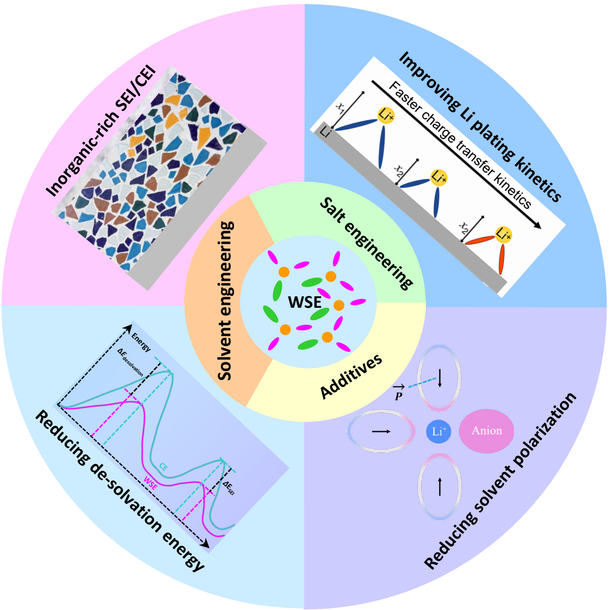
Energy Materials and Devices

Review

Weakly solvating electrolytes for next-generation lithium batteries: design principles and recent advances

Zhijie Wang and Biao Zhang ✉

Graphical Abstract



The emerging weakly solvating electrolytes (WSEs) have attracted intensive research interests in recent years. This contribution reviews the working mechanisms, design principles, and recent advances in developing WSEs. A summary and perspective about future research directions in this field is also provided. The insights will benefit both academic and industrial communities in designing safe and high-performance next-generation Li batteries.

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Received: August 3, 2023
Revised: August 21, 2023
Accepted: August 23, 2023

https://www.sciopen.com/journal/3005-3315

https://mc03.manuscriptcentral.com/emd

Citation: Wang Z., Zhang B. Weakly solvating electrolytes for next-generation lithium batteries: design principles and recent advances. *Energy Mater. Devices*, 2023, 1, 9370003. https://doi.org/10.26599/EMD.2023.9370003

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Review https://doi.org/10.26599/EMD.2023.9370003

Weakly solvating electrolytes for next-generation lithium batteries: design principles and recent advances

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Received: August 3, 2023 / **Revised:** August 21, 2023 / **Accepted:** August 23, 2023

ABSTRACT

Lithium (Li) batteries are major players in the power source market of electric vehicles and portable electronic devices. Electrolytes are critical to determining the performance of Li batteries. Conventional electrolytes fall behind the ever-growing demands for fast-charging, wide-temperature operation, and safety properties of Li batteries. Despite the great success of (localized) high-concentration electrolytes, they still suffer from disadvantages, such as low ionic conductivity and high cost. Weakly solvating electrolytes (WSEs), also known as low-solvating electrolytes, offer another solution to these challenges, and they have attracted intensive research interests in recent years. This contribution reviews the working mechanisms, design principles, and recent advances in the development of WSEs. A summary and perspective regarding future research directions in this field is also provided. The insights will benefit academic and industrial communities in the design of safe and high-performance next-generation Li batteries.

KEYWORDS

weakly solvating electrolytes, solvation structure, salt design, solvent engineering, lithium batteries

1 Introduction

Lithium (Li) ion batteries (LIBs) have revolutionized modern life[1]. These batteries have achieved great commercial success in the last 30 years, but their energy density has been approaching its theoretical limit[2]. In addition, the current LIB configuration cannot meet the ever-growing demand for batteries with high safety, long lifespan, fast-charging capability, and broad temperature adaptability[3, 4]. Li metal batteries (LMBs) use metallic Li directly as the anode, and they have attracted intensive research interests in recent years because of their energy density, which can be boosted up to 500 Wh kg^{-1}, which is more than twice that of LIBs[5]. However, LMBs currently face challenges, including Li dendrite growth, unstable Li–electrolyte interfaces, and safety hazards, which hinder their practical applications[6, 7].

Electrolytes play a critical role in determining the electrochemical performances of LIBs and LMBs[8]. The commercialization of LIBs was marked by the invention of ethylene carbonate (EC)-based electrolytes[1]. Nevertheless, these electrolytes are nonfunctional at low temperatures mainly because of the high melting point of EC (over 34℃). In addition, unlike in graphite anode, they cannot form a stable solid–electrolyte interphase (SEI) on Li metal anode[9]. On the contrary, ether electrolytes were initially excluded from LIBs because of their low volatility and flammable nature[10]; however, they are thermodynamically more stable against Li than their carbonate-based counterparts and therefore show more promise for use in LMBs[11].

The solvation structure determines the electrochemical performance of electrolytes[12]. Conventional electrolytes (CEs) feature highly dissociated Li salts (typically $LiPF_6$)[13] and an electrolyte solvation sheath occupied by solvent molecules (Fig. 1). This condition leads to a high desolvation energy, but the low-temperature and rate performance are sacrificed[14]. The decomposition of solvated solvent molecules results in the formation of organic-rich SEI and cathode–electrolyte interphase (CEI), which

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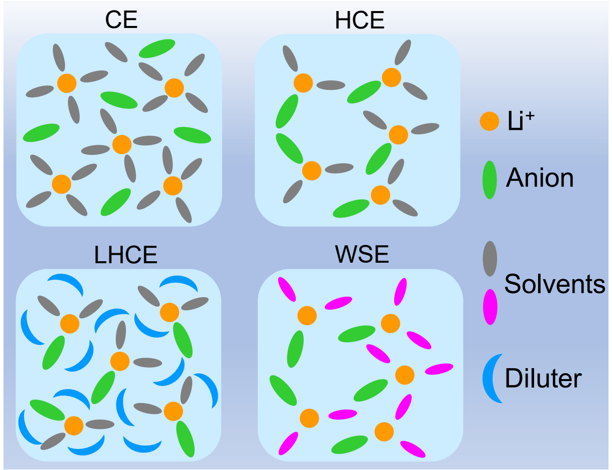

Figure 1 Schematic illustration of the solvation structures of CEs, HCEs, LHCEs, and WSEs.

exhibits sluggish Li^+ conduction kinetics[15]. To address these issues, researchers developed high-concentration electrolytes (HCEs)[10, 16], in which solvent molecules and anions participate in Li^+ solvation sheaths. This solvation structure can reduce the activity of solvent molecules, construct anion-derived inorganic SEI/CEI, and widen the electrochemical window; however, it also has drawbacks, such as high viscosity and poor wettability. The introduction of nonsolvating solvents (normally hydrofluoroethers) as dilutes in HCEs can be used to prepare localized high-concentration electrolytes (LHCEs)[17, 18], which can effectively reduce viscosity and improve wettability while preserving the anion-participated solvation structure. However, LHCEs suffer from low ionic conductivity because the Li^+ solvation sheaths are capsuled by the diluents, and their mobility speed is limited. In addition to HCEs and LHCEs, weakly solvating electrolytes (WSEs), also known as low-solvating electrolytes, offer another strategy for improving the electrochemical performance of LIBs and LMBs. The solvation sheaths of WSEs contain the solvent and anion that coordinate with Li^+ via weak interactions (Fig. 1). Compared with HCEs, WSEs at dilute conditions enable the formation of an anion-rich solvation structure, which reduces viscosity. Compared with LHCEs, the solvation process of WSEs (without using nonsolvating diluents) involves the participation of all solvents, which improves ionic conductivity. Therefore, WSEs can deliver superior electrochemical performance in LIBs and LMBs.

This paper aims to review the design strategies and recent advances in the development of WSEs for Li batteries, including LIBs and LMBs. First, the four functions of WSEs in the improvement of electrochemical performance are summarized. Then, the design principles of WSE development, including salt, solvent, and additive engineering, are discussed. Finally, a comprehensive summary and perspective are provided to guide future research directions. The insights will help the academic and industrial communities in the design of safe, long-lifespan, and high-energy-density Li batteries.

