD55 exhibited exceptional compatibility with LMAs, as evidenced by the significantly higher average CE of Li||Cu half-cells (99.5%) at a current density of 0.5 mA/cm^2 compared to HCEs with similar solvation structures but lacking TTE. Additionally, LHCE-LiTD55 demonstrated high oxidation stability and retained 90% of capacity after 200 cycles at 4.5 V when assembled in Li||NCM523 full cells. Furthermore, the cells using LHCE-LiTD55 exhibited outstanding discharge performance at low temperatures (−40 °C) and demonstrated excellent cycling stability at elevated temperatures (80 °C).

As shown in Fig. 8, BEYENE et al [75] discovered a dual salt electrolyte consisting of LiTFSI and LiDFOB as lithium salt, a small amount of $LiPF_6$ as additive, and fluoroethylene carbonate (FEC) and TTE as co-solvents at a volume ratio of 2:3. This innovative electrolyte system could induce the uniform deposition of lithium in Cu||NMC anode-free cells. And the deposited lithium effectively passivates the anode due to the synergistic effect of fluorinated FEC solvent and LiDFOB. In addition, incorporating fluorinated TTE solvent as a diluent can efficiently passivate the high-voltage cathode. As a result, by employing this dual lithium salt system, Cu||NMC cathode-free cell demonstrates exceptional coulombic efficiency (98.6%) and capacity retention rate (63%) at 4.5 V.

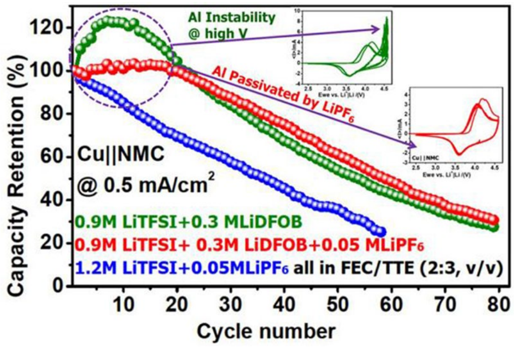

Fig. 8 Comparison of capacity retention rate of three electrolytes (Reproduced with permission [75], Copyright 2022, Elsevier)

4.3 Functional additive chemistry

Electrolyte additives are deemed crucial constituents of the electrolyte, despite their volume or mass accounting for less than 5%, and optimizing the additive formulation for the electrolyte emerges as the simplest and most effective approach [76].

4.3.1 Sacrificial additive

Usually, the main purpose of introducing additives is to form a stable SEI layer rich in inorganic species in LMBs, such as Li_3N, LiF, and LiCl, which exhibit minimal strain during cycling to cope with changes in anode volume. This type of additive is commonly referred to as sacrificial additive. Generally, sacrificial additives have a lower LUMO level than solvent molecules, so they can preferentially get electron and be reduced during the charge and discharge process, thus forming an inorganic-rich SEI [77].

As shown in Fig. 9, XIA et al [78] found that the addition of potassium trifluoro (trifluoromethyl) borate (PTB) as an additive to a solution containing 1.1 mol/L LiFSI in DME/TTE (2:3, molar ratio), can improve the interaction between Li^+ ions and DME/FSI^- species, leading to enhanced stability of the DME solvent against oxidation/reduction reactions and selectively promoting the reduction of FSI^- to stabilize the anode interface. Furthermore, the involvement of —CF_3—BF_3— moiety at the cathode interface can facilitate the formation of a SEI rich in LiF compound, thus efficiently inhibiting electrolyte decomposition. The full cell using Li||NMC90 demonstrates remarkable capacity retention reaching up to 84.1% after 170 cycles at a voltage up to 4.5 V.

