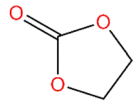
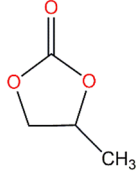
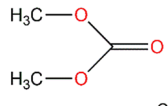
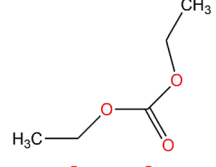
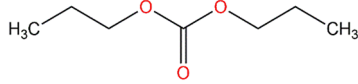
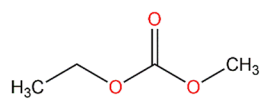


Table 1 Physical properties of traditional carbonate-based solvents

Carbonate electrolyte solvents	Structural formula	Melting point (°C)	Boiling point (°C)	Dielectric constant
Ethylene carbonate (EC)		35–38	248	89.6
Propylene carbonate (PC)		–55	240	64.9
Dimethyl carbonate (DMC)		2–4	90	3.12
Diethyl carbonate (DEC)		–43	125.8	2.82
Dipropyl carbonate (DPC)		83	302	2.6
Ethyl methyl carbonate (EMC)		–53	110	2.958

dense, stable interphase through molecular engineering for instance, using strongly coordinating solvents to tailor the solvation structure. This approach kinetically stabilizes both high-voltage cathodes and lithium–metal anodes. This evolution in focus, from isolated molecular properties to collective interfacial thermodynamics, provides a critical foundation for developing next-generation battery electrolyte solvents.³⁶ Consequently, the need for high-performance electrolyte solvents has become increasingly urgent.^{30,37} Such electrolyte solvents must maintain high ionic conductivity and a broad electrochemical stability window while providing improved low-temperature performance, enhanced safety,³⁸ and more stable interfacial properties.^{39,40} Furthermore, they must fulfill the specific chemical and electrochemical demands of emerging electrode materials.^{33,41}

Future research should prioritize the development of advanced lithium-ion battery electrolyte solvents through molecular functionalization and optimization of experimental protocols.^{42,43} Such methods can operate under harsh temperature and voltage conditions, thus accelerating the popularization of high energy density batteries in next-generation applications.⁴⁴

Results and discussion

1. Fluorinated solvents

Fluorinated solvents are garnering significant attention in the realm of lithium metal battery electrolyte research because of their potential to significantly improve battery performance.

A key property of these solvents is their ability to promote the formation of stable solid electrolyte interphase (SEI) films enriched with lithium fluoride (LiF) on the surface of electrodes, particularly lithium metal anodes.⁴⁵ For instance, fluoroethylene carbonate (FEC) is a representative fluorinated solvent with a unique dual reaction mechanism that helps build SEI protective layers (Fig. 2b). The primary role of the SEI is to function as an electron-insulating layer, preventing direct electron tunneling from the electrode to the electrolyte and thereby avoiding continuous reductive decomposition of the electrolyte. The thickness of the SEI directly determines the width of this electron tunneling barrier. The advantage of fluorinated solvents in constructing the SEI lies in their ability to form an LiF-rich interphase. However, as LiF possesses a wide band gap and is an excellent electron insulator, an LiF-rich SEI layer can achieve the same electron-blocking effect even at a reduced thickness.⁴⁶ In contrast to a homogeneous single phase, the solid-electrolyte interphase (SEI) is more accurately described as a stratified structure with a distinct compositional gradient. An ideal SEI features an inorganic-rich inner layer (adjacent to the electrode), composed primarily of LiF, Li₂O, and Li₂CO₃, and an organic-rich outer layer (facing the electrolyte) containing species such as polycarbonates and alkyl carbonates.⁴⁷ This architected gradation is functionally critical: the inorganic inner layer, especially LiF, exhibits a high Young's modulus and exceptional electronic insulation, which collectively passivate the electrode surface, block electron tunneling, and suppress lithium dendrite penetration. The inorganic constituents



The LiF in SEI films prevents continued decomposition at the interface, which improves the overall stability of the electrolyte and thus maintains battery performance over a longer operating time.^{50,51} Specifically, this LiF-based interfacial stabilization mechanism can effectively inhibit the growth of lithium dendrites and improve the oxidative stability of cathode materials under high voltage conditions, with enhanced compatibility between the electrolyte and electrode interfaces. Collectively, these factors contribute to improved cycling stability and safety of lithium metal batteries (Fig. 2d).

Extensive studies have shown that the molecular structure of fluorinated solvents as well as commonly used fluorinated lithium salts such as LiPF₆, LiTFSI, and LiFSI play a critical role in defining the microscopic solvation structure of the electrolyte as well as the reaction kinetics at the electrode/electrolyte interface. Notably, the number and positional arrangement of fluorine atoms within the molecule can have a profound effect on the chemical composition and microstructure of the resulting SEI film. Furthermore, the spatial configuration and proximity of fluorine atoms relative to other functional groups (*e.g.*, ester or ether groups) have important effects on the physical and chemical properties of the solvent (*e.g.*, polarity and reduction potentials) as well as on the overall behavior of the electrolyte system.

For example, in linear fluorinated solvent molecules, if a strongly electron-withdrawing trifluoromethyl (–CF₃) group occupies the α position (Fig. 2e), it significantly diminishes the overall polarity of the molecule. This decline in polarity directly reduces the solvent's ability to dissolve lithium salts and dissolve lithium ions, thereby reducing the ionic conductivity of the electrolyte. Interestingly, the α -fluorinated molecules demonstrate higher reactivity on the lithium metal anode surface and are more likely to preferentially decompose to form LiF. However, this does not inherently equate to superior interface stability on the lithium anode. Conversely, when the –CF₃ group resides at the γ position, it produces a relatively weak electron-withdrawing effect throughout the molecule. Therefore, taking into account the solvation capacity, interfacial reactivity and ultimate stability of the interfaces formed, β -fluorinated molecules may strike a more favorable balance in optimizing the properties of fluorinated solvents.

The strategic design of partially fluorinated molecular structures inhibits excessive aggregation of lithium ions and anions in the electrolyte, and improves lithium-ion mobility in the bulk electrolyte and at the interface, while maintaining high interfacial stability. Thus, these advances synergistically optimize the electrochemical performance of the battery (Fig. 2f).

Fluorinated solvents are recognized as exemplary candidates for advanced electrolyte design due to several inherent

advantages, including a high dielectric constant, a wide window of electrochemical oxidative stability (typically 4.3–5.0 volts *vs.* Li/Li⁺, which exceeds that of conventional carbonate solvents) (Table 2), and relatively low flammability. Nevertheless, a crucial consideration involves the strong electron-withdrawing characteristic of fluorine atoms, which may adversely affect the reduction stability of electrolyte at the negative electrode (low potential), potentially leading to premature decomposition of the lithium metal anode.

Nonetheless, substantial experience has demonstrated the irreplaceable role of fluorinated solvents in facilitating the development of highly efficient and stable SEI and cathode electrolyte interphase layers (CEI). They can successfully inhibit the generation of side-reaction gases (*e.g.*, H₂, CO, CO₂, *etc.*) during the cycling process and significantly improve the long-term cycling stability and safety of batteries. These wide-ranging properties make fluorinated solvents highly desirable and are expected to drive the design of next-generation high-performance electrolyte solvents and improve the overall efficacy of lithium metal batteries.

Additionally, meticulous molecular engineering enables fluorinated electrolyte solvents to utilize their unique function of C–F bonds to provide considerable resilience under extreme operating conditions such as wide temperature ranges and high voltages. The pronounced electron adsorption of the C–F bond gives excellent antioxidant properties at high potentials and reduces certain harmful decomposition pathways (Fig. 2g). At low temperatures, the intrinsic steric hindrance provided by fluorine-containing molecular units promotes disordered alignment, which significantly improves electrolyte mobility and facilitates ion transport. Critically, these electrolyte solvents effectively promote the formation of high-energy interphases (SEI and CEI) enriched with LiF. This high interfacial energy layer possesses dual protective capabilities: physically hindering the uncontrolled proliferation of lithium dendrites and slowing down the degradation process of the cathode materials under high voltage scenarios. Moreover, the inherent non-flammability of fluorinated electrolyte solvents is mainly due to the ability of the C–F bond to effectively quench the highly reactive free radicals during combustion and to destroy the combustion chain reaction, which provides important protection for the safe operation of batteries under extreme electrochemical conditions and ensures structural integrity and functional reliability.

Future SEI design strategies are guided by a clear set of target parameters. With regard to thickness, an ultrathin layer is critical for minimizing ionic transport resistance. Although the optimum is system-specific, it generally lies within the nanoscale regime of 10–50 nm. Such control can be achieved

Table 2 Fluorinated solvent classes and the battery performance

Solvents	Cell configuration	Protocol	Discharge capacity	Ref.
FEC	Li NCM811	–30 to 60 °C, > 4.5 V (<i>vs.</i> Li ⁺ /Li)	200 cycles, > 80%	52
FEMC	Li NCA	–85 to 70 °C, > 5.0 V (<i>vs.</i> Li ⁺ /Li)	400 cycles, > 90%	53
DFEC	Li NCM811	–20 to 80 °C, > 5.0 V (<i>vs.</i> Li ⁺ /Li)	200 cycles, > 80%	52



through tailored electrolyte formulations that suppress excessive SEI growth.⁴⁶ In terms of composition, an LiF-rich SEI remains a leading strategy with emphasis placed not only on increasing total LiF content, but more importantly, on ensuring its homogeneous distribution to avoid a heterogeneous, mosaic-like morphology. The ultimate aim is a multilayered SEI with an ideal compositional gradient: a dense, uniform inorganic inner layer and a soft, porous organic outer layer. Through advanced molecular and electrolyte design, such hierarchically structured interfaces are progressing from concept to reality, paving the way for high-energy-density batteries.⁵⁴

1.1. Fluorinated carbonate. Carbonate molecules exhibit considerable reactivity at the lithium metal anode interface, typically forming loose and porous solid electrolyte interface (SEI) film. This poses challenges for lithium-ion batteries such as reduced coulombic efficiency and reduced cycling stability. It is shown that the introduction of fluorine substitutes into carbonate solvent molecules significantly improves the cycling stability of the electrode interface while expanding the

temperature and voltage windows of the electrolyte. This provides an important avenue for optimizing the performance of lithium-ion batteries.⁶⁰ Currently, fluorinated carbonate solvents such as fluorinated ethylene carbonate (FEC)⁶¹ and fluorinated ethyl methyl carbonate (FEMC) are widely recognized as promising alternatives (Fig. 3a). Carbonate molecules exhibit considerable reactivity at the lithium metal anode interface, typically forming loose and porous solid electrolyte interface (SEI) film.⁶² This leads to challenges such as diminished coulombic efficiency and reduced cycling stability in lithium-ion batteries. It has been shown that the introduction of fluorine substitution into carbonate solvent molecules can significantly improve the cycling stability of the electrode interface while expanding the voltage window of the electrolyte. This provides an important avenue for optimizing the performance of lithium-ion batteries.

The effects of various electrolyte compositions on the formation of SEI and long-term cycling stability of lithium-ion batteries were systematically compared. SEIs formed in EC/DMC using

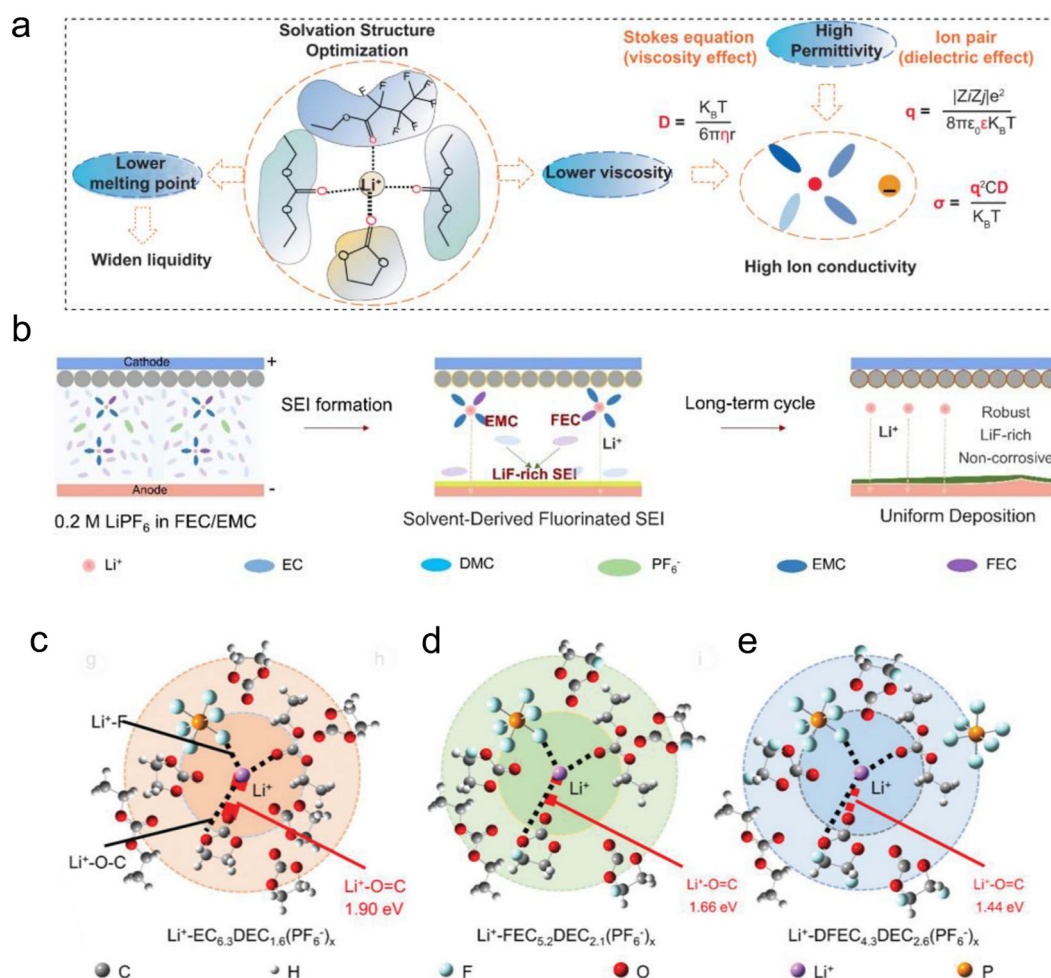


Fig. 3 (a) Relationship of solvation structure and physical properties of electrolyte.⁶⁵ (b) Schematic of different chemical energy storage systems, their SEI formation processes, and long-term cycle performance of lithium-metal batteries using 0.2 M LiPF₆ in FEC/EMC. (Reproduced from ref. 66 with permission from John Wiley and Sons, copyright 2022).⁶⁶ (c) Schematics of the solvation structure in (c) 1 M LiPF₆-EC/DEC, (d) 1 M LiPF₆-FEC/DEC, and (e) 1 M LiPF₆-DFEC/DEC electrolytes. (Reproduced from ref. 67 with permission from John Wiley and Sons, copyright 2021).⁶⁷



1 M LiPF₆ do not contain LiF,⁶³ which can lead to dendrite growth and subsequent corrosion over time. Similar results are also observed with 0.2 M LiPF₆ in EC/DMC, where dendrites are formed continuously during the cycling process. However, when 0.2 M LiPF₆ is used in the FEC/EMC electrolyte, a fluorine-rich solvent-derived SEI is formed, which is not only stable and robust but also effective in preventing the formation of dendrites, thus providing excellent cycling stability and a non-corrosive environment (Fig. 3b).⁶⁴ This highlights the critical role of electrolyte composition in improving SEI quality and hence battery performance.

During the decomposition process, FEC produces a substantial amount of LiF, which forms a dense and stable SEI film. This film can effectively protect the lithium metal anode, thus improving the cycling performance of the battery. Simultaneously, FEMC improves the oxidation stability of the electrolyte, allowing the battery to operate safely at higher voltages.⁶⁸ Concurrently, fluorinated carbonate solvents demonstrate superior electrochemical properties across a wide range of thermal spectra, creating the conditions for batteries to be used over a wide range of temperatures. Cheng *et al.* devised a controlled fluorination strategy for carbonate solvents to accelerate the Li desolvation kinetics, thereby significantly improving the performance of lithium-ion batteries at sub-zero temperatures. Using fluoroethylene carbonate (FEC) and difluoroethylene carbonate (DFEC) as model systems (Fig. 3c–e), they demonstrated that increasing fluorination progressively weakens the Li-solvent ion-dipole interactions. