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# Low Concentration Electrolyte: A New Approach for Achieving High Performance Lithium Batteries

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**Abstract**

The conventional perspective suggests that low-concentration electrolytes (LCEs) face challenges in achieving stable charge/discharge properties due to the decreased ionic conductivity resulting from lower $Li^+$ concentrations. However, the successful utilization of LCEs in lithium/sodium-ion batteries has brought them into the forefront of consideration for high performance battery systems. It is possible to achieve improved interface stability and ion transport performance for LCEs through adjusting electrolyte components like salts, solvents, and additives. This review provides timely update of the recent research progress, design strategies and remaining challenges of LCEs to answer several questions: i) What is the key factor for designing LCEs? ii) How to balance the low salt concentration and good ionic conductivity? iii) What is the interphasial mechanism of anode/cathode in LCEs? Firstly, the development of LCEs is discussed with typical examples. Subsequently, effectiveness of solvents on overall performances of LCEs is comprehensively summarized in detail. Finally, the challenges and possible research direction of LCEs are discussed. This review provides critical guidance for designing novel electrolytes for secondary batteries.

*Keywords:* Lithium-ion batteries; Electrolytes; Low salt concentration; Interphasial

chemistry Batteries

## 1. Introduction

Lithium-ion batteries (LIBs) have attracted great attention due to their exceptional high-energy density and environmentally friendly nature compared to other energy storage systems. Since the 1990s, LIBs have been widely used not only in small light electronic devices such as cameras, mobile phones, laptop computers, and portable measuring instruments, but also in space, military, and other special applications, especially as the main power source for electric or hybrid electric vehicles [1-4]. The electrolyte is a major part of secondary ion batteries, which acts as a medium for $Li^+$ between cathode and anode. Therefore, the physicochemical properties of electrolytes are closely related to the cell performances such as high-voltage and wide temperature operation properties, fast charging capability as well as safety. As an indispensable component in LIBs, the electrolyte needs to withstand good reduction and oxidation stability at both anode and cathode sides. In addition, high ionic conductivity and low viscosity are two other important factors to determine the performance of electrolyte.

Currently, LIBs used in electric vehicles are composed of layered transition metal oxides as cathode, graphite as anode, and organic electrolytes. The electrolyte formulation for LIBs is a 1 M (mol $L^{-1}$) solution of lithium hexafluorophosphate ($LiPF_6$) in a mixed solvent of ethylene carbonate (EC) and linear carbonates (e.g., dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethyl methyl carbonate (EMC)) and other functional additives. Which, EC exhibits excellent film-forming ability, being capable of forming a passivating film (solid electrolyte interphase: SEI) that is ion-conductive and electronically insulating at low potentials (~0 V vs. $Li^+$/Li). A SEI layer formed by EC decomposition prevents continuous electrolyte decomposition or solvent co-intercalation into graphite [5]. $LiPF_6$ possesses optimal overall performance compared to other salts such as $LiClO_4$, $LiBF_4$, and LiDFOB, etc., more importantly, its hydrolysis products enable the formation of a passivation layer on the surface of aluminum current collectors, preventing their corrosion at high potential [6, 7]. However, carbonate-based electrolytes still suffer from drawbacks such as a narrow electrochemical window and temperature range [8, 9]. Additionally, the volatile and flammable nature of carbonate solvents, coupled with the susceptibility of $LiPF_6$ to hydrolysis and poor thermal stability further induce significant safety concerns [10]. Many strategies have been deliberately designed to improve the overall performances of electrolytes including regulation of solvation structure by introducing novel solvents and salts, tuning the concentration of salts, and developing film-forming additives to extend the electrochemical window of electrolytes. In recent years, high concentration electrolytes (HCEs) have attracted much attention due to their excellent performances [11]. Increasing the salt concentration will enhance the interactions between cations and anions/solvents as well as reduce the content of free solvent molecules. Therefore, the solvation structure of HCEs is mainly composed of contact ion pairs (CIPs) and aggregates (AGGs), while the solvent-separated ion pairs (SSIP) structures and free solvent molecules are greatly reduced [3, 12, 13]. CIPs and AGGs are complexes formed by lithium ions bonding with anions through coulombic interactions, where AGGs have two or more lithium ions coordinated to the same anion [14]. The abundance of CIPs and AGGs allows anions to extensively enter the solvated structure and participate in SEI/CEI formation, resulting in higher inorganic content in the CEI/SEI further enhancing the interphasial stability [15]. For example, Qian et al.[13] applied 4 M LiFSA/DME in a Li||Cu battery and achieved stable cycling for up to 500 hours (1000 cycles at a current density of 4 $mA/cm^2$) with high coulombic efficiency (>98%). However, HCEs also suffer from disadvantages such as high viscosity, poor wettability towards separators and cathodes, and poor performance at low temperatures [3]. More fatally, the cost of lithium salt accounts for a high proportion of electrolytes, hence, greatly increasing the cost of electrolytes, which will severely impede the practical application of HCEs [16].

Recently, researchers have employed inert cosolvents as diluents to overcome these drawbacks, which are miscible with the solvent but immiscible with the salt within HCEs [17]. The addition of diluent makes HCEs change to local high concentration electrolytes (LHCEs). LHCEs retain the solvated structure of HCEs while possessing the distinctive characteristic of viscosity much lower than HCEs and excellent wettability towards electrodes and separators [17, 18]. But to date, diluents in LHCEs are limited only to fluorinated ethers such as 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropylether (HFE), 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) and bis(2,2,2-trifluoroethyl) ether (BTFE), with low boiling points, and volatility, which are difficult to apply for high-temperature secondary batteries [19]. Diluents in LHCEs can significantly reduce the viscosity of electrolytes, but diluents are even more expensive than lithium salts [20]. Therefore, even if the salt concentration is reduced in the whole solvation structure, the total cost of electrolytes remains high.

More recently, designing low/ultra-low salt concentration electrolytes (LCEs) is becoming a promising strategy to conquer these issues. However, how to balance the low salt concentration and high ionic conductivity is becoming one of the major challenges. The successful utilization of LCEs in sodium-ion batteries by Hu et al. has brought them to the forefront of consideration for lithium-ion batteries as well [21]. HCEs have proven that ionic conductivity is not the decisive factor affecting battery performance, while a good interphasial chemistry and relatively lower solvation energy barrier are important factors to ensure stable battery operation [3, 12, 13, 22]. Up to now, substantial progress has been made in utilizing LCEs in secondary batteries, but a comprehensive review focus on progress of LCEs is lacking. An in-depth understanding of designing principle and interphasial mechanism of LCEs provides a timely and critical overview of the development of electrolyte systems.

In this review article, we particularly focus on the fundamental designing principle of LCEs, strategies for regulating solvation structure as well as effective approaches for optimizing interphasial chemistry. Major solvents for LCEs including carbonates, ethers and other type organic solvents are comprehensively summarized.