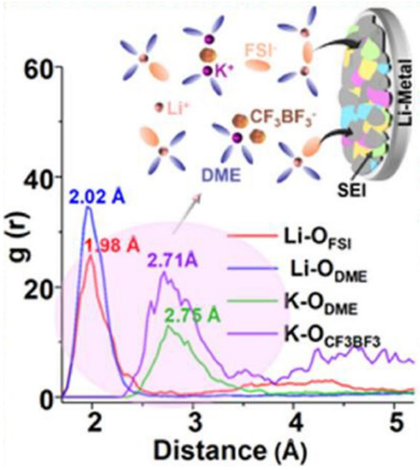

Fig. 9 Mechanism of action and electrochemical performance of PTB additive (Reproduced with permission [78], Copyright 2022, Elsevier)

As shown in Fig. 10, FU et al [79] discovered that the addition of a novel functional additive, hexachloro-1,3-butadiene (HCBD), to ether-based electrolytes, can selectively react with LMAs to produce LiCl-rich SEIs. The formed SEI can effectively regulate the deposition/stripping kinetics of Li^+, thereby inducing uniform lithium nucleation and reducing side reactions between LMA and electrolyte during extended cycles. As a result, the assembled Li||Li symmetric cell exhibits exceptional cycling stability with a lifespan of 7000 h at a current density of 1 mA/cm^2 and a hysteresis voltage of approximately 10 mV. Furthermore, after undergoing 350 cycles at 1*C*, the assembled Li||$LiFePO_4$ full cell demonstrates high specific capacity of 141.1 mA·h/g and outstanding rate performance.

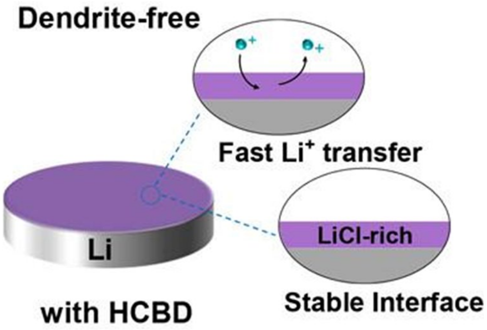

Fig. 10 HCBD additive in LMA to construct SEI (Reproduced with permission [79], Copyright 2022, American Chemical Society)

4.3.2 Adsorptive additive

It has been found that in addition to sacrificing additives, surface adsorbents can also be added into the electrolyte to adjust the interfacial chemistry. In the electrolytes with sacrificial additives, the oxidation of solvent molecules dominates the formation of interfacial phases. However, in the presence of adsorbent additives, the adsorption mechanisms of adsorbent additives play a more important role [80−83].

A typical representative of adsorption additives is nitrates (such as lithium nitrate $LiNO_3$), which can adsorb on the cathode surface and regulate the electrochemical double layer (EDL) structure. When the inner layer of EDL is occupied by negatively charged anions, these anions will repel ether molecules from contacting the cathode surface, thereby inhibiting the tendency of ether molecules to lose electrons on the cathode surface and improving the oxidation stability of ether based electrolytes [84].

As shown in Fig. 11, YU et al [85] found that the addition of a small amount of lithium nitrate (200 mmol/L) to an electrolyte composed of DME and 1 mol/L LiFSI can enhance the antioxidant ability of the dilute ether electrolyte, resulting in an increased voltage stability up to 4.4 V when paired with high-voltage $LiCoO_2$ and NMC532 cathodes, and the cells display excellent cycling performance. By accumulating NO_3^- ions in the inner layer of the cathode EDL, continuous expulsion of DME molecules from the cathode inhibits ether by-product decomposition. The electrolyte exhibits outstanding compatibility with $LiCoO_2$ and NMC532 cathodes at 4.3 V, showing capacity retention rates of 94.2% and 90.4%, respectively, after more than 600 cycles.

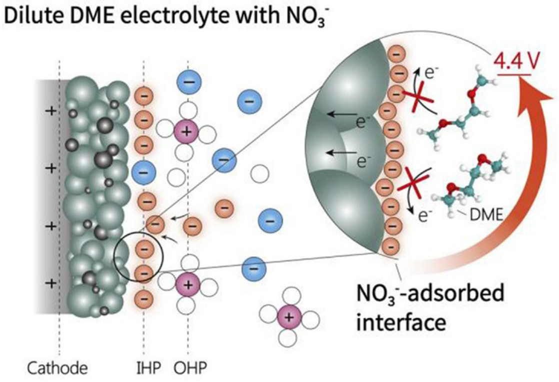

Fig. 11 Mechanism for solvent exclusion in the presence of NO_3^- (Reproduced with permission [85], Copyright 2022, Elsevier)

In addition to the anion-dominated adsorption mechanism, the spontaneous adsorption mechanism of polymer molecules has also been widely studied. Polymer adsorbent additives will induce the formation of a SEI layer rich in organic polymers and inorganic composite components on the LMA surface, thereby improving the coulombic efficiency and cycling stability of LMBs.

As shown in Fig. 12, JIN et al [86] discovered that polyethylene glycol (PEG400) with low relative molecular mass can spontaneously adsorb onto Li and Zn metal cathodes, and induce the formation of stable organic−inorganic hybrid SEIs. This stable interfaces can promote ion migration and suppress side reactions. By utilizing DOL-PEG400 (DOL + 1 mol/L LiTFSI + 0.5 mol/L $LiNO_3$ + 2 mg/mL PEG400) as the electrolyte, high coulombic efficiency can be achieved while extending the cycle life of Li||Cu half-cells. The Li||LFP full cells with a N/P ratio of 3 and an E/C ratio of 5 g·A/h can deliver a capacity retention rate of 87.5% after 250 cycles at 0.5*C*.

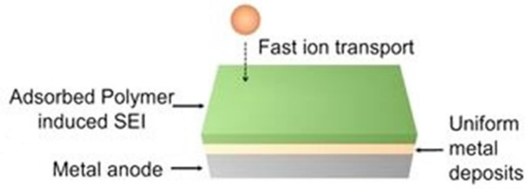

Fig. 12 Schematic diagram illustrating single-polymer chain and corresponding SPEI formed at metal anode (Reproduced with permission [86], Copyright 2023, Wiley)

4.4 Redesign of solvation structure

4.4.1 High salt−solvent ratio electrolyte

The presence of unstable free solvent molecules is the primary factor contributing to side reactions at the electrode−electrolyte interface [87]. HCE can enhance the incorporation of anions into the solvated structure of Li^+ by increasing the salt concentration (salt solvent ratio ≥1:2), thereby promoting the formation of a significant number of CIPs and AGGs and reducing the proportion of free solvent molecules. The reduction in free solvent molecules can effectively suppress the oxidative decomposition of electrolytes at high voltage, thus enhancing their passivation ability towards electrodes and ensuring the stable cycling of batteries under high voltage. However, CIPs and AGGs with lower LUMO levels exhibit preferential reduction on the anode surface, facilitating the formation of an inorganic-rich anion-derived SEI and improving the interface stability [88].

As shown in Fig. 13, REN et al [56] synthesized a HCE (4 mol/L LiFSI in DME) by increasing the concentration of LiFSI in DME. The synergistic effect between the lithium salt and the ether solvent induced a unique CEI layer, which maintained structural integrity of cathodes under high voltage. As a result, the assembled Li||NMC333 full cell exhibited a capacity retention of 92% after 500 cycles at 4.3 V.

However, the excessive utilization of lithium salts in HCEs still faces some challenges, including high viscosity, poor electrode wettability, relatively low ionic conductivity, and high cost, all of which impede their large-scale applications [89]. In order to address these limitations, the researchers have developed a series of electrolyte systems known as LHCEs [90−92], which typically introduce inert fluorinated diluents (such as HFE and fluoride benzenes) into HCEs. These LHCEs can not only retain the solvated structural characteristics observed in CIP and AGG in HCEs, but also tackle issues related to low wettability, increased viscosity, and elevated costs associated with high salt concentrations.

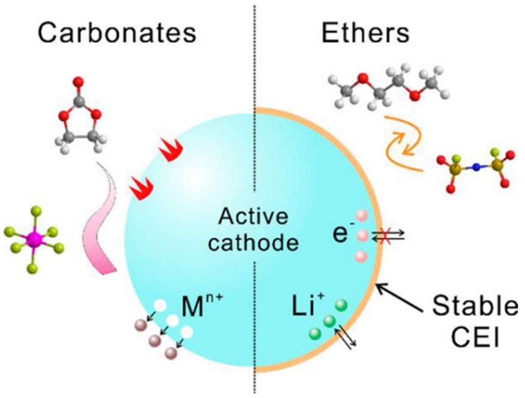

Fig. 13 Ether-based HCEs form stable CEI layer on highly catalytically active cathode surface (Reproduced with permission [56], Copyright 2019, American Chemical Society)

As shown in Fig. 14, PENG et al [89] proposed a high-performance BTF-LHCE (5 mol/L LiFSI in DME/BTF (volume ratio of 1:2)) by incorporating a low-cost and low-density diluent, benzotrifluoride (BTF), into 5 mol/L LiFSI in DME. The resulted BTF-LHCE exhibits excellent wettability, high lithium ion mobility, and superior ionic conductivity. Moreover, it can form an robust SEI rich in LiF and Li_3N on the LMA surface. With this electrolyte, an ultra-high average CE of 99.83% can be achieved within 400 cycles (up to 99.8% within 200−400 cycles), which is among the best values reported to date. The corresponding Li||NCM622 full cell demonstrates stable cycling for over 60 cycles at 4.6 V even with a very low N/P ratio (0.9) and an ultra-high loading NCM622 cathode (26.5 mg/cm^2). Additionally, the assembled Li||NCM622 pouch cell exhibits high energy density of 349.4 W·h/kg.

As shown in Fig. 15, LUO et al [93] reported an electrolyte composed of 4 mol/L LiDFOB as lithium salt, difluoroethylene carbonate (DFEC) as co-solvent, and DME as solvent. In contrast to conventional LHCEs, DFEC, with lower LUMO level, can function both as an additive and diluent

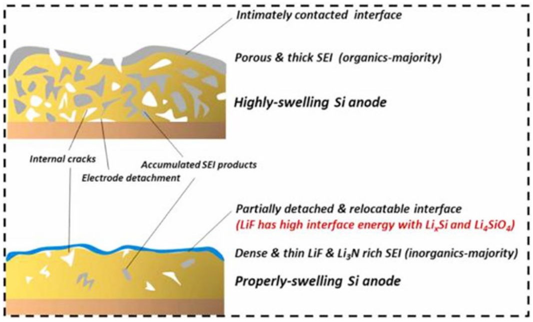

Fig. 14 Schematic illustration showing structure evolution of Si anodes cycled in CBE (top) and BTF-LHCE (bottom) (Reproduced with permission [89], Copyright 2022, Elsevier)

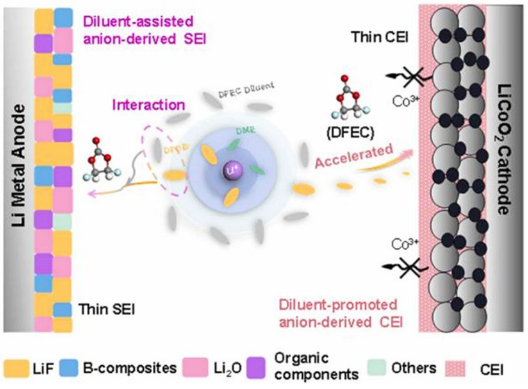

Fig. 15 Electrolyte structures and corresponding formed SEI/CEI layers for Li||LHCE||LCO cells (Reproduced with permission [93], Copyright 2023, Elsevier)

to induce the anion-derived interface layer, thereby suppressing the side reactions and dendrite growth, expediting Li^+ desolvation/transfer kinetics, and ensuring the exceptional coulombic efficiency (~98.25%). Moreover, this electrolyte can effectively passivate the highly catalytic surface of $LiCoO_2$ (LCO) cathode to prevent further decomposition. As a result, the high loading LCO electrode (~10.7 mg/cm^2) demonstrated a capacity retention exceeding 80% after 1000 cycles at 0.3C and 4.5 V, and the pouch cell exhibited a high capacity retention of approximately 93.6% after 60 cycles.

Although the design of LHCEs can effectively enhance the oxidation stability of electrolytes and suppress side reactions at the electrolyte−electrode interface, ensuring the safe operation of LMBs remains a challenge due to the low flash points commonly associated with HFE diluents [94].

4.4.2 Weakly solvated electrolyte

The decomposition of solvent molecules usually induces the formation of SEI/CEI rich in organic compounds, leading to a slow Li^+ conductivity [95]. To address these challenges and improve the stability of ether-based electrolytes at high voltages, the weak solvent strategy, alongside HCEs and LHCEs, is considered as an effective approach. In weakly solvated ether-based electrolytes (WSEE), both the solvent and the anion can coordinate with Li^+. However, due to the weaker coordination between solvent molecules and Li^+ [96], solvation structures abundant in anions (CIPs and AGGs) are formed, while reducing electrolyte viscosity and increasing ionic conductivity.

In the dilute DPE-based electrolytes, the coordination ability between Li^+ and anions (FSI^-) is stronger than that with higher salt concentrations, resulting in a higher abundance of non-coordinated ether molecules, which are commonly considered as the primary contributor to decreased stability observed in ether-based electrolytes under high voltage. As shown in Fig. 16, LI et al [97] found that dipropyl ether (DPE), a highly nonpolar ether compound, exhibits a low binding capacity for Li^+ ions, which prevents Li^+ from binding to it and promotes the formation of AGG even at low salt concentrations of 1 mol/L. In addition, the cathode surface is occupied by aggregates consisting of Li^+−FSI^- due to the attraction between the cathode and FSI^-, which significantly inhibits the side reactions between free ether molecules and the cathode by altering the structure of EDL. This study demonstrates that lack of improvement in thermodynamic stability does not necessarily indicate incompatibility between electrolyte systems and high-voltage cathodes. Instead, rearranging the decomposition order of solvation components within the electrolyte and adjusting the electrical double layer structure on the cathode surface can also stabilize electrode−electrolyte interface.

As shown in Fig. 17, ZHANG et al [98] demonstrated a weakly solvated electrolyte based on tetrahydropyran (THP) (2 mol/L LiFSI + 0.4 mol/L $LiNO_3$ in THP) to modulate the solvation structure and interfacial behavior of Li^+. The results show that the limited coordination capacity of THP towards Li^+ significantly enhances the interaction

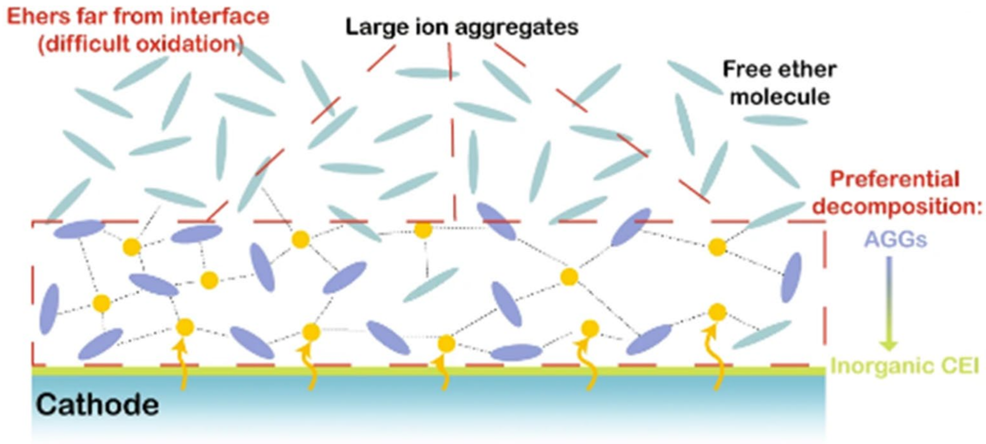

Fig. 16 Illustrations of interfacial model of WSEEs at NCM cathode surface (Reproduced with permission [97], Copyright 2023, Nature Publishing Group)

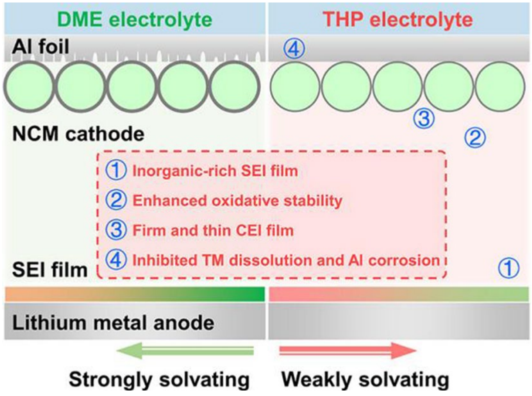

Fig. 17 Illustrations of interfacial model of THP electrolyte at NCM cathode surface (Reproduced with permission [98], Copyright 2023, American Chemical Society)

between Li^+ and anions, resulting in an increased content of AGGs in the electrolyte. The anion-rich solvation structure of Li^+ in THP-based WSEE can facilitate the formation of a SEI rich in inorganic components, a stable CEI layer, and a protective passivation layer on the aluminum current collectors. This optimized interfacial behavior promotes dense lithium deposition, and high-voltage stability, as well as suppresses transition metal dissolution and corrosion of aluminum current collectors. Ultimately, when assembled into a full cell configuration with $LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2$ cathode material, the capacity retention rate reaches 99.6% after 100 cycles at either 4.3 V or even 4.5 V.

In addition to certain ethers with weakly solvated ability, most ethers lacking weakly solvated ability can attain weak solvation through the steric hindrance effect, thereby facilitating the formation of CIPs and AGGs.

Recently, as shown in Fig. 18, PARK et al [99] demonstrated that 1,2-dimethoxypropane (DMP) can effectively utilize the steric hindrance effect between methyl and methoxy groups to reduce the binding ability of solvent to Li^+ and induce the formation of solvation structures rich in CIP and AGG with strong interactions between anions and Li^+. Accordingly, the 2 mol/L LiFSI-DMP electrolyte exhibits exceptional oxidative stability, leading to the formation of a uniform and robust CEI on the cathode surface. Remarkably, when tested in a Li||NCM811 full cell configuration at a current density of 1*C*, it demonstrates an impressive capacity retention rate of 86.0% after more than 180

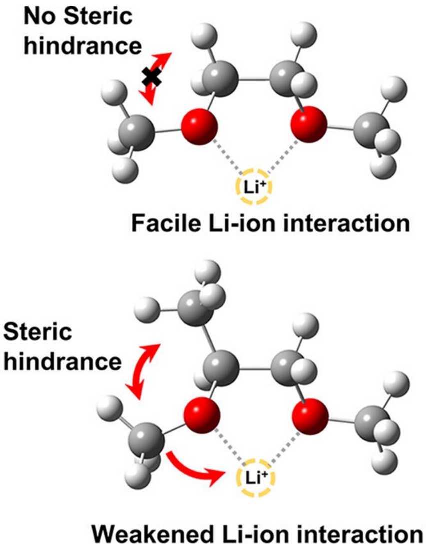

Fig. 18 Schematic illustration of steric hindrance and interaction with Li-ion for DME and DMP (Reproduced with permission [99], Copyright 2023, American Chemical Society)

Table 2 Chemical composition, action mechanism, research progress and related literature of ether electrolytes of four ether electrolytes

Classification of high-voltage ether electrolytes	Chemical composition	Action mechanism	Research progress	Related literature
Typical ether electrolyte	1 mol/L lithium salt and common ether solvents	Free ether solvents interacting with electrodes	–	–
HCEs or LHCEs ether-based electrolyte	High concentration lithium salt and common ether solvents (and inert fluorinated diluents)	CIPs and AGGs interacting with electrodes	92% after 500 cycles at 4.3 V (NCM333, 4.3 V)	[56]
			80.56% after 300 cycles at 0.6*C* (NCM622, 4.3 V)	[89]
			80% after 1000 cycles at 0.3*C* (LCO, 4.5 V)	[94]
Fluorinated ether-based electrolyte	1 mol/L lithium salt and fluorinated ether solvent	fluorinated ether solvents interacting with electrodes	84% after 200 cycles at 0.5*C* (NCM811, 4.3 V)	[43]
			100 % after 112 cycles at 0.5*C* (NCM811, 4.3V)	[69]
			95.9% after 150 cycles at 1/3*C* (NCM811, 4.7 V)	[71]
Weakly solvated ether-based electrolyte	1 mol/L lithium salt and weakly solvated ether solvent	CIPs and AGGs interacting with electrodes	100% after 150 cycles (NCM811, 4.3 V)	[97]
			100% after 100 cycles (NCM523, 4.5 V)	[98]
			86.0% after 180 cycles at 1*C* (NCM811, 4.3 V)	[99]

cycles, while maintaining a capacity retention rate of 93.0% after over 160 cycles at a high current density (~5 mA/cm^2).

Table 2 lists the chemical composition, action mechanism, research progress and related literature of ether electrolytes of four ether electrolytes.

5 Summary and outlook

5.1 Summary

Ether-based electrolyte is a strong candidate for the next generation advanced electrolyte system for LMBs owing to its exceptional capacity to dissolve lithium salts, superior lithium ions conductivity, and outstanding reduction stability for lithium metal. Thus far, however, some main challenges such as poor oxidation stability at high voltages (>4.3 V), unstable electrode−electrolyte interfaces, and safety concerns posed by low-lightning ether-based solvents still remain, and substantial research effort would be required to overcome these challenges. In recent years, many modification methods such as solvent molecular design, multi-lithium salt synergy, additive optimization, or solvation structure regulation have been employed to improve the oxidation stability of electrolyte and the reversibility of lithium ion, and restrain the side reaction of interface. This work provides a detailed overview of the progress of various strategies, and some consensus is reached:

(1) Introducing electron-withdrawing groups or spatial groups on solvent molecules can effectively reduce coordination sites between solvents and Li$^+$, thereby promoting desolvation process of Li$^+$ and forming a anion-derived interface layer.

(2) The high-voltage stability of electrolytes can be enhanced through synergistic effects arising from dual/multiple lithium salt thermodynamics (HOMO energy level) and kinetics (CEI layer structure additive).

(3) Functional additives are beneficial to building a stable interface layer between electrolyte and electrode and inhibit side reactions between heterogeneous interfaces.

(4) Special solvation structure design, such as HCEs, LHCEs, or weakly solvated electrolyte, can weaken the interaction between Li^+ and solvent molecules, thereby enhancing the stability of electrolyte under high voltage and reducing interface side reactions.

5.2 Outlook

Despite certain achievements in achieving ether-based electrolytes for high-voltage LMBs, there remain critical issues that necessitate further investigation and discourse in future research:

(1) Explore stable electrolyte systems

Ether-based electrolytes have unparalleled advantages in LMBs, and numerous challenges such as the continuous degradation and reconstruction of the SEI, significant decomposition and side reactions under high voltages, have been addressed to a certain extent. However, LMBs are bound to be used under some extreme conditions such as high temperature, low temperature and high rate, and thus it is necessary to design new ether-based electrolytes with wide application temperatures and high rate impact resistance.

(2) Further explore the mechanism of voltage stability and interface stability for electrolytes

Poor oxidation stability is the main challenge that hinders the practical application of ether-based electrolytes. Previous researchers have conducted extensive work to broaden the electrochemical window of ether-based electrolytes, such as solvent molecular design, multi-lithium salt synergistic strategies, multifunctional additives, construction of high concentration or local high concentration electrolytes, and weak solvation electrolytes. However, there is no systematic consensus on the mechanism for improving voltage stability, and the stability mechanism of the electrode electrolyte interface is not yet clear. Further explanation is needed by combining theoretical calculations and advanced characterization techniques.

(3) Explore the evolution of multiphase interface states of batteries throughout the entire life cycle.

Currently, the formation and evolution processes of electrode−electrolyte interface are not yet clear due to the limitations of effective characterization techniques. Therefore, it is imperative to develop advanced characterization techniques that can accurately and intuitively obtain properties of electrode−electrolyte interface. For example, in-situ techniques can be used to track the structure and compositional evolution of electrode−electrolyte interface, providing strong evidence for analyzing their operating mechanisms. Cryo-electron microscopy and scanning transmission electron microscopy can provide clearer and more intuitive information about morphology and structural of interfaces. The differential electrochemical mass spectrometry (DMES) can track gas production during battery cycling processes, while atomic force microscope (AFM) can provide surface morphology of interface as well as accurate measurements of their mechanical properties.

(4) Full cells validation to promote practicality

The currently reported electrochemical properties about ether-based electrolytes are generally obtained under laboratory conditions, and there is still a considerable distance from large-scale practical applications. In this regard, in order to facilitate the rapid transformation and application of scientific research achievements, the validation of batch pouch cells is imminent, and the process parameters suitable for actual production still need to be explored and adjusted gradually.

In conclusion, further exploration and optimization of the interface between high-voltage ether-based electrolyte systems and electrodes can facilitate the practical application of ether-based electrolytes. Simultaneously, promoting the advancements in electrolyte science, particularly in interface chemistry, can significantly augment our comprehension of battery chemistry and stimulate innovation in battery devices.

CRediT authorship contribution statement

Hai-peng ZHU: Conceptualization, Investigation, Reference curation, Writing − Original draft; **Qiang-feng ZHANG:** Investigation, Reference curation; **Zhao CHEN:** Investigation, Illustration; **Zi-yu PENG:** Visualization, Reference curation; **Lin MEI:** Writing − Review & editing; **Chun-xiao ZHANG:** Project administration, Resources, Writing − Review & editing, Funding acquisition; **Wei-feng WEI:** Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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高压锂金属电池醚基电解液的最新进展

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摘　要：醚基溶剂通常对锂金属具有更好的亲和力，因此，醚基电解液(EBEs)更倾向于在锂金属表面形成均匀且薄的固体电解质界面(SEI)，确保锂金属电池(LMBs)的长循环稳定性。然而，EBEs 仍然面临着在高电压下氧化分解的挑战，这会腐蚀正极的晶体结构并破坏电极−电解质界面的稳定性，甚至造成安全隐患。回顾了 EBEs 的类型和关键挑战，详细讨论了提高 EBEs 的高压稳定性和构建稳定的电极−电解质界面的策略。最后，探讨了 EBEs 组分优化和高电压 LMBs 中电解质−电极界面调控的未来前景和潜在方向。

关键词：醚基电解液；锂金属电池；高电压；溶剂化结构；电极−电解质界面

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