2 Function of WSEs

2.1 Lowering the desolvation energy

The migration of Li^+ in batteries occurs in four steps: the migration of solvated Li^+ in the bulk electrolyte, the desolvation process of solvated Li^+, the transport of naked Li^+ in SEI/CEI, and the diffusion of Li^+ in electrode materials[19]. The speed of these steps can be affected by factors, including the thickness and porosity of electrodes, particle size of active materials, and operating temperatures. Therefore, Li^+ migration kinetics is complicated in real working conditions. At the current stage, the desolvation process consumes the most energy and is considered the rate-determining step[20], especially in fast-charging and low-temperature applications. In WSEs, given the weakened Li^+–solvent interaction, the energy barrier for the desolvation process of solvated Li^+ is greatly reduced compared with that in CEs (Fig. 2a). Therefore, the rate performance and low-temperature adaptability of Li batteries could be boosted.

2.2 Construction of inorganic-rich electrode–electrolyte interphases

The SEI/CEI diffusion process is also important. Li^+ diffusion through the SEI may play a more critical role than desolvation in realizing fast kinetics under some circumstances[21]. The anion-solvated Li in WSEs migrates to the anode and cathode surfaces. Anions can decompose to form inorganic SEI/CEI species, including Li_2O and LiF. These inorganic species possess higher ionic conductivity, lower electric conductivity, and higher modulus than solvent-derived organic ones. On the anode side, the inorganic-rich SEI can reduce the energy barrier for Li^+ transport, suppress the dendritic growth of Li, and passivate the electrodes from the side reaction with the electrolyte. On the high-voltage layer-oxide cathode side, it can alleviate active element loss, suppress oxygen gas release, and prevent the attack of charged high-valence elements in electrolytes (Fig. 2b). Therefore, the safety properties and lifespan of Li batteries can be improved.

2.3 Reducing the polarization degree of solvated solvent molecules

In the solvation sheaths of CE, the polarization of solvent molecules occurs due to the electrostatic Li^+ (Fig. 2c). The solvent molecules have negatively charged inner sides (close to Li^+) and positively charged outer sides. The sites with induced positive

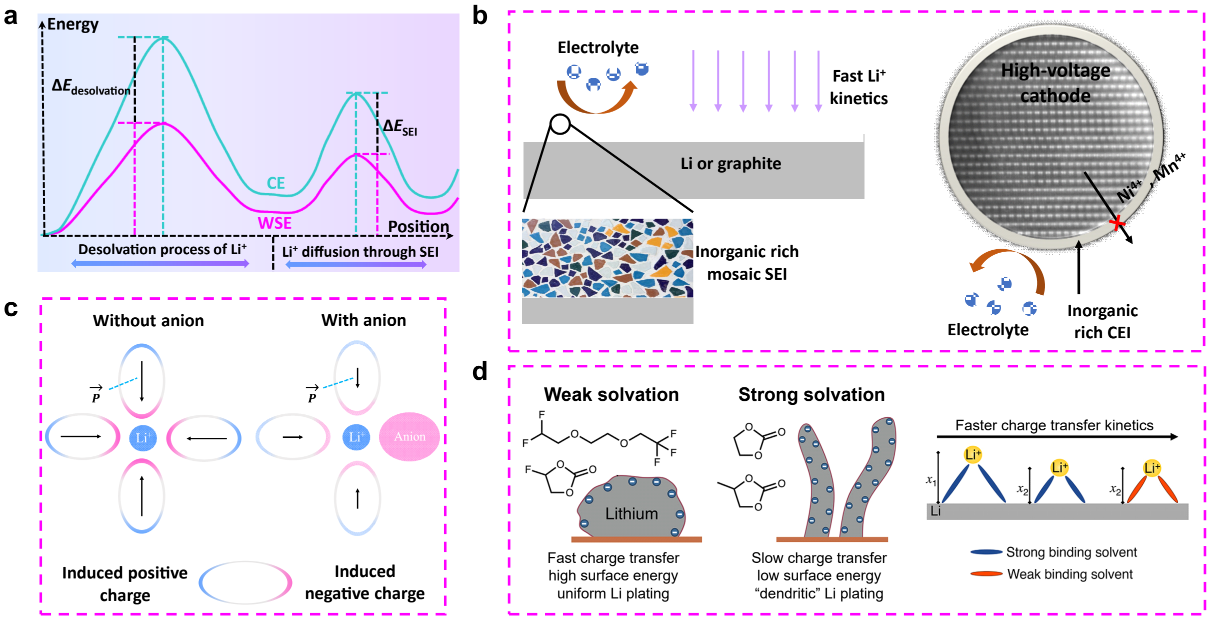

Figure 2 Functions of WSEs. (a) Reduction of desolvation and SEI diffusion energy barriers. Reproduced with permission[25]. Copyright 2023, American Chemistry Society. (b) Construction of inorganic-rich SEI and CEI. (c) Reduction of the polarization degree of solvated solvent molecules. Reproduced with permission[26]. Copyright 2022, the authors. (d) Regulation uniform Li deposition. Reproduced with permission[23]. Copyright 2022, American Chemistry Society.

charge exhibit increased regional electrophilicity and are thus susceptible to accepting electrons and decomposing on the anode surface[22]. In WSEs, anions participate in solvation sheaths, which can reduce the polarization degree of solvent molecules and lower their possibility of electron acceptance. Therefore, WSEs possess a thermodynamically more stable solvent than CEs, which minimizes the consumption of electrolytes and reduces the levels of unstable solvent-derived organic SEI species.

2.4 Improvement of Li plating kinetics

Boyle et al. proposed a different insight into the relationship between the solvation structure and Li plating kinetics. They reported that the reversibility of the Li plating/stripping process is more strongly correlated with the intrinsic exchange current density (j_0^{ct}) of charge transfer at the fresh Li–electrolyte interfaces than interfacial resistance; in addition, the rapid ion diffusion through the SEI is not the main cause of uniform Li plating[23, 24]. They pointed out that a weak solvation structure increases the j_0^{ct}, drives the Li/Li$^+$ equilibrium potential to reach more positive values, and improves Li surface energies, which create more favorable conditions for uniform Li plating and high Li reversibility. They also suggested the potential of screening fluorinated solvents to improve j_0^{ct} for the development of WSEs.

3 Strategies for designing WSEs

3.1 Basic principles

The main principle of WSE design is the tuning of the interaction strength of Li$^+$–solvent and Li$^+$–anion. CEs exhibit a considerably larger electrostatic force between Li$^+$ and the solvent ($f_{\mathrm{Li^+-solvent}}$) compared with that between Li$^+$ and the anion ($f_{\mathrm{Li^+-anion}}$). In the case of weakly solvating solvents, ($f_{\mathrm{Li^+-solvent}}$) decreases and reaches a balance with ($f_{\mathrm{Li^+-anion}}$), and a solvent-regulated WSE forms. Inversely, when low-dissociation Li salts are used, the ($f_{\mathrm{Li^+-anion}}$) increases, and the solvents are "pushed" away from Li$^+$ in the solvation sheaths. Thus, an anion-regulated WSE can also be achieved in this case (Fig. 3a)[27].

Gutmann donor number (DN) can be used to assess the attraction capability of solvents or anions to Li$^+$ (Fig. 3b)[28, 29]. Li salts with a high anion DN (such as lithium chloride, LiCl) do not show promise in the development of WSEs because they are hard to dissolve/dissociate. Meanwhile, Li salts with a moderate anion DN, such as lithium bis(trifluoromethanesulfonyl)imide (LiFSI), lithium triflate (LiOTF), and lithium nitrite ($LiNO_3$), are the most popular candidates. Li salts with a low anion DN, such as $LiPF_6$ and $LiBF_4$, are highly dissociated and can be used in WSEs but only under relatively high-concentration conditions or when paired with low-solvation fluorinated solvents[27, 30]. The screening of solvents with a suitable DN is also critical in the improvement of WSEs. Low-DN solvents cannot dissolve or dissociate Li salts, whereas those with a high DN can strongly dissociate Li salt and solvated Li$^+$ and are thus more likely to result in solvent-dominated solvation structures. When solvents and salt anions have comparable DNs, the attraction between the solvent molecules and Li$^+$ can reach a delicate balance

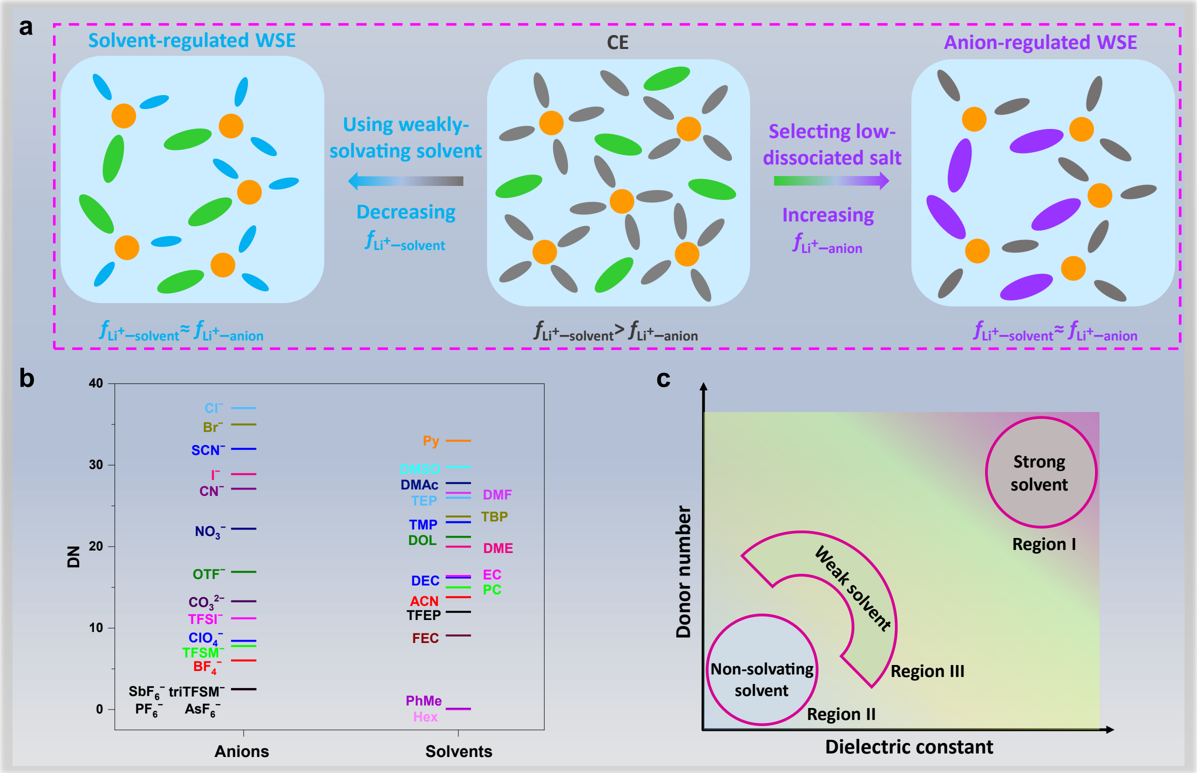

Figure 3 Design principles for WSEs. (a) Schematic illustration of salt and solvent engineering for WSE development. Reproduced with permission[27]. Copyright 2023, John Wiley. (b) Gutmann DN of common anions and solvents. Reproduced with permission[26]. Copyright 2022, the authors. (c) Schematic illustration of the distributions of strong, weak, and nonsolvating solvents.

compared with that between anions and Li^+, and an anion-participated solvation structure can be obtained at diluted salt concentrations[26]. Thus, partial dissociation of Li salts occurs. In addition to DN, the dielectric constant (ε) is a scaling factor used in solvent selection[31, 32]. Strong solvents have high DN and ε (region I in Fig. 3c) and high dissolving capacity and dissociating capability, and those with low DN and ε are nonsolvating solvents (region II in Fig. 3c) that cannot dissolve nor dissociate Li salts. Suitable candidates for the construction of WSE solely include solvents with moderate DNs and ε (region III in Fig. 3c), and they can be regarded as weak solvents or “soft” solvents[33].

DN and ε are experimental parameters and insufficient for the complete determination of the solvating power of solvents from a theoretical perspective. He’s groups recently reported that electrostatic potential (ESP) can compensate for such a deficiency and be used as a theoretical descriptor for screening solvents[34]. The absolute value of the lowest negative ESP ($|ESP_{min}|$) represents the solvating power of solvents, and the strong highest positive ESP (ESP_{max}) reflects the polarization of solvent molecules. If $|ESP_{min}|$ is substantially higher than ESP_{max}, then the solvent has a high, strong solvating power. By contrast, if $|ESP_{min}|$ is lower than ESP_{max}, then the solvent is nonsolvating and can be used as an antisolvent. Only solvents with an $|ESP_{min}|$ that is comparable with ESP_{max} and have a weak solvating power are suitable for the development of WSEs.

3.2 Salt engineering for the development of WSEs

The main strategies in this aspect include the utilization of Li salts with moderate anion DNs and the synthesis of novel salts.

$LiNO_3$ is a low-dissociation salt and has the advantages of low cost, low corrosivity, and anode film-forming function[35, 36]. This salt is widely used as an additive in ordinary ether electrolytes, in which NO_3^- coordinates with Li^+[37]. The wide application of $LiNO_3$ is due to the close DNs of NO_3^- and ordinary ether solvents, such as 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (Fig. 3b). Therefore, the ethers cannot fully dissociate $LiNO_3$ salt. Thus, $LiNO_3$ can be used to develop WSEs in ether solvents. In carbonate electrolytes, however, $LiNO_3$ has a solvability of as low as 10^{-5} g L^{-1}[38] mainly because of the notably higher DN of NO_3^- carbonate solvents. When small amounts of high-DN solvents, such as organic phosphates[39] and sulfones[40], are used as cosolvents, NO_3^- can be introduced to the solvation sheaths of carbonate-based electrolytes. However, these cosolvents normally contain high concentrations of $LiNO_3$, and the concept of this strategy is similar to that of LHCEs.

Other common low-dissociation salts include LiOTF, LiTFSI, lithium difluoro(oxalato)borate (LiDFOB), LiFSI, and lithium difluorophosphate (LiDFP). Although the accurate DNs of $DFOB^-$, FSI^-, and DFP^- anions have not been reported yet, they have been described to participate in the solvation process of Li^+ in diluted electrolytes[41, 42], which reflects their moderate DNs. Xia et al. proved that by utilizing 1 mol L^{-1} LiFSI as the signal salt, the stable cycling of graphite anode can be obtained in a DOL solvent[43]. The main mechanism is the formation of a weakly solvating solvation structure through the combination of LiFSI (a low-dissociation salt) and DOL (a soft solvent). In addition, the solvated FSI^- decomposes on the graphite surface and forms an F-rich SEI that can prevent the cointercalation of DOL into graphite (Fig. 4a). Similarly, Liu et al. introduced LiTFSI and $LiNO_3$ into the DOL solvent as dual salts and obtained a coordinating structure of $Li^+[DOL]_{10.26}[FSI^-]_{0.71}[NO_3^-]_{0.29}$[44]. An F-, N-, and S-containing inorganic-rich thin SEI was constructed on the graphite anode (Fig. 4b), and it showed a high ionic conductivity and can provide fast ionic transportation kinetics across the SEI. These designs prove that apart from HCEs, LHCEs, and fluorinated electrolytes, WSEs offer another solution to form a stable SEI on graphite anodes in ether electrolytes.

The development of new Li-dissociation salts is also an effective strategy. Sang et al. synthesized a class of benzenethiolate-based Li salts that can form an anion-dominated solvation structure in ether solvents at a standard concentration of 1 mol L^{-1} while maintaining a moderate ionic conductivity[45]. However, the electrolyte exhibited a low oxidation voltage of 2.6 V. Min et al. developed a high-voltage lithium difluoro (1,2-dihydroxyethane-1,1,2,2-tetracarbonitrile) borate salt (LiDFTCB), which is a novel cyano-functionalized analog of LiDFOB (Fig. 4c)[46]. The severe salt decomposition was alleviated in the LiDFTCB electrolyte, and a thinner SEI/CEI formed on graphite/$LiCoO_2$. Consequently, the gassing issue at high temperatures was suppressed. The type and properties of solvents should also be carefully considered in salt engineering. The synthesis of novel salts can be a promising direction, but obtaining salts with a comprehensive performance remains challenging.

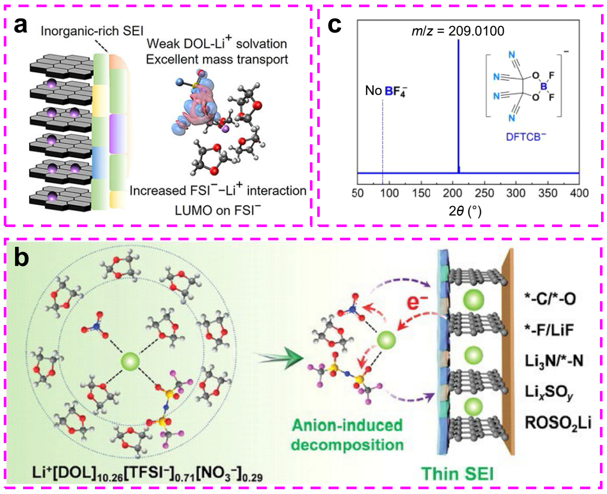

Figure 4 Salt engineering for the development of WSEs. (a) Schematic illustration of the function of the LiFSI-DOL WSE in the formation of a stable SEI on the graphite surface. Reproduced with permission[43]. Copyright 2023, American Chemistry Society. (b) Schematic illustration of the solvation structure of LiTFSI–$LiNO_3$–DOL electrolyte and the anion-derived SEI. Reproduced with permission[44]. Copyright 2022, the authors. (c) Nuclear magnetic resonance (NMR) spectrum and structure of $DFTCB^-$. Reproduced with permission[46]. Copyright 2023, John Wiley.

3.3 Solvent engineering for the development of WSEs

Compared with the limited reports on salt engineering, extensive progress has been attained in solvent engineering because of the more available options for solvent selection. Based on the source of solvents, the solvent engineering strategy can be divided into the screening of existing solvents and the synthesis of new ones.

3.3.1 *Screening of existing solvents*

Carbonate ester solvents

Linear carbonates generally have lower DN and ε than cyclic carbonates, and thus, they can be used as weak solvents. Liu et al. reported that with the addition of diethyl carbonate cosolvent to propylene carbonate (PC)-based electrolytes, even PF_6^-, which has a low DN of 2.5, can be introduced to the Li^+ solvation sheaths[47]. They proved that the solvated PF_6^- can reduce the lowest unoccupied molecular orbital energy level of the electrolyte and thus improve the reduction stability of the PC solvent. In addition, dimethyl carbonate (DMC) was used to construct a $DFOB^-$-rich solvation structure, which contributed to the formation of a robust SEI that restrained the cointercalation of the DMC solvent into graphite[48]. This work provides a possible solution for the development of EC-free carbonate electrolytes and the improvement of the low-temperature performance of LIBs.

Ether solvents

The general principles for the reduced solvating power of ethers are increasing the proportion of nonsolvating alkyl units, reducing solvating ethereal O atoms, and adding steric hindrance groups to ether molecular skeletons.

Zhang's group proposed the transition from a solvent-dominated to an anion-dominated solvation structure when the solvent was changed from DME to 1,3-dioxane (1,3-DX) and 1,4-dioxane (1,4-DX)

(Fig. 5a)[49]. They proved that as the ε of these three solvents decreased gradually, their solvating power reduced correspondingly. Accordingly, the amounts of Li^+–anion complexes in the solvation sheaths increased, and the proportion of contact ion pairs (CIP) and aggregate (AGG) coordination was promoted (Fig. 5b). The anion-derived SEI in 1,4-DX-based WSE enabled the fast charging of graphite anode. Kolosov's group further conducted in-depth research on the SEI formation mechanism in an ordinary EC-based electrolyte and 1,4-DX-based WSE (Fig. 5c)[50]. They revealed that the EC-based electrolyte showed the formation of a solvent-derived nonhomogeneous SEI with an inorganic–organic dual-layer structure. By contrast, the 1,4-DX-based electrolyte presented the formation of an SEI dominated by the nanostructure of the electrical double layer. The solvated FSI^- accumulated and formed a negative-charge layer near the graphite surface and decomposed on the basal and edge planes before solvent decomposition. Therefore, a thin and uniform inorganic-rich SEI formed on the edge section and basal plane of graphite. In addition to graphite, the 1,4-DX-based WSE electrolyte can form inorganic-rich SEI on Li metal anodes[51].

Tetrahydrofuran (THF) is a cyclic ether known for its low-solvating power, and it has been used to develop electrolytes for low-temperature and fast-charging batteries[52-56]. However, its application is hindered by its low oxidation voltage. Zhang et al. used tetrahydropyran (THP) to develop a WSE with a high oxidation voltage (>4.3 V)[57]. The THP molecule had an additional $-CH_2$ unit in the ring and exhibited a lower binding energy with Li^+ (−1.94 eV) than THF and DME (−2.00 and −2.82 eV, respectively). They proposed that the extension of the $-C_xH_y$ group to the ether ring will decrease the electronegativity of ethereal O atoms and increase the

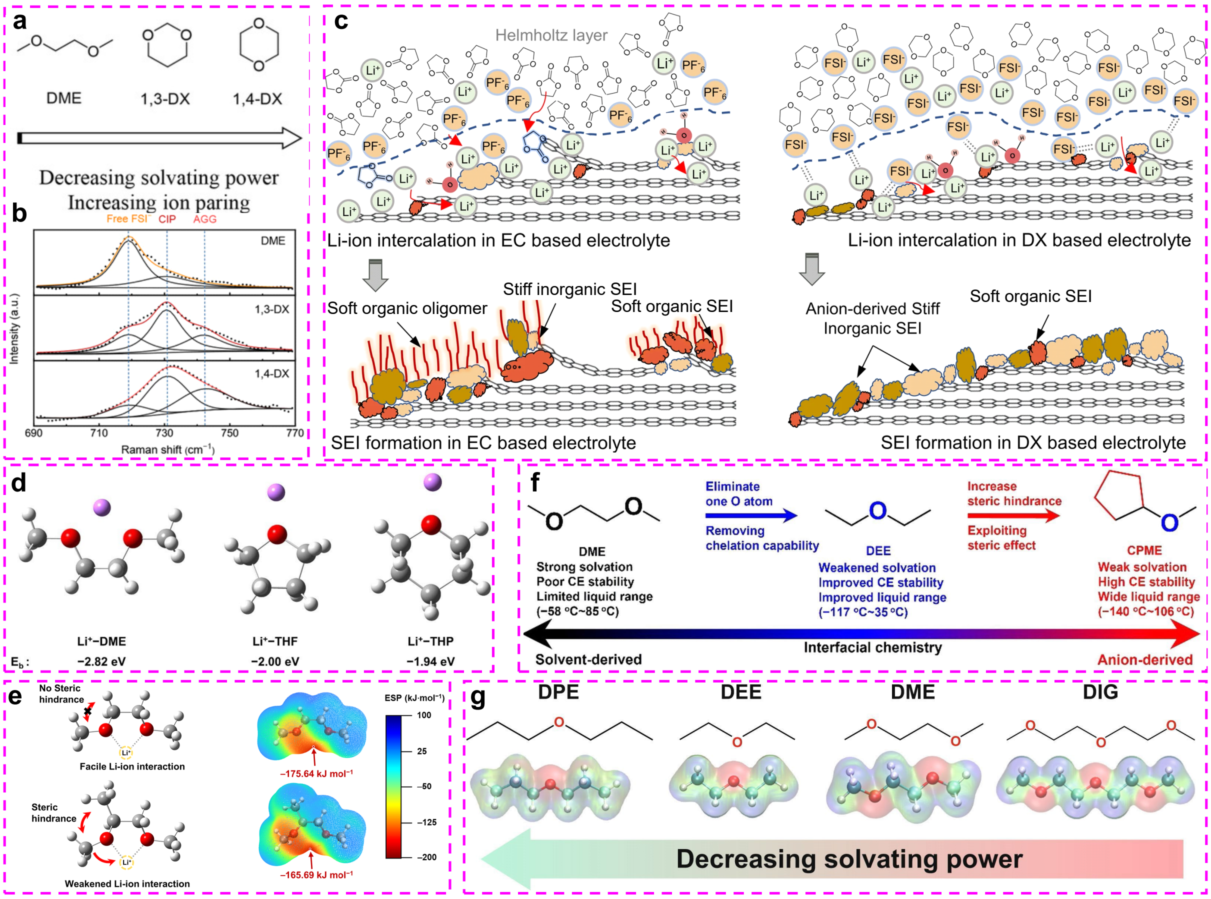

Figure 5 Screening of existing ether solvents. (a) Schematic illustration of the chemical structures of DME, 1,3-DX, and 1,4-DX and the evolution of their solvation structure. (b) Raman spectra of electrolytes based on the three ethers. Reproduced with permission[49]. Copyright 2020, John Wiley. (c) Schematic illustration of the SEI formation and Li^+ intercalation mechanism in an ordinary EC-based electrolyte and 1,4-DX-based WSE. Reproduced with permission[50]. Copyright 2023, the authors. (d) Structure and the calculated binding energy for the Li^+–solvent complexes. Reproduced with permission[57]. Copyright 2023, American Chemistry Society. (e) Structure of the Li^+–solvent complexes and ESP mapping of DME and DMP. Reproduced with permission[58]. Copyright 2023, American Chemistry Society. (f) Chemical structure and properties of DME, DEE, and CPME. Reproduced with permission[67]. Copyright 2023, John Wiley. (g) Chemical structure, ESP mapping, and comparison of the solvating powers of DIG, DME, DEE, and DPE. Reproduced with permission[68]. Copyright 2023, the authors.

steric hindrance to coordinate Li^+.

Additional linear ether solvents are available because their diverse molecular structures provide more opportunities to tune their solvability. In addition, linear ethers present a higher stability than cyclic ones and can inhibit the possible ring-opening reaction. DME is the most typical linear solvent and normally forms a solvent-dominated solvation structure in diluted electrolytes. The grafting of an additional $-CH_3$ group on the middle $-C_2H_4-$ chain in DME (which corresponds to 1,2-dimethoxypropane, 1,2-DMP)[58] and extension of the $-C_2H_4-$ chain to $-C_3H_6-$ (which corresponds to 1,3-dimethoxypropane, 1,3-DMP)[59] can effectively increase steric hindrance and reduce the ε and dipole moments while maintaining a reasonable Li salt solubility. Both 1,2-DMP and 1,3-DMP exhibit a reduced solvating power compared with DME (Fig. 5e), which facilitates the formation of CIP and AGG electrolyte species and inorganic-rich SEI/CEI. Thus, 1,2-DMP- and 1,3-DMP-based electrolytes enable the stable cycling of 4.3 V-class LMBs under practical conditions. Shortening the $-C_2H_4-$ between two ethereal O atoms in DME to $-CH_2-$ (which corresponds to dimethoxymethane, DMM) can weaken the Li^+–solvent interaction[60]. The electrolyte consisting of 1 mol L^{-1} LiFSI in DMM delivers a high Li deposition/stripping efficiency of 97.87% at −40℃, and the practical Li-SPAN cell can operate for more than 120 cycles at such a low temperature.

Furthermore, an extension of the terminal methyl groups in DME to ethyl groups (which correspond to 1,2-diethoxyethane or ethylene glycol diethyl ether) can weaken the solvating power and allow more anions to participate in the solvation process at identical concentrations[61-63]. The anion-derived SEI/CEI can support highly reversible Li anodes and high-voltage cathodes. Our group proved that the decomposition of solvents on electrodes can be suppressed by using ethylene glycol dibutyl ether, in which the terminal alkyl groups are further extended to *n*-butyl groups, and that of anions can be promoted[64]. Therefore, a thin and inorganic-rich SEI/CEI formed on the Li anode/NCM811 cathode. The reversibility of Li anode increased to 99.41% at 60℃, and the cycling stability of high-temperature NCM811-Li batteries was prolonged by more than four times.

Ethereal O atoms serve as coordinating sites of ethers[65]. Thus, reducing the number of ethereal O atoms can remarkably decrease the solvating power of ethers. Diethyl ether (DEE) has one ethereal O atom, and its attraction to Li^+ is notably lower than those of DME and DOL. Holoubek et al. reported that in the electrolyte of 1 mol L^{-1} LiFSI in DEE, the presence of FSI^- in the solvation sheaths substantially lowered the desolvation energy[66]. This can help in eliminating the tip-drive deposition behavior of Li^+ in conventional ether electrolytes (1 mol L^{-1} LiFSI in DOL/DME), promote homogenous Li plating, and therefore greatly improve Li reversibility at low temperatures. Nevertheless, its real-life applications are hindered by the low boiling point of DEE (34.6℃) and low oxidation voltage. Zhang et al. demonstrated the improved boiling point (106℃) and reduced melting points (−106℃) of cyclopentyl methyl ether (CPME) compared with DEE (Fig. 5f)[67]. The cyclopentane ring improved the steric hindrance and further reduced the solvating power and desolvation energy of Li^+–solvent complexes. Therefore, CPME-based electrolytes delivered a higher oxidation voltage and a better low-temperature performance than DEE-based ones. In addition, when screening solvents, factors other than decreasing solvating power must be considered. The maintenance of solvating power at a certain level will ensure reasonable ion mobility, salt solubility, and battery voltage polarization. Li et al. performed in combination the elimination of ethereal O and the extension of terminal alkyl groups by screening a non-polar dipropyl ether (DPE) solvent (Fig. 5g)[68]. They demonstrated that with the decreased solvating power of solvents, the solvation structure released Li^+ more easily, and the anion decomposed on the high-voltage cathode (NCM811) surface. In addition, the AGG cluster showed the highest occupied molecular orbital (HOMO) energy, with a value even higher than that of free solvents, which can theoretically explain the decomposition preference of anion-rich solvation sheaths on the cathode side. With the anion-derived CEI, NCM811-Li batteries exhibited a stable operation at a cut-off voltage of 4.3 V in the diluted electrolyte of 1.8 mol L^{-1} LiFSI in DPE.

All the above-mentioned weak ethers have a lower O/C ratio compared with DOL or DME, and the O/C ratio in ether molecules is positively associated with the solvating power[69]. However, with the increased number of $-C_xH_y$ groups and the elimination of ethereal O atoms, ether solvents present a notably increased flammability[70]. This condition adds safety risks to Li batteries. In addition, these weak ether-regulated WSEs normally have an oxidation voltage lower than 4.5 V, and the batteries generally cycle at a cut-off voltage of <4.4 V, which leads to the sacrifice of the energy density of Li batteries.

Fluorinated solvents

The weakened solvating power of fluorinated solvents is mainly attributed to the electron-withdrawing F atoms, which reduce the regional electron density of Li^+-coordinating sites (normally O atoms) in solvents. In addition, fluorinated solvents display improved oxidation voltage and reduced flammability. Furthermore, the decomposition of fluorinated solvents and anions contributes to the formation of fluorinated inorganic-rich SEI/CEI[71, 72].

Fluoroethylene carbonate (FEC) and difluoro ethylene carbonate are cyclic carbonates with reduced solvability compared with EC[73, 74]. Ethyl (2,2,2-trifluoroethyl) carbonate[75], 2,2,2-trifluoroethyl methyl carbonate (FEMC)[76], and bis(2,2,2-trifluoroethyl) carbonate (BTFC)[77] are the representatives of fluorinated linear carbonates. The existing fluorinated ethers are normally used as antisolvents or diluents rather than solvents or cosolvents because of their remarkably decreased solubility and solvating power. Fluorinated carboxylic esters exhibit desirable compatibility with graphite/Li anodes and high-voltage cathodes. They have low melting points and high boiling points and, therefore, attract considerable attention in the development of WSEs. Ethyl difluoroacetate (EDFA), methyl 2,3,3,3-tetrafluoro propionate, methyl difluoroacetate (MDFA), methyl 2,2-difluoro-2 (fluorosulfonyl) acetate (MDFSA)[33], and ethyl trifluoroacetate (ETFA)[78] are widely used as solvents for low-temperature electrolytes. In addition, fluorinated sulfonamide-based solvents, such as N,N-dimethyltrifluoromethane-sulfonamide[79], and fluorinated amides, such as 2,2,2-trifluoro-N, N-dimethylacetamide[80], possess lower solvating powers and form a robust F-rich SEI/CEI on Li anodes/high-voltage cathodes. In addition, the bulky ethoxy (pentafluoro) cyclotriphosphazene (PFPN) solvent has multiple functions (Fig. 6a)[81]. The fluorinated cyclotriphosphazene ring is responsible for the flame-retardant and filming-formation properties, but it is nonsolvating and can increase steric hindrance. The ethoxy group reduces viscosity, and the O and N atoms provide a coordinating site, which ensures the entry of PFTN to the solvation sheaths.

To date, in most reported WSEs, fluorinated solvents are mixed with other fluorinated and/or ordinary solvents rather than used as a single solvent. This form of usage stems from the consideration of maintaining the comprehensive properties of electrolytes, including salt solubility, ionic conductivity, viscosity, flammability, and electrochemical windows. For example, Lu et al. reported a nonflammable WSE with a mixture solvent of DME/FEC/PFPN (3/3/4 by vol)[81]. Cao et al. developed a WSE based on a mixed solvent of FEC/BTFC/ETFA (2/2/6 by vol) and a standard salt concentration (1 mol L^{-1} LiFSI)[77]. This electrolyte design reduced the desolvation energy of solvated Li$^+$ by more than half compared with that of conventional carbonate electrolyte and formed an inorganic-rich SEI (Fig. 6b). Therefore, the Si anode exhibited a performance that was boosted up to 200 cycles and an ultrahigh capacity of over 2000 mAh g^{-1} at −20℃. Wang et al. developed a WSE using 1 mol L^{-1} LiFSI in MDFA/MDFSA/TTE (at a volume ratio of 4/1/5), which supported a 4.5 V pouch-type LIB with a graphite anode operating for more than 350 cycles and a capacity retention of 83.8% at a low temperature of −30℃[33]. Mo et al. revealed that the moderately fluorinated EDFA has a lower Li$^+$ coordination energy than the less-fluorinated ethyl fluoroacetate and a higher capability to dissociate LiFSI salt than highly fluorinated ETFA; thus, it can achieve a delicate balance between the weakened solvating power and electrolyte ionic conductivity[82]. The electrolyte of 1 mol L^{-1} LiFSI in EDFA/FEC (9/1 by vol) can support NCM811-graphite works at a wide temperature range of −40℃–45℃. Cai et al. proposed an idea of quasi-LHCE (*q*-LHCE), which can be developed by replacing the EC and ethyl methyl carbonate (EMC) in a common carbonate electrolyte (1 mol L^{-1} LiPF$_6$ in EC/DMC/EMC) with FEC and FEMC and increasing the salt concentration to 2 mol L^{-1} (Fig. 6c)[76]. The *q*-LHCE has a weakly solvating structure and can form an anion-derived SEI/CEI. This electrolyte supports a 4.5 V-class practical LiCoO$_2$–Li

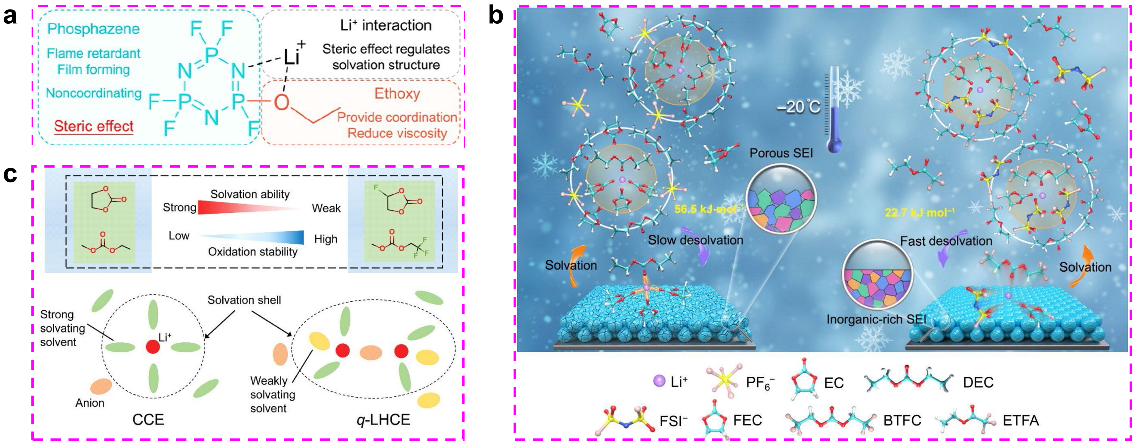

Figure 6 Fluorinated solvents for the development of WSE. (a) Chemical structure and functions of PFPN and the illustration of its solvation structure. Reproduced with permission[81]. Copyright 2023, American Chemistry Society. (b) Schematic illustration of the WSE with FEC/BTFC/ETFA mixed solvent and its working mechanism. Reproduced with permission[77]. Copyright 2023, American Chemistry Society. (c) Schematic illustration of the design concept of *q*-LHCE. Reproduced with permission[76]. Copyright 2023, John Wiley.

battery that works at a wide temperature range of −20℃ −45℃ with minimized Li consumption.

Other solvents

In addition to the solvents discussed above, Si-based electrolytes show potential application in WSEs. Dimethyl dimethoxy silicane (DMSi) has a low ε of 3.66, it has been used to develop an anion-rich solvation structure[83]. However, the average Li reversibility is only ~97%. The reversibility of Li can be improved to 99.6% by extending the methyl groups of DMSi to ethyl groups (which correspond to dimethyldimethoxysilane). In addition, by substituting a methyl group of DMSi with a trifluoropropyl group, a dimethoxy(methyl)(3,3,3-trifluoropropyl) silane solvent can be obtained. The resulting WSE with a moderate concentration of 3 mol L^{-1} can successfully support the long-term cycling of a practical $LiCoO_2$−Li battery at a high cut-off voltage of 4.6 V[84].

3.3.2 *Synthesis of new solvents*

The synthesis of new solvents is a crucial strategy for the development of WSEs and the achievement of exceptional battery performance. The recent progress in this direction mainly focused on the development of fluorinated ethers because of the following reasons. (1) Ether solvents have a higher reductive stability than esters, amides, and sulfones and are therefore thermodynamically more stable against Li and graphite anodes; (2) the coordinating behaviors of esters, amides, and sulfones are governed by strong C=O, P=O, or S=O bonds, but those of ether solvents are dominated by ethereal O atoms, in which the local charge density is notably weaker; therefore, the fluorination of ethers will have a more evident effect on the solvating power and electrochemical performance.

Cui and Bao's groups conducted several pioneering works. They grafted ether groups at the ends of fluorinated tetraethylene glycol (FTEG) and fluorinated triethylene glycol (FTriEG) via covalent bindings (Fig. 7a)[85]. The obtained fluorinated ethers exhibited an oxidatively stable inner core and ionic conductive terminal ether groups. The product properties can be regulated through the adjustment of the length of inner fluorinated segments and terminal ether groups. This design enabled the delivery of an ultrahigh oxidation voltage of 5.6 V in the electrolyte with a standard salt concentration of 1 mol L^{-1}. However, the highest ionic conductivity only reached 0.27 mS cm^{-1}, which limits the battery performance at high rates. They further synthesized 1,4-dimethoxylbutane (FDMB) via a two-step approach and used DME as the backbone[86], which has a remarkably smaller molecular size than those obtained in previous works. The electrolyte of 1 mol L^{-1} LiFSI in FDMB delivered a superior oxidation voltage of >6 V, and the ionic conductivity at room temperature improved to 3.5 mS cm^{-1}. The electrolyte boosted the Li plating/stripping reversibility to 99.52% and promoted the lifespan of practical NCM−Li batteries to over 420 cycles at 1/3 C, along with a capacity retention of 90% and a high CE of 99.98%. They also demonstrated that the rate performance of LMBs can be evidently improved by extending the $-C_2F_4-$ group to the $-C_6F_{12}-$ group in the middle of ether[87]. In addition, they revealed the better effects of partial fluorination of the terminal methyl groups ($-CHF_2$) than full fluorination ($-CF_3$) when DEE was used as the backbone[88]. This finding was due to partial fluorination, which can increase the local dipole moment and improve intermolecular polarity and interaction. The electrolyte with partially fluorinated ethers as solvents delivered high Li$^+$ kinetics, high oxidative stability, and high Li reversibility.

Ali's group used a one-pot facile method to synthesize 2-ethoxy-4-(trifluoromethyl)-1,3-dioxolane (cFTOF) based on a triethyl orthoformate (TOF) ether backbone (Fig. 7b)[89]. They pointed out that the direct substitution of a fluorinated group to ethereal O atoms will greatly sacrifice the solvating power of TOF. Thus, they utilized a cyclic structure to deliver a $-CF_3$ group to the TOF skeleton. In the cFTOF molecule, the covalently bonded $-CF_3$ group can improve oxidation stability, and the five-membered ring retains the solvating power of ethereal O atoms. This design remarkably promoted the formation of CIP and AGG species in the solvation structure. The electrolyte of 1 mol L^{-1} LiFSI in cFOTF delivered an oxidation voltage of >5.8 V, which is at least 1.8 V higher than that of 1 mol L^{-1} LiFSI in TOF. A similar concept was applied to synthesize a new ether, 2,2-dimethoxy-4-(trifluoromethyl)-1,3-dioxolan (DTDL)[90]. The electrolyte of 1 mol L^{-1} LiFSI in DTDL maintained an anion-rich solvation structure and excellent Li$^+$ mobility (a high Li$^+$ transference number of 0.75). In addition, the solvating behavior and electrochemical performance can be tuned effectively by grafting the carbon skeleton of common ethers, such as DME and DOL, with a $-CF_3$ group. They synthesized 1,1,1-trifluoro-2,3-dimethoxypropane (TFDMP), which can be regarded as DME with the covalent attachment of a $-CF_3$ group on the central alkyl moiety (Fig. 7c)[91], and achieved a recorded ionic conductivity of 7.3 mS cm^{-1} in fluorinated electrolytes. They also synthesized 4-(trifluoromethyl)-1,3-dioxolane, which can be regarded as DOL grafted with a $-CF_3$ group in C4[92]. This design not only improved the oxidation voltage to >5 V but also inhibited the open-ring polymerization of DOL.

Fluorination remarkably increases the density of solvents (normally >1.3 g cm^{-3}) and thus leads to a

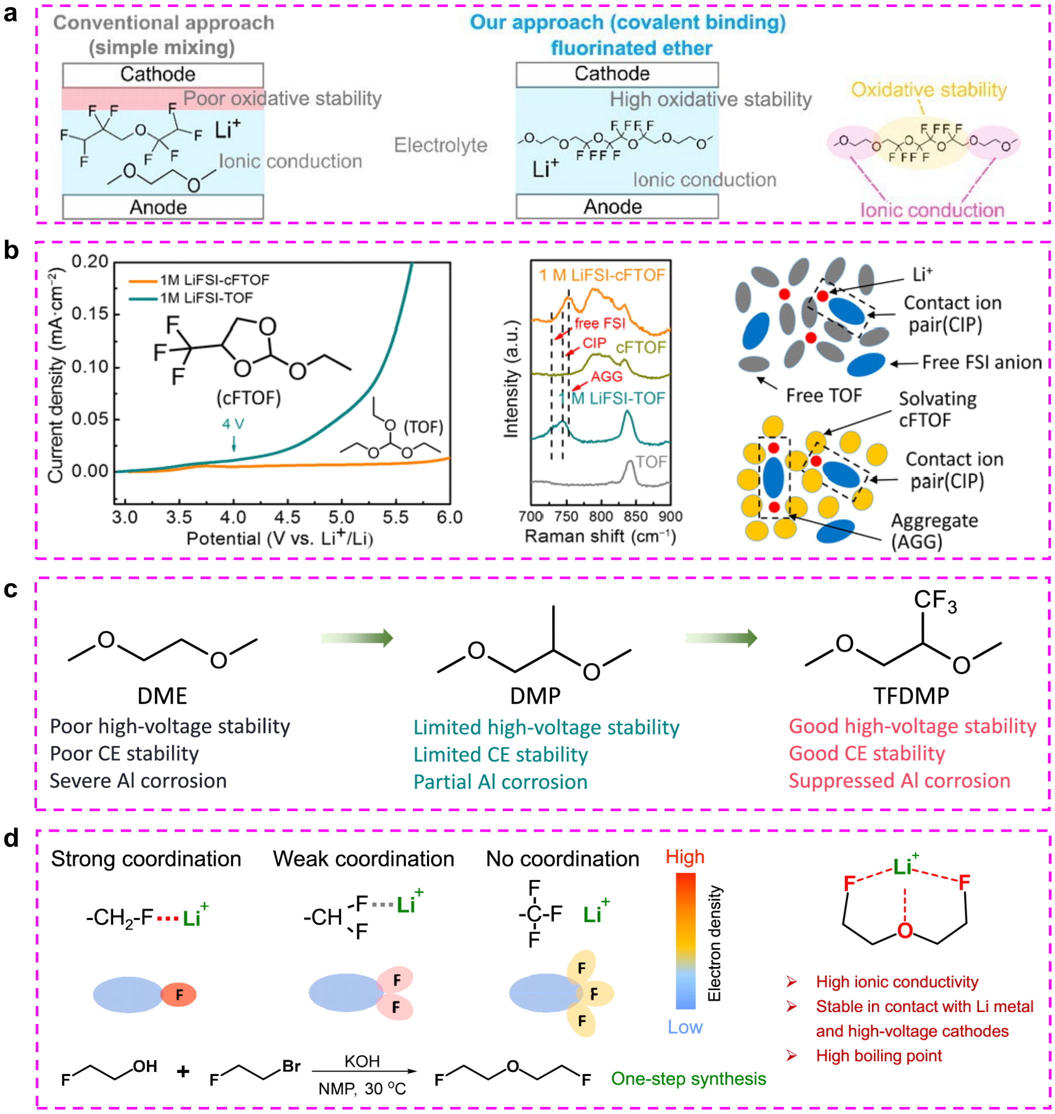

Figure 7 Synthesis of new solvents. (a) Design concept of FTEG- and FTriEG-based fluorinated ethers. Reproduced with permission[85]. Copyright 2020, American Chemistry Society. (b) LSV curves and solvation, Raman spectra, and schematic illustration of the solvation structure of electrolytes with cFTOF and TOF solvents. Reproduced with permission[89]. Copyright 2022, John Wiley. (c) Chemical structures DME, DMP, and TFDMP and their electrochemical properties. Reproduced with permission[91]. Copyright 2023, the authors. (d) Synthesis route and electrochemical properties of BFE and schematic illustration of the effects on the solvating power of fluorination degree. Reproduced with permission[93]. Copyright 2023, the authors.

compromise in the energy density of batteries. To improve this property, Zhang et al. developed monofluoride bis(2-fluoroethyl)ether (BFE) with a one-step approach and achieved a low density of 0.98 g cm^{-3} (Fig. 7d)[93]. In addition, the monofluoro substituent gave rise to a solvent with a weak solvating power. The two methylene groups in BFE can weaken the intermolecular interaction of F and O atoms and promote the favorable five-member-ring coordination with Li^+. Moreover, BFE has a high oxidation voltage and boiling point. Given these advantages, the electrolyte of 2 mol L^{-1} LiFSI in BFE, which is the best CE in LMBs reported thus far, delivered a high Li reversibility of 99.75%. In addition, NCM811–Li batteries can operate in a wide temperature range of −60℃–60℃, and the NCM811–Li pouch cell delivered a high energy density of 426 Wh kg^{-1}.

In brief, the novel solvents with covalently bonded F-containing groups possess a remarkably reduced solvating power, and anion-rich solvation structures can be obtained using $LiPF_6$ salt. These solvents exhibited a substantially better electrochemical performance than the mixture of ordinary solvents with hydrofluoroethers. Therefore, the WSEs based on new fluorinated solvents can exhibit higher oxidation voltage and ionic conductivity than LHCEs. However, their yields and costs are still unsatisfactory and pose difficulties in their commercialization. Importantly, fully or highly fluorinated solvents are resistant to natural degradation because of the strong C–F covalent bonds in the $-CF_3$ and $-CF_2H$

groups[94]. This condition can lead to environmental hazards and additional burdens in the disposal or recycling of spent Li batteries. Reduction of the fluorination degree of solvents will be effective in addressing the mentioned challenges while maintaining a reasonably weak solvating power.

3.4 Functional additives for the development of WSEs

The addition of insoluble nanoparticles to electrolytes will produce a suspension electrolyte. Li_2O and Li_3N nanoparticles in suspensions can weaken the Li^+–solvent interaction and reduce the coordinating number of solvents[95, 96]. Consequently, the desolvation of Li^+ can be facilitated, and the decomposition of solvents can be decreased (Fig. 8). Furthermore, Li_2O and Li_3N are lithiophilic and can guide the uniform deposition of Li^0. The research focusing on this direction is still at the preliminary stage. Thus, future studies should explore more functional inorganic particles that are electrochemically stable in the electrolytes and their potential as additives.

4 Summary and perspectives

In summary, WSEs have different solvation environments compared with CEs, HCEs, and LHCEs. These electrolytes can greatly improve electrode–electrolyte properties, widen the electrochemical window, and boost the low-temperature and rate performance of Li batteries. We have systemically revealed the working mechanisms of WSEs in improving battery performance, summarized the design principles of WSEs, and reviewed recent advances in WSE development. The key to constructing WSEs is reaching a balance between the interactions of Li^+ with solvent and anions. Salt and solvent engineering is a major strategy applied in the development of WSEs, and a few reports demonstrated the use of inorganic nanoparticles in preparing suspension electrolytes. Low-dissociation salts, including $LiNO_3$, LiOTF, LiFSI, LiTFSI, LiDFOB, and LiDFP, are popular choices in salt engineering, and high-dissociation salts, such as $LiPF_6$, have been applied in fluorinated solvents. Salt engineering is normally combined with the selection of appropriate solvents. In the scope of ordinary solvents, ethers are the most popular choice for the development of WSEs, along with some linear carbonates and Si-containing solvents. Strategies of extending alkyl groups, reducing ethereal O atoms, and causing steric hindrance groups are widely applied to screen ether solvents, but these ethers may increase flammability and result in safety hazards. Fluorinated solvents deliver a reduced solvating power and notably superior electrochemical performance. The existing fluorinated solvents are usually used in a mixture with other solvents, and the synthesized novel fluorinated compound is used as a single solvent. Currently, WSEs with novel fluorinated solvents present the best electrochemical performance, and this direction shows remarkable promise for future applications. The design concepts of WSEs can be extended to other batteries, such as Na, K, Mg, and Zn systems. Future research should focus on the simplification of synthesis procedures, improvement of yields, and cost reduction, as summarized below.

(1) Development of comprehensive Li salts. Existing salts have limited types, and the options for anion selection are limited. Recent advances have been observed in the synthesis of new salts, but most of them still present the disadvantages of low oxidation voltage, poor solubility, or unsatisfactory electrochemical performance. In addition, the decomposi-

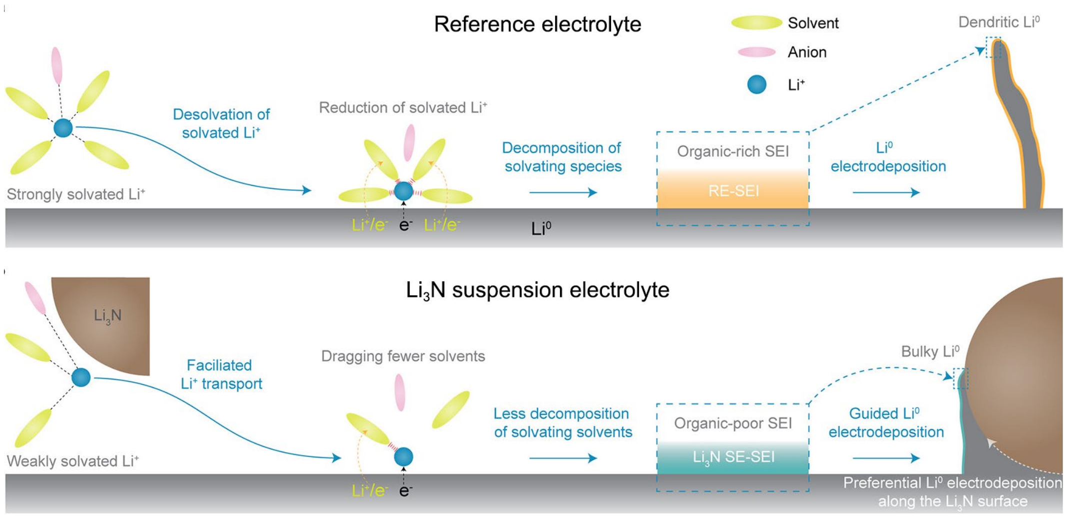

Figure 8 Schematic illustration of the working mechanism of Li_3N nanoparticles in a suspension electrolyte. Reproduced with permission[96]. Copyright 2023, American Chemistry Society.

tion of current organic anions, such as FSI^-, $TFSI^-$, and $DFOB^-$, forms an inorganic-rich SEI/CEI, and some organic by-products are generated. In this regard, the development of inorganic salts with large anions can be promising because of the following reasons. (i) A large radius reduces the charge density around the anion and weakens the Li^+–anion ionic bonds; (ii) such inorganic salts can attain a solubility that is comparable to that of organic salts and notably higher than those of most common inorganic salts, including $LiPF_6$, $LiBF_4$, and LiBOB; (iii) the decomposition of pure inorganic anions can considerably increase the proportion of inorganic species in SEI and CEI and boost the performance of Li batteries.

(2) Reduction of solvent flammability. Except for fluorinated solvents, most of the solvents used in WSEs, such as linear carbonates and low-solvating ethers, are highly flammable. This property increases the safety risks associated with Li batteries. Mixing these solvents with fluorinated solvents can reduce the flammability to some extent but still cannot solve the safety problem. In this direction, modifying organic phosphates, which are intrinsically nonflammable but have a strong solvating capability, with electron-withdrawing groups, such as Cl, F, and cyan groups, can effectively decrease their solvating power and, therefore, promote their potential application in the development of WSEs. In addition, Si-containing solvents are attractive solvent candidates for WSEs and have reduced flammability and solvating power. To date, only a few papers on this topic have been published because of the poor battery performance of most Si-containing solvents. Screening high-performance Si-containing solvents is, therefore, highly desirable.

(3) Controlling the costs of fluorinated solvents. Commercially available fluorinated solvents are notably more expensive than most ordinary solvents. In regard to the newly synthesized fluorinated solvents, the high price of precursors, complicated procedures, and low yields also remarkably increase the cost, which limits their practical application. Therefore, costs can be reduced by applying strategies that optimize the synthesis routes and improve yields.

(4) Utilization of artificial intelligence in science tools. The traditional trial-and-error strategies used in the development of WSEs are time- and resource-consuming. With the use of big data and machine learning techniques, researchers can effectively predict the properties of many solvents and salts, study their solvation structure, and analyze their electrochemical performance prior to practical experiments. This research direction can guide the proper screening of electrolyte composition and optimization of recipes with minimized cost. The related study is at the initial stage, and the top priorities currently include the statistical analysis of existing data and the training of reliable models. This direction needs the interdisciplinary cooperation of computer science, materials science, and chemistry.

(5) Understanding the mechanism of WSEs in the stabilization of high-voltage cathodes. Previous research mostly focused on the correlations between the weak Li^+-solvating behavior of WSEs to the SEI composition and the electrochemical performance of Li or graphite anode. However, no in-depth research has been conducted on the correlations on the cathode side. Studies should investigate the electrostatic induction of solvated anions to solvents and its influence on the decomposition behavior of solvents on the cathode side, especially in the charging process. In addition, some inorganic species, such as Li_3N, LiN_xO_y, and Li_2S, are useful in SEI but unstable at high voltages. Thus, the final decomposition products of solvated anions on the cathodes differ from those on the anode side. However, the detailed decomposition routes have not been investigated.

(6) Monitoring of the dynamic evolution of solvation structures during temperature change. In most reported WSEs, the electrolyte solvation structure was characterized or simulated at room temperature. However, the dissociation degree of Li salts and solvating power can be altered during temperature change, and therefore, the Li^+-coordinating structure and electrochemical performance can be adjusted accordingly. Investigation of the viscosity, ionic conductivity, Raman, Fourier transform infrared spectroscopy, and NMR spectra and theoretical simulation of the electrolyte solvation structure can help in the design of all-climate electrolytes.

(7) Improving the high-temperature performance of Li batteries in WSEs. Elevated operating temperatures lead to additional safety concerns and more severe performance decay of Li batteries. Nevertheless, the electrochemical data of state-of-the-art WSEs are generally evaluated at room or low temperatures, and the long-term cyclability at high temperatures has rarely been studied, particularly when using lean electrolytes under conditions of high area capacity and low n/p ratio. In addition, despite the few recently designed WSEs for high-temperature Li batteries, the discussion of improved electrochemical performance stems from the perspective of constructing inorganic-rich SEI/CEI. More fundamental mechanisms, such as the changes in HOMO energies of solvated clusters and/or oxidative decomposition preference of electrolyte compositions at high temperatures, should be revealed in-depth.

Acknowledgments

This work was supported by the Hong Kong Polytechnic University (No. CDBJ). Z. Wang thanks the funding support from the Centrally Funded Postdoctoral Fellowship Scheme of the Hong Kong Polytechnic University (No. 1-YXAU).

Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

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