## 2. Properties of LCEs

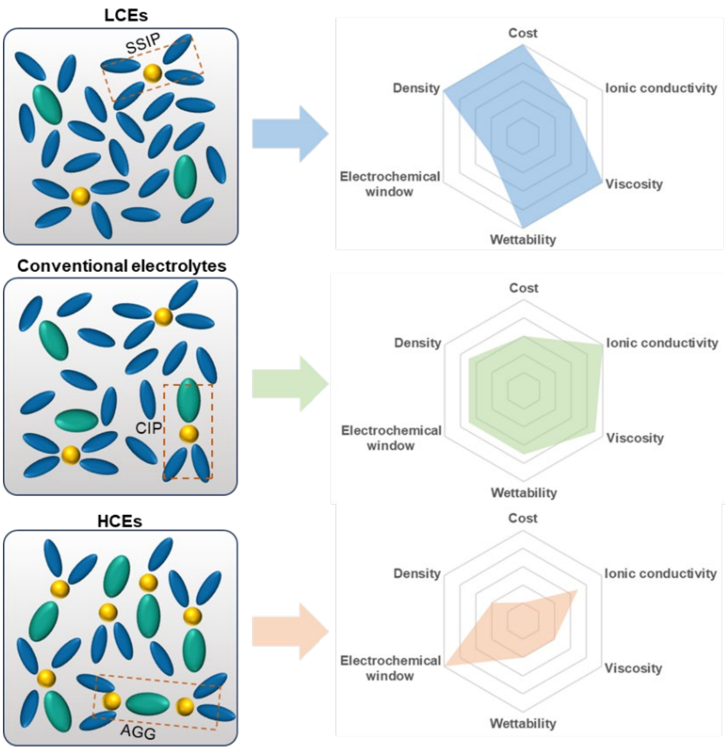


**Figure 1.** The solvation structure and performance comparisons of LCEs, conventional electrolytes and HCEs.

Electrolytes typically include a solution of salt dissolved into a single solvent or solvent mixture with different salt concentrations, solvent ratios, and additives. When the lithium salt dissolved in solvents to form $Li^+$ and salt anions, the solvation sheath including $Li^+$ ($Li^+$-solvent) complex formed due to the stronger interaction between $Li^+$

and solvents. It should be noted that the structure of the solvation sheath is determined by the properties of salts, solvents, and salt concentration. The solvation structure typically includes $Li^+$-anion and $Li^+$-solvent complexes. The relative interaction intensity of these complexes determines the existence of CIPs, AGGs, and SSIPs, relating to the ionic conductivity, viscosity, reduction/oxidation stability as well as the composition of electrode/electrolyte interphase.

As shown in Figure 1, the solvation structures of electrolytes are various with different salt concentrations. It can be seen that CIPs and AGGs are dominant in the solvation structure of HCEs, while SSIPs are dominant in conventional electrolytes and LCEs. Although SSIPs constitute the main portion of conventional electrolytes, they still contain a certain amount of CIPs and a small quantity of AGGs.When the salt concentration decreases, the fraction of SSIPs and free solvents increases. Previous study shows that SSIPs in LCEs exhibit low binding energy and weak solvation characteristics, enabling LCEs to achieve relatively fast interfacial charge transfer kinetics and low-temperature performance[23]. The physicochemical properties of the electrolyte also exhibit certain trends with varying salt concentrations. The superior film-forming properties of HCEs expand their electrochemical window, however, excessive salt concentration increases their cost and hinders commercial application. Moreover, the high density of HCEs decreases the energy density of the battery, while high viscosity, poor wetting properties, and low ionic conductivity contribute to sluggish ion transport. LCEs offer significant advantages in terms of cost, density, viscosity, and wettability compared to HCEs and conventional electrolytes. Nevertheless, the presence of excessive free solvents and low salt concentration leads to poor electrochemical stability and low ionic conductivity in LCEs. Therefore, it requires a great effort to carefully optimize the composition and salt concentrations of

LCEs.

## 3. Low Concentration Electrolytes for lithium batteries

Among various electrolyte formulations, carbonate-based and ether-based electrolytes are the most commonly utilized in practical applications. Carbonate-based electrolytes, which have been employed in commercial LIBs for over four decades, exhibit excellent oxidation stability (with an anodic limit of around 4.3 V) and compatibility with graphite anodes [24, 25]. However, conventional EC-based electrolytes exhibit poor compatibility with lithium metal anode (LMA), resulting in the formation of a low-quality interface that promotes uncontrolled lithium dendrite growth. Such an issue becomes more pronounced at low salt concentrations. Therefore, various strategies, including the utilization of inert diluents, fluorinated carbonate solvents, and new lithium salts, have been developed to enhance the compatibility between carbonates and LMAs. Ether-based electrolytes are widely employed in lithium metal batteries (LMBs) due to their favorable compatibility with lithium metal anodes. However, the electrochemical window of the conventional ethers is below 4 V, making them suitable for low-voltage LMBs such as lithium-sulfur (Li-S) batteries [26]. Recent studies have shown that ether-based LCEs exhibit significant inhibitory effects on the shuttle effect of polysulfides in Li-S batteries [27, 28]. Novel electrolyte systems and organic solvents are also being developed to broaden the applicability of LCEs in various battery systems.

### 3.1 Carbonate-based solvents

Carbonate-based solvents have remained the predominant choice for lithium battery electrolytes [1-3]. Therefore, directly regulating the components of carbonate-based electrolytes is undoubtedly the most economical method. The carbonate solvents have lower oxidation stability and high reactivity toward LMAs [9]. The instability of the electrolytes becomes more serious due to the large amount of free solvent in the carbonate-based low-concentration electrolytes [29]. Therefore, an interface film with high ionic conductivity and low electronic conductivity is the ideal scheme to realize its application. Recent research has demonstrated that the anion-dominated solvation structures play a crucial role in film-forming in HCEs and LHCEs [3, 30]. In light of this understanding, it is possible to develop LCEs with exceptional electrochemical compatibility by substituting solvating co-solvents with non-solvating alternatives. As shown in Figure 2a, the limited coordination between $Li^+$ and the solvents inherently promotes anion-ion interactions, thereby facilitating the formation of AGGs [31].

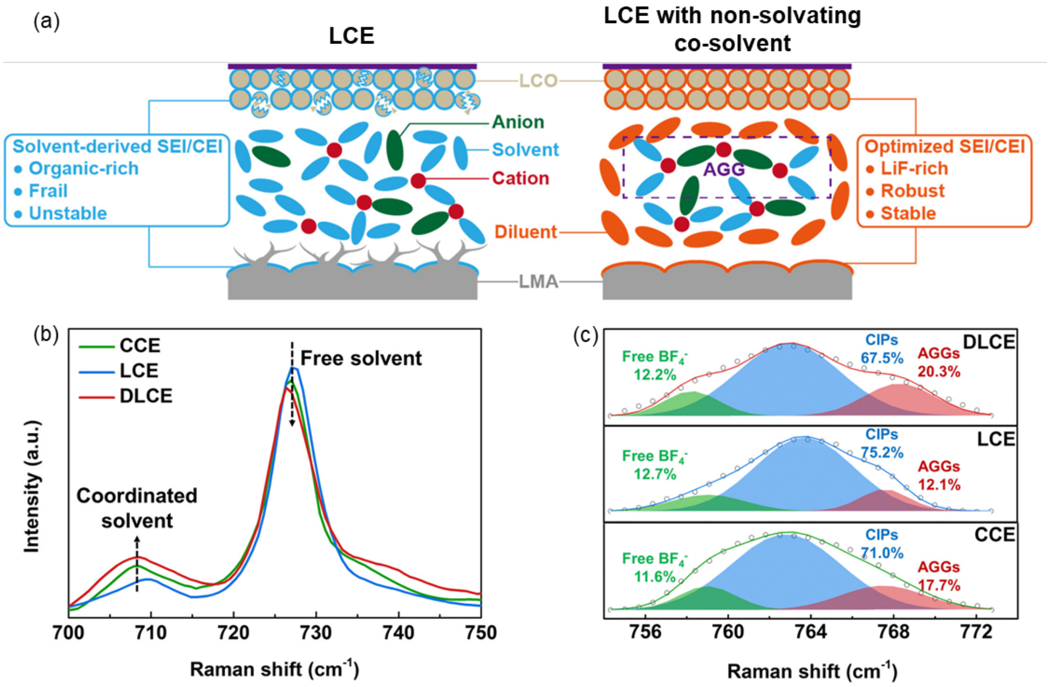


**Figure 2.** (a) Solvation and interfacial structures of the LCE and LCE with non-solvating co-solvent. Raman spectra of different electrolytes in the wavenumber range of (b) 700-750 $cm^{-1}$ ($FEC_{O\text{-}C\text{-}O}$) and (c) 754-774 $cm^{-1}$ ($BF_4^-$). Reprinted with permission from Ref 31. Copyright © 2021 The Author(s).

Jiang et al. [31] used the non-solvating solvent fluorobenzene (FB) as a co-solvent in a typical dual-salt LCE. This substitution resulted in the formation of a diluted low-concentration electrolyte (DLCE) comprising 0.3 M LiDFOB and 0.2 M $LiBF_4$ in a mixture of DEC/FEC/FB (3.5:1.5:5 by volume). Raman spectroscopy (Figure 2b) provides conclusive evidence regarding the enhanced interaction between lithium ions and solvent molecules in DLCE. FB-contained DLCE reduces the quantity of free solvents and further improves the oxidation stability of the electrolyte. Moreover, a certain amount of CIP is converted into AGGs as shown in Figure 2c. These positively charged AGGs allow more $BF_4^-$ to enter the double layer at the solid-liquid interface, enhancing the kinetics of $BF_4^-$ decomposition to form LiF-rich SEI. The undesired side reactions are effectively also suppressed due to the improvement in solvated structure and interface characteristics. Corresponding Li-$LiCoO_2$ cells in DLCE show excellent cycling stability even at a high charge cutoff voltage of 4.6 V.

Guan et al. introduced the inert cosolvent TTE into 0.4M $LiPF_6$ EC-DMC to regulate the solvation structure of the electrolyte [32]. The introduction of TTE also enhances the interaction between lithium ions and solvent molecules, and enables LCE to form a robust CEI on $LiFePO_4$ cathodes. As a result, Li|| $LiFePO_4$ cell in 40% TTE contained electrolytes demonstrates best rate performance and the capacity of 122.8 mA h $g^{-1}$ was achieved at a fact charging rate of 5C. More importantly, introduction of TTE in LCEs effectively enhances the safety performance of LIBs due to the reduced the flammability of the electrolyte.

Previous studies have shown that LiF-rich SEI/CEI demonstrates high densification, good passivation performance, enables uniform ion flux, and reduce interface resistance [33-35]. Therefore, fluorinated solvents are introduced to build fluorine-rich interface [36]. For one aspect, the inevitable decomposition of fluorinated solvents induces fluorine-containing interface layer, thereby improving the electrochemical stability and enhancing the mechanical properties of the interface [37]. For example, fluoroethylene carbonate (FEC) and EC show different decomposition mechanisms. FEC undergoes reduction to form poly(VC) and LiF as its primary decomposition products [38] while, the decomposition of EC yields organo-rich compounds such as $(CH_2OCO_2Li)_2$ and $(CH_2CH_2OCO_2Li)_2$, along with minor traces of $Li_2CO_3$ [39]. On another note, fluorinated solvents with low solvating ability promotes more anions to participate in the solvated structure, producing an interface layer derived from anions upon decomposition [37, 40].

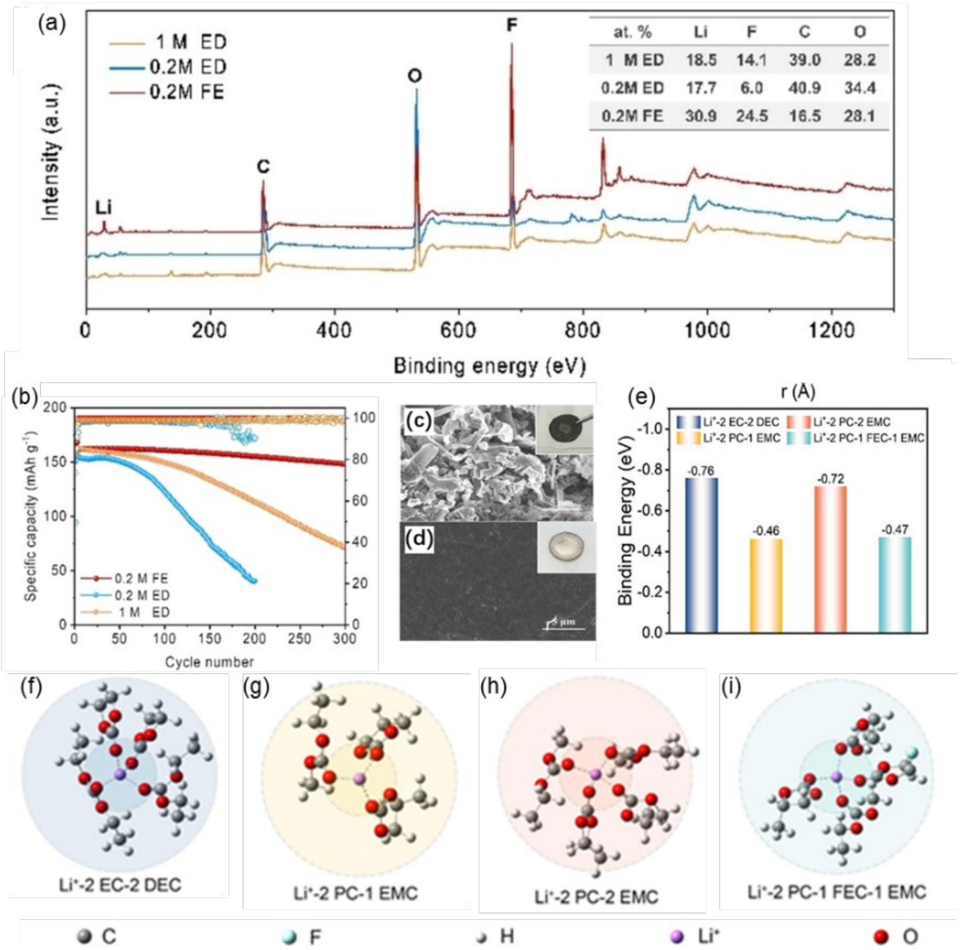


**Figure 3.** (a) The total XPS spectra of SEI layers on Li anodes in $LiCoO_2||Li$ batteries after 200 cycles 1 M $LiPF_6$ in EC and DMC (note as 1 M ED) , 0.2 M $LiPF_6$ in EC and DMC (note as 0.2 M ED), 0.2M $LiPF_6$ in FEC and EMC(note as 0.2M FE), the inset table corresponds to atomic ration of elements; (b) The long-term cycle performances of $LiCoO_2||Li$ full cells at 0.5 C in 1 M ED, 0.2 M ED, and 0.2 M FE at room

temperature; Reprinted with permission from Ref 41. Copyright © 2022 Wiley - VCH GmbH. Morphologies of the Li metal harvested from the Li||Li symmetric cells after cycling in (c) 1 M $LiPF_6$ in EC and DMC (3:7 by weight ratio), (d) 0.1M LiDFP and 0.4M LiBOB in EC and DMC; Reprinted with permission from Ref 16. Copyright © 2020 WILEY - VCH Verlag GmbH & Co. KGaA, Weinheim. (e) Binding energy of representative Li+ solvation structure in three electrolytes by DFT calculations. Schematics of representative Li+ solvation structure in (f) STD, (g-i) E1 and E2 electrolytes. Reprinted with permission from Ref 50. Copyright © 2022 Elsevier B.V. All rights reserved.

Deng et al. [41] used the typical fluorinated solvent FEC and EMC as a co-solvent with good film forming property to achieve a 0.2 M $LiPF_6$ LCE and used in high-voltage LMBs. Extensive quantum chemistry calculations showed that compared with 1M $LiPF_6$ -EC/DMC (STD), the solvated molecules formed by lithium ions coordinating with FEC and EMC in LCE have a higher reducing potential. And among all the free molecules, free EC molecules have the lowest reduction potential of 0.22 V, while free FEC molecules have a higher reduction potential of 0.57 V, even higher than the lithiated $Li^+$(EC) molecules. This means that once FEC is added in the electrolyte, the reduction potential will be increased. X-ray photoelectron spectroscopy (XPS), as shown in Figure 3a, also confirms that LCE produces LiF-rich SEI layer and reduce undesirable decomposition components caused by side reactions. The corresponding $LiCoO_2$||Li battery using LCE shows stable electrochemical performance at high voltage (4.4V) with a capacity retention of 91.1% after 300 cycles at 0.5C current rate (Figure 3b).

Utilization of strongly chelating salts such as lithium bis(fluorosulfonyl)amide (LiFSI), lithium difluoro(oxalato)borate (LiDFOB), and lithium tetrafluoroborate ($LiBF_4$) can also achieve stable interface [42, 43]. Despite its widespread commercialization and balanced performance, $LiPF_6$ has several disadvantages such as inadequate thermal stability and high sensitivity to moisture [43], inducing the formation of highly reactive species, such as $POF_3$ and HF [44, 45]. Mixed salt electrolytes have garnered significant attention due to their enhanced overall performances induced by the synergistic effect of different anions [46]. Introducing multiple lithium salts within the electrolyte mixed salt electrolytes with cooperative effects can be formulated [46-48]. These electrolytes offer the potential to enhance thermal stability and facilitate the formation of stable interface layers on both the cathode and anode [43].

Zheng and coworkers explored the LCEs based on dual-salt (0.1 M LiDFP and 0.4 M LiBOB, LiFSI, or LiTFSI) dissolved in EC and DMC (3:7 by weight ratio) [16]. LiDFP can decompose at the high-voltage cathode and graphite anode surface to form a passivation layer. Moreover, it also explored the potential benefit on LMA. The decomposition of LiDFP enables the formation of LiF-rich and P–O species contained SEI. The SEM images and surface morphology of LMA (Figure 3c, d) cycled in 1M $LiPF_6$ EC/DMC show a needle-like lithium deposition. In contrast, the LMA cycled in LCEs shows a very smooth and uniform surface morphology, confirming the formation of uniform and dense SEI. Taking the advantages of stable SEI formed in dual-salt LCEs, the coulombic efficiencies (CE) of Li/Cu cells increased from 83.3% for conventional carbonate electrolyte to 97.6%, 94.5%, and 93.6% for LiDFP-LiBOB, LiDFP–LiFSI, and LiDFP–LiTFSI electrolytes, respectively. When applied in a Li-$LiFePO_4$ full cell, LiDFP-LiBOB-based electrolyte demonstrated best performances with a high-capacity retention of 94.5% after 300 cycles at a current density of 2.0 mA $cm^{-2}$.

Similarly, lithium difluoro(bisoxalate)phosphate (LiDFBOP) can also be preferentially reduced in the electrolyte, resulting in an interfacial film containing LiF and $Li_xPO_yF_z$ with large Young's modulus and high ionic conductivity, thus effectively inhibit the growth of lithium dendrites and accelerate the migration of lithium ions in the SEI layer [49]. Wang et al. [50] proposed LCEs based on LiDFBOP: 0.1 M LiDFBOP + 0.4 M LiBOB and 0.1 M LiDFBOP + 0.2 M LiBOB + 0.2 M $LiPF_6$ in PC/FEC/ EMC). These LCEs not only enable the formation of dense and stable SEI but also have a lower desolvation energy barrier than STD, as illustrated in Figure 3e-i. According to the calculated binding energies, the typical solvation structure formed in LCEs has weaker ion-dipole interactions. Low desolvation energy of the two LCEs enables good capacity retention at low temperatures, resulting in high discharge capacities of 140 mAh $g^{-1}$ and 146 mAh $g^{-1}$ at -25℃ (10 cycles, 0.5C), respectively.

LCEs with carbonate solvents exhibit improvements in viscosity, wettability, and other relevant characteristics through solvation structure optimization. Furthermore, LCEs also acquire the capability to form robust and stable interface films on the electrodes, thereby significantly enhancing the stability and overall performance of the lithium batteries.

3.2 Ethers-based solvents

Ether-based electrolytes are widely used in lithium-sulfur batteries. However, the utilization of lithium-sulfur batteries is impeded by challenges such as the polysulfide shuttle effect and the strict demand for low electrolyte/sulfur (E/S) ratio and high cathode loading [51, 52]. The dissolution of polysulfides in lithium-sulfur batteries leads to various issues, including capacity degradation, self-discharge, and the formation of unstable interfacial layers. The absence of a passivating layer on the electrode surface results in continuous electrolyte decomposition until depletion. To achieve a high energy density lithium-sulfur battery system, a low E/S ratio and a high sulfur loading on the cathode are necessary [52-54], further highlighting the necessity for enhanced cathode stability, accelerated reaction kinetics, improved electrolyte wetting, and more stable interfacial layers to ensure reasonable charging rates and prolonged cycle life [28].

For the standard electrolyte system of LiTFSI/$LiNO_3$/1,2-Dimethoxyethane (DME)/ 1, 3-Dioxolane (DOL), little attention has been paid to dilute and ultra-dilute electrolytes, which are considered to exacerbate the dissolution and shuttling effects of polysulfides [55, 56]. However, studies have shown that LCEs can inhibit the dissolution of short-chain polysulfides, thereby significantly reducing the shuttling effect of polysulfides [27, 28].

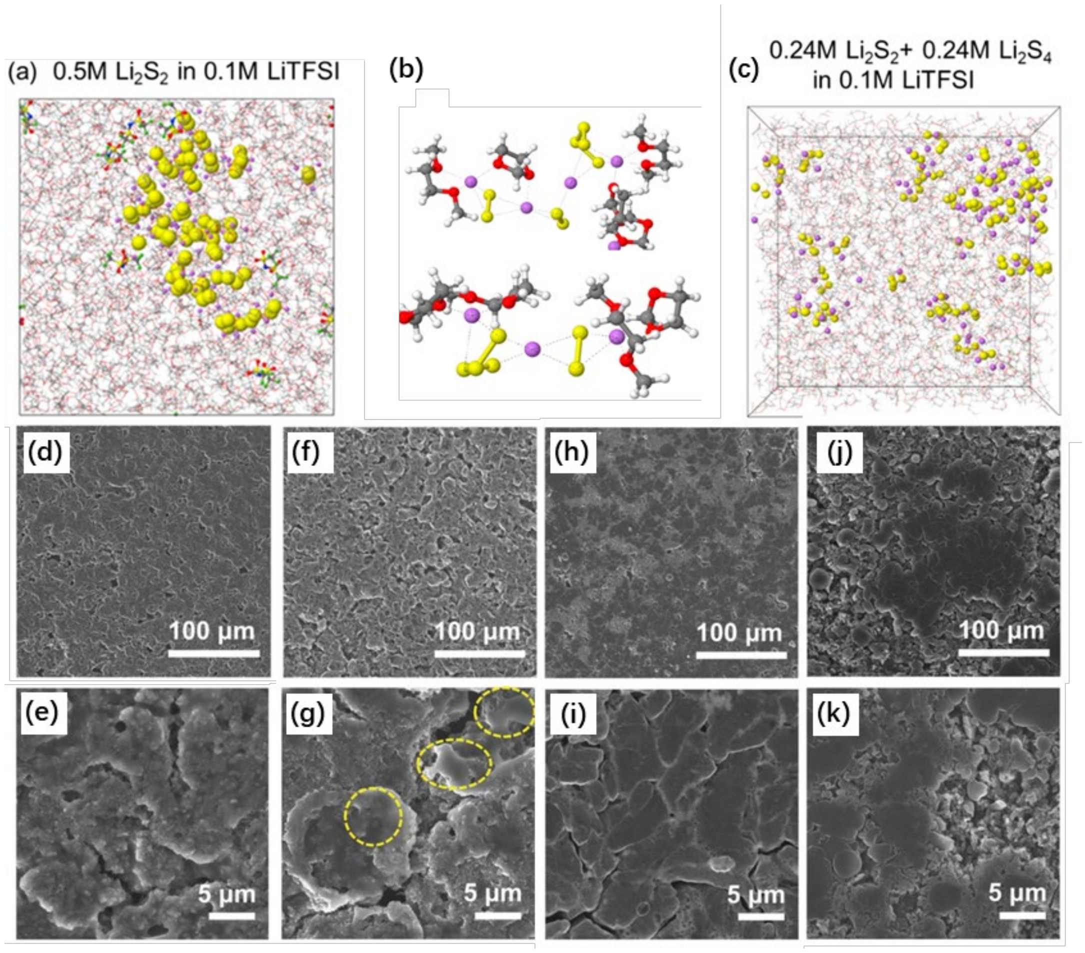


**Figure 4.** Snapshots of MD simulation boxes highlighting (a) $S_2$ anions and (b) $S_2$ and $S_4$ anions (shown in yellow), solvent and $TFSI^-$ are shown as a wire frame; (c) the $Li_2S_2$–$Li_2S_4$ clusters from simulations; Reprinted with permission from Ref 28. Copyright © 2020, American Chemical Society. Morphology characterization of cycled electrodes in Li–S batteries operated at 0 °C: top-surface SEM images of G–S cathodes after 500 cycles in d,e) 0.1 M and f,g) 1.0 M electrolytes; SEM images of cycled Li metal anodes after 500 cycles in h.i) 0.1 M and j,k) 1.0 M electrolytes. The yellow dotted circles in (g) indicate the uneven shuttle deposition of lithium polysulfides. Reprinted with permission from Ref 27. Copyright © 2022 Wiley - VCH GmbH.

Through MD simulations (Figure 4a), Wu et al. [28] found that in LCE (0.1 mol $L^{-1}$ of LiTFSI in DME-DOL with 1 wt. %$LiNO_3$), $Li^+$ bridged $Li_2S_2$ into large particles dispersed in the electrolyte, thereby preventing the dissolution of short-chain polysulfides into the electrolyte. As shown in Figure 4b and 4c, $Li_2S_2$–$Li_2S_4$ clusters are formed by participating in the aggregation of $Li_2S_2$ particles, which simultaneously reduces the diffusion rate of $Li_2S_2$ and $Li_2S_4$ (compared with conventional concentrated electrolytes). In addition to its significantly low viscosity and exceptional wetting characteristics on sulfur cathodes, the utilization of LCEs in carbon-sulfur cathodes has demonstrated superior rate capability and enhanced cell stability. Notably, these improvements are evident in terms of both capacity retention and the absence of charge transfer resistance growth, surpassing the performance observed in standard 1 M or concentrated electrolyte systems. Chu et al. [27] also confirmed less solubility of short-chain polysulfide ($Li_2S_2$) in 0.1 M electrolyte. The graphene-sulfur (G-S) composite cathode and LMA after cycling in LCEs exhibited suppressed polysulfide shuttle effects and electrolyte-lithium anode interface issues under low-temperature conditions. Conversely, the G-S cathode using a 1M electrolyte showed uneven deposition of lithium polysulfides (Figure 4d-k).

Fluorinated solvents, particularly perfluorinated solvents, exhibit higher steric hindrance and weaker association with polysulfides compared to nonfluorinated solvents (Figure 5a,b), owing to the higher electronegativity and larger van der Waals radius of fluorine atoms [57, 58]. Consequently, electrolytes incorporating fluorinated solvents as co-solvents demonstrate limited solubility for polysulfides.

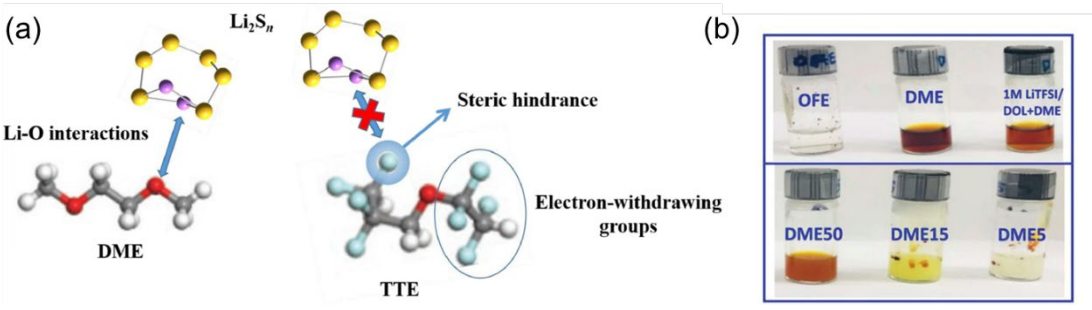


**Figure 5.** (a) Schematic diagram of the interaction between the lithium polysulfide and DME or fluorinated ether. Reprinted with permission from Ref 58. Copyright © 2019 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved. (b) Digital photos for saturate Li2S8 in different solutions after 2 weeks standing; The darker the color, the higher the solubility of the polysulfide. Reprinted with permission from Ref 57. Copyright © 2019 WILEY‐VCH Verlag GmbH & Co. KGaA, Weinheim.

Glaster et al. [59] conducted a systematic investigation on the influence of fluorinated solvents in local low-concentration electrolytes (LLCEs) on battery discharge behavior. By increasing the proportion of HFE in sulfolane /HFE mixed solvents, the formation of long-chain polysulfides from sulfur was significantly suppressed, resulting in reduced polysulfide dissolution. In comparison to DME/DIOX electrolytes, LLCEs displaye higher capacities due to their lower viscosity, improved wettability, and reduced polysulfide solubility.

The development of low-temperature lithium-sulfur batteries (LSBs) has been impeded by challenges such as hindered planar $Li_2S$ growth, lithium polysulfide (LiPS) conversion issues, and poor stability of the anode, leading to poor sulfur utilization and inferior cycling performance. Recently, LCEs have emerged as a promising solution for addressing the aforementioned issues. According to growth pattern analyses by both morphology observation and theoretical models, Guan et al. [23] discovered that in low-concentration electrolytes (LCEs), $Li_2S$ nucleation transitions to a progressive mode with fewer initial nuclei. This transition promotes the vertical growth of $Li_2S$ and facilitates a more thorough lithium-sulfur conversion reaction under cold conditions

(Figure 6a). In contrast, $Li_2S$ in the 1M electrolyte tends to form a greater number of initial nuclei, resulting in smaller grains and a thinner deposition layer at the end of the process (Figure 6b).

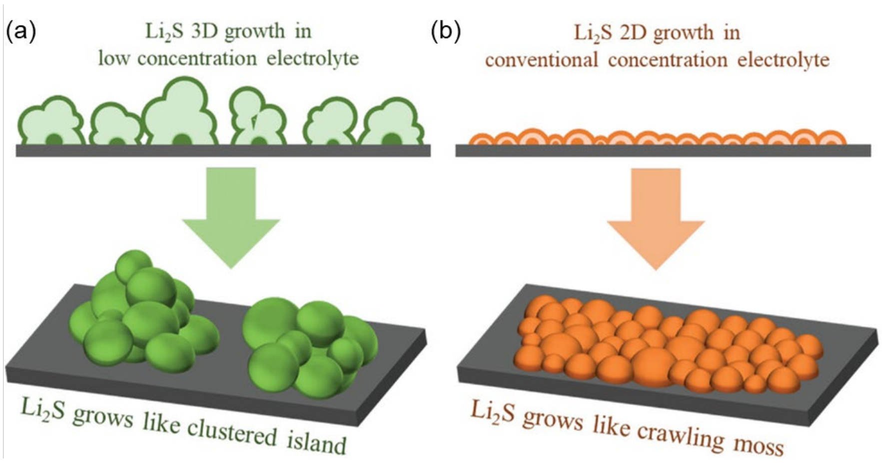


**Figure 6.** The sectional and 3D schematic diagrams of $Li_2S$ growth with different initial nuclei density in (a) low and (b) conventional concentration electrolytes. Reprinted with permission from Ref 23. Copyright © 2023 Wiley - VCH GmbH.

Moreover, it should be noted that the reduction of salt concentration does not necessarily result in a loss of film-forming capability. A investigation revealed that even electrolytes with salt concentrations as low as 0.1 M are capable of reproducing the composition of CEI formed in electrolyte compositions with higher concentrations (1 M and 3 M) [60]. The sulfur cathode surface with the LCE composed of 0.05 M $LiPF_6$ and 0.05 M LiTFSI contains a substantial amount of LiF, along with a significant presence of $Li_3N$, a compound crucial for effective electrode protection. Furthermore, LCEs exhibite comparable capacities and hysteresis to those of 1 M LiTFSI electrolytes, implying that salt concentrations higher than 0.1-0.2 M may incur unnecessary increases in both electrolyte weight and cost.

In terms of the lithium deposition behavior, a previous study showed that conventional ether-based electrolytes exhibit poor film-forming performance on LMAs under low-concentration conditions [61]. Spectral analysis and corresponding theoretical calculations reveal that LCEs possess a higher abundance of SSIPs, resulting in an unstable SEI layer primarily composed of decomposition products from organic solvents. Through repeated plating/stripping processes, LMAs in LCEs display mossy and porous lithium deposits as shown in Figure 7a, along with pronounced dendritic structures. Conversely, electrolytes with relatively higher concentrations can exhibit uniformly distributed lithium deposits that are parallel to the lithium substrate, accompanied by smaller volume expansion. However, the low-concentration effect enables rapid kinetics during charge transfer processes. This is attributed to the relatively lower binding energy of SSIP ion-solvent complexes (Figure 7b,c), which reduces the energy barrier for the $Li^+$ de-solvation process in LCEs. Therefore, compatibility of LCEs with of both cathode and anode should be considered.

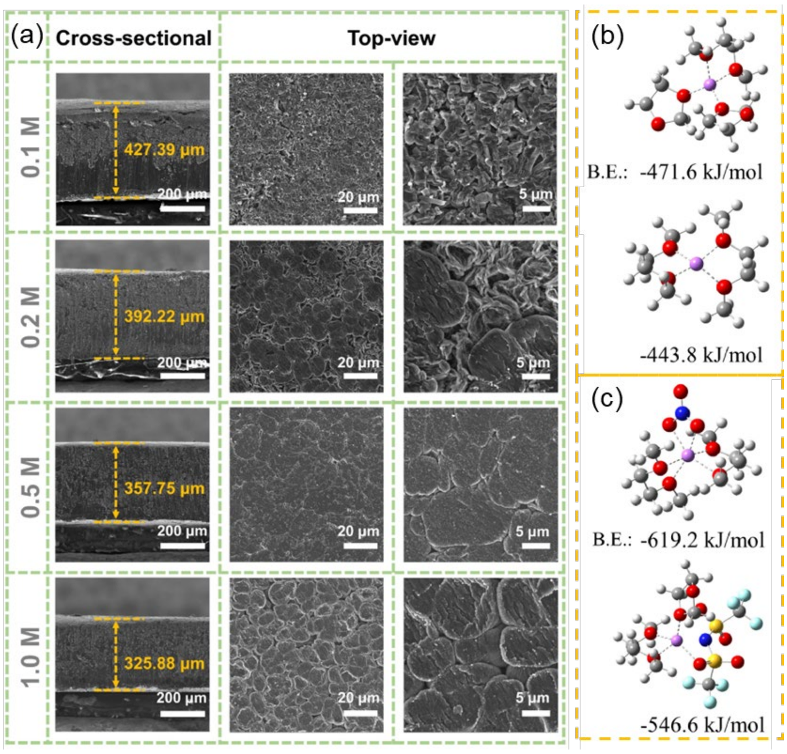


**Figure 7.** (a) Morphology characterization of cycled Li metal anodes in different electrolytes: SEM morphology evolution of deposited lithium metal with various scales from the top view and cross-section view, displaying various surface morphology and different thickness variations of lithium deposition after 30 cycles. Representative Li-solvation structures with their predicted binding energy in (b) 0.1 M and (c) 1.0 M electrolytes. Reprinted with permission from Ref 61. 

In practical applications of lithium-sulfur batteries, meeting the requirements of high cathode loading and low E/S ratio is essential. In this regard, LCEs offer significant advantages owing to their favorable wettability toward separator and electrode and low viscosity. If LCEs can ensure low polysulfide solubility and favorable film-forming capability, they hold promising potential for employment in lithium-sulfur batteries.

**3.3 Other solvents**

Based on the observations above mentioned, modification of the solvation structure holds potential for optimizing the composition of SEI/CEI, lowering the energy barrier for $Li^+$ desolvation, and improving the oxidation stability of electrolytes. Moreover, optimized solvation structure enables LCEs display higher working voltage, wider working temperature ranges, and enhanced fast charging performances. Currently, numerous studies are focused on the design of novel electrolyte systems to address the limitations associated with LCEs.

Ionic liquids (ILs) have garnered significant attention in the field of LIBs due to their advantageous, including non-volatility, non-flammability, wide electrochemical stability window, and strong solvation capabilities [62-64]. Furthermore, certain IL-based electrolytes have been found to facilitate the formation of SEI on electrode surfaces through cation and/or anion decomposition [63, 65]. Considering high viscosity associated with ILs, the utilization of ILs in LCEs is another effective approach.

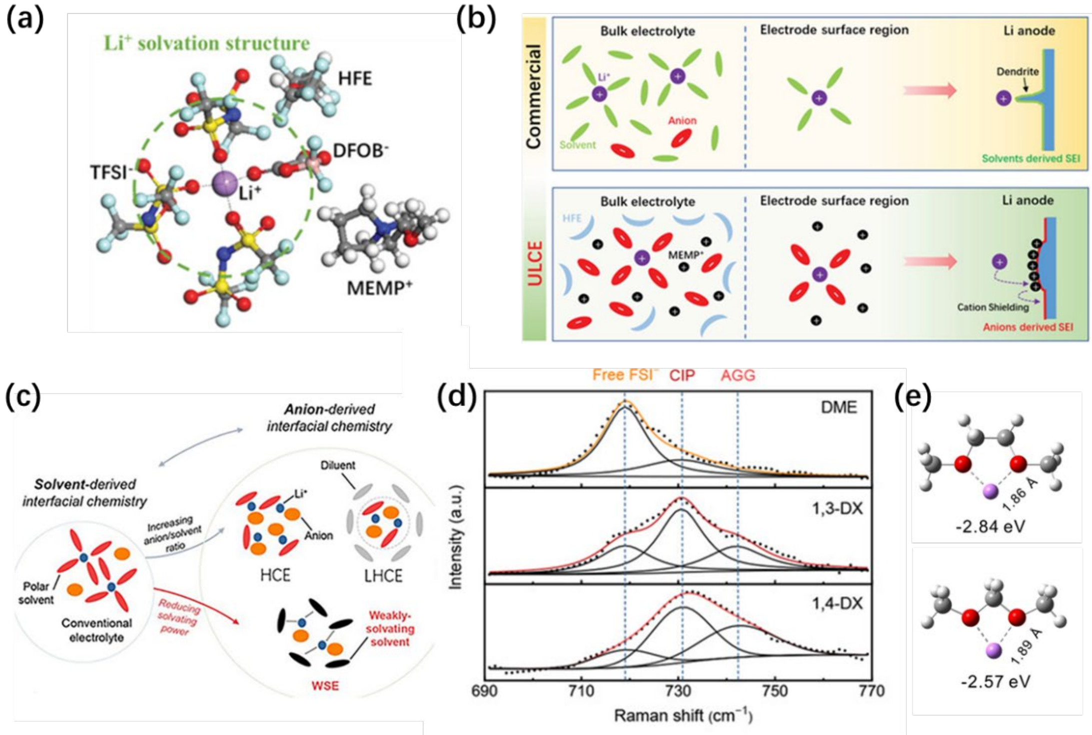


**Figure 8.** (a) Typical $Li^+$ solvation structure in ULCE extracted from MD simulation snapshot; (b) Schematic illustrations of the solvation structure and electrode surface chemistry of commercial electrolyte and ULCE. Reprinted with permission from Ref 66. Copyright © 2022 Wiley - VCH GmbH. (c) The solvation structures of high-concentration electrolyte (HCE), localized high-concentration electrolyte (LHCE), and weakly solvating electrolyte (WSE); (d) Raman spectra of 1.0 M LiFSI dissolved in DME and weak solvating solvents (1,3-dioxane, denoted as 1,3-DX, and 1,4-dioxane, denoted as 1,4-DX); Reprinted with permission from Ref 67. Copyright © 2020 Wiley - VCH GmbH. (e) The binding energies of Li+-solvent complex. up: Li+-DME; down: Li+-weak solvating solvent dimethoxymethane. Reprinted with permission from Ref 69. Copyright © 2022 Wiley - VCH GmbH.

The addition of fluorinated ether inert diluents to HCEs has proven effective in addressing challenges such as elevated viscosity and reduced ionic conductivity [17, 18]. This approach can also be applied to resolve similar issues encountered in ILs. It has been proposed to incorporate an HFE diluent into the 0.1 M LiDFOB ultra-low-concentration ionic liquid ([MEMP][TFSI]) electrolyte (ULCE) [66]. The resulting electrolyte exhibits desirable characteristics such as non-flammability, cost-effectiveness, wide operating temperature range, and excellent electrochemical stability. Notably, the unique solvation structure of ULCE contributes to the formation of anion-derived SEI films and uniform lithium deposition behavior on the LMA. Figure 8a depicts a schematic diagram of the $Li^+$ solvation structure in ULCE. In this structure, $Li^+$ are predominantly coordinated with $DFOB^-$ from the Li salt and $TFSI^-$ from the [MEMP][TFSI] ionic liquid, while the $[MEMP]^+$ cations do not actively participate in solvating the $Li^+$ sheath. When solvated $Li^+$ migrate to the electrode surfaces, $DFOB^-$ and $TFSI^-$ preferentially decomposed, resulting in the formation of the SEI on the LMA. Importantly, under the influence of the electric field, $MEMP^+$ cations also migrate to the LMA surface, acting as an electrostatic shield and enabling even distribution of $Li^+$ flow on the electrode surface (Figure 8b). Consequently, compared to the pronounced growth of Li dendrites observed in commercial carbonate electrolytes, the combined effects of a robust anion-derived SEI and cation shielding in ULCE effectively suppress Li dendrite growth. As a result, ULCE exhibits an average CE of approximately 99% in Li/Cu cells and demonstrates stable cycling performance in Li/Li symmetric cells.

The concept of weakly solvated electrolytes (WSEs) as potential electrolytes in LIBs has emerged as a subject of significant interest [67]. WSE solvents possess a reduced solvating capacity, which promotes a transition from solvent-driven interfacial chemistry to anion-driven interfacial chemistry (Figure 8c). In essence, as the solvating ability of the solvent diminishes, anions gradually replace the solvent in the primary solvating sheath (Figure 8d). Consequently, the resulting anion-derived SEI/CEI is governed by the distinctive solvation structure, thereby exhibiting excellent charge transport kinetics and high stability at the electrode interface [68]. Furthermore, WSEs exhibit a low energy barrier for desolvation (Figure 8e), enabling favorable cycling performance even at low temperatures [69]. By carefully selecting an appropriate weak solvation solvent, solvation structures similar to those observed in HCEs can be achieved at lower salt concentrations.

A low-concentration bisalt electrolyte (LBE) is prepared by dissolving a 0.5 M dual-salt (LiFSI\LiTFSI) in the weakly solvating solvent 1,4-dioxane (DX) [70]. The molecular dynamics simulation results demonstrate that the 87% of salt anions ($FSI^-$ and $TFSI^-$) exist in an ion-associated state, while the remaining 13% are free anions. This observation indicates a strong coordination between $Li^+$ ions and the salt anions ($FSI^-$ and $TFSI^-$) within the LBE system. This solvation structure facilitates the involvement of anions in decomposition processes, leading to the formation of an interfacial film rich in inorganic components. Such a film enhances the diffusivity of $Li^+$ ions and mitigates undesired side reactions between the electrodes and electrolytes, enabling the Li||LFP cell with a capacity retention of 78.5% after 400 cycles.

Examples of LCEs in this paper are listed in **Table 1**. Caution should be taken when comparing performance due to the inherent non-comparability of results across varying chemistries and cell designs. Carbonate-based LCEs, due to their relatively higher oxidation stability, can be applied to most layered oxides cathode materials. The regulation of the formulation improves their compatibility with lithium metal, although there is still some distance from practical applications. Ether-based electrolytes, with poorer oxidation stability, are primarily used in Li-S and organic batteries. While the reduction in salt concentration diminishes the solubility of polysulfides, thereby suppressing the shuttle effect of polysulfides, it also exacerbates the parasitic reactions between the electrolyte and the lithium metal anode. Therefore, novel solvents and/or electrolyte addictives are needed for further widen the potential applications of LCEs.

## Table 1. LCEs with all types of solvents

| | Electrolyte formulation | Cell system | Capacity (mAh $g^{-1}$) or Capacity retention/current density or C rate/Temperature (°C) | CE of Li‖Cu cell | Cycle voltage range/Cell system | Operating Temperature(°C) | Ref. |
|---|---|---|---|---|---|---|---|
| Carbonate-based solvents | 0.2M LiPF6 in EMC:FEC 1:1 by volume | Li‖$LiCoO_2$ | 91.1% after 300 cycles/0.5 C/25℃ | 95.40% | 2.8-4.4V/Li‖LCO | 25~45 | [41] |
| | 0.1 M LiDFBOP + 0.4 M LiBOB and 0.1 M LiDFBOP + 0.2 M LiBOB + 0.2 M $LiPF_6$ in PC:FEC:EMC 5:3:2 by volume | Li‖NMC712 | 140mAh $g^{-1}$ and 146 mAh $g^{-1}$ after 10 cycles/0.5C/-25℃ | 98%&97.7% | 2.8-4.3V/Li‖NMC712 | -25~70 | [50] |
| | 0.1 M LiDFP and 0.4 M LiBOB, LiFSI, or LiTFSI in EC:DMC 3:7 by weight ratio | Li‖$LiFePO_4$ | 95.4% after 300cycles (LiDFP-LiBOB)/2.0 mA cm-2/25℃ | 97.6%&94.5%&93.6% | | | [16] |
| | 0.3 M LiDFOB and 0.2 M $LiBF_4$ in DEC/FEC/FB 3.5:1.5:5 by volume | Li‖$LiCoO_2$ | 85.6% after 120 cycles/1.0 mA cm-2/25℃ | 98.30% | 3-4.6V/Li‖LCO | -20~25 | [31] |
| | 0.4M $LiPF_6$ EC:DMC:TTE 1:1:4 by volume | Li‖$LiFePO_4$ | 122.8 mAh $g^{-1}$/5C/25℃ | | 2.8-4.3V/Li‖NMC811 | | [32] |
| Ethers-based solvents | 0.1 M LiTFSI in DME:DOL 1:1 with 1 wt. %$LiNO_3$ | Li‖CC-S | 95% after 200 cycles/0.5C/25℃ | | | | [28] |
| | 0.1 M LiTFSI in DME:DOL 1:1 with 1 wt. %$LiNO_3$ | Li‖G-S | 900mAh $g^{-1}$ after 200 cycles/0.1C/0℃ | | | | [27] |
| | 0.1 M LiTFSI, 0.05 M LiTFSI + 0.05 M $LiPF_6$ and 0.1 M $LiPF_6$ in DME:DOL 1:1 with 1 wt. %$LiNO_3$ | Li‖S/KB | 70% after 200 cycles/0.2C/25℃ | | | | [60] |

<table>
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<tr><td></td><td>0.1 M LiFSI in DME:DOL 1:1 with 1 wt. %$LiNO_3$</td><td>Li||S/KB</td><td>400mAh $g^{-1}$ after 100 cycles/0.5C/-20°C/2.3mg cm-2(cathode mass loading)</td><td></td><td></td><td>-20</td><td>[23]</td></tr>
<tr><td></td><td>0.1-1 M LiTFSI in DME:DOL 1:1 with 1 wt. %$LiNO_3$</td><td></td><td></td><td></td><td></td><td></td><td>[61]</td></tr>
<tr><td></td><td>0.1 M LiTFSI in Sulfolane:HFE 1:1-1:10</td><td>Li||S-KB</td><td>about 1200 mAh $g^{-1}$/0.1C/25℃</td><td></td><td></td><td></td><td>[59]</td></tr>
<tr><td>Other solvents</td><td>0.1M LiDFOB in [MEMP][TFSI]:HFE 1:1 by volume</td><td>Li||NMC622</td><td>96% after 100 cycles/0.2C/25℃</td><td>~99%</td><td>2.8-4.5V/Li||NMC622</td><td>-60~70</td><td>[66]</td></tr>
<tr><td></td><td>0.5 M LiFSI\LiTFSI in 1,4-dioxane</td><td>Li||LFP</td><td>78.5% after 400 cycles/0.5C charge-1C discharge/25℃</td><td>99.20%</td><td></td><td>25~50</td><td>[70]</td></tr>
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## 4. Conclusion and Outlook

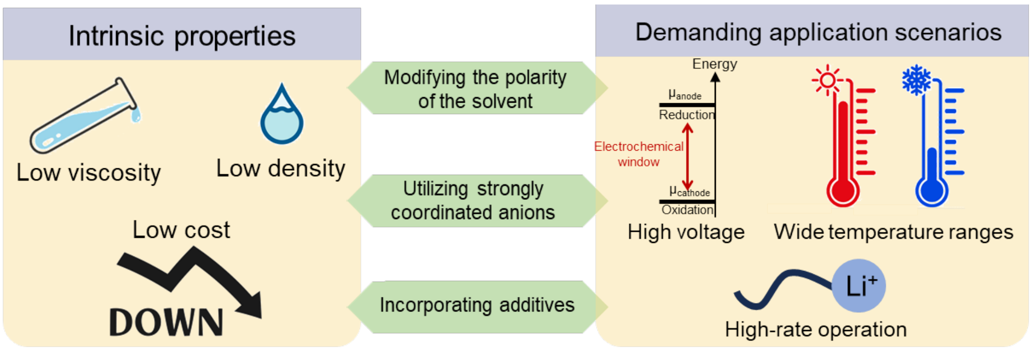


**Figure 9.** Summary of low concentration electrolyte design in Lithium batteries.

LCEs have gradually attracted attention in research for their advantages such as low cost, low density, and low viscosity. However, their application in lithium batteries has encountered challenges primarily attributed to their low ionic conductivity and limited interfacial stability. By modifying the electrolyte composition to adjust the solvation structures of $Li^+$, the electrochemical properties of the electrolytes can be improved. This article demonstrates various approaches employed by researchers to alter the solvation structure in LCEs, including modifying the polarity of the solvent, utilizing strongly coordinated anions, and incorporating additives. These approaches enable LCEs to adapt to demanding application scenarios characterized by high voltage, wide temperature ranges, and fast charging. Nevertheless, it is important to note that LCEs still possess certain limitations:

Safety is a critical concern in the commercialization of LIBs, particularly regarding the electrolytes employed. The successful commercialization of electrolytes necessitates a high level of reliability and safety assurance. The use of flammable solvents, such as carbonates, in LCEs poses greater safety risks due to the substantial proportion of solvents present.

Another aspect to consider is the environmental performance of the electrolytes. To promote the formation of inorganic-rich interfacial films, fluorinated solvents and salts containing fluorine groups are commonly employed in the electrolyte formulation. While efforts have been made to update fluorinated solvents for different battery chemistries, their potential environmental impact throughout the production, storage, application, and recycling processes has often been overlooked. The degradation behavior of fluorinated organics differs significantly from that of non-fluorinated organic compounds. For instance, highly fluorinated molecules exhibit exceptional structural stability, making them resistant to environmental degradation. As a result, greater attention should be directed towards the use of fluorine-containing solvents during manufacturing processes and their subsequent recycling to mitigate the severity of fluorine pollution.

The interphasial mechanism of anode/cathode materials in LCEs should be investigated. Although it has been widely accepted that solvation structure directly effects the composition of SEI/CEI and formation of “good” SEI/CEI is also essential for improving overall performances of battery system, especially at the extreme conditions. However, there is still no clear picture about how a “good” SEI/CEI forms and what the difference of CEI/SEI formed in LCEs comparing with conventional of high concentration electrolyte systems. The previous discoveries clarified that LiF is a critical component for “good” SEI/CEI of LIBs. However, in the previous work published by Hu et al. [20] proposed a controversial conclusion that the enhanced low temperature performances of sodium ion battery are attributed to the formation of organic-dominant SEI. Therefore, it still requires the development of advanced characterization techniques together with theoretical calculation for understanding the interphasial mechanism in LCEs.

Organic materials are promising candidates for next-generation secondary batteries due to their tunable structure, molecular diversity and fast charging kinetics comparing with TM-based layered cathodes. However, most of organic materials processes poor electronic conductivity, especially in the high active materials loading configuration. Typically, large amount of carbon sources is used for enhancing electronic conductivity to improve the utilization of active material. Therefore, the wettability of LCEs toward not only the separator but also the high loading electrodes should be optimized. As mentioned in the previous section, dual-salt strategy effectively improves the interphasial stability at both anode and cathode sites. However, the salt composition should be carefully screened to balance the film-forming capability and wettability of electrolytes.

The application of LCEs in the extreme condition such as fast charging and low/high temperature is still needed to be examined. In addition, the feasibility of using LCEs in practical application, especially for high energy pouch cell testing should be also confirmed. More importantly, compatibility of LCEs with Ni-rich NMCs, Li-rich cathodes, those demonstrate high energy density, should be also investigated.

In conclusion, future research efforts should be directed towards investigating a wider variety of solvents that possess characteristics such as non-flammability, environmental friendliness, wide electrochemical windows, and high dielectric constants. Additionally, the development of high-performance additives that can effectively coordinate with LCEs holds promise for enhancing their overall performance.

**Author contributions**

Z.S., E.H. and J.Z. co-organized this work and are responsible for the overall work; L. L., Z. S. and N.W. drafted this paper; Y.C. and X.C. revised and enriched the content of the paper. All authors have read and agreed to the published version of the manuscript.

**Competing financial interests**

The authors declare no competing financial interests.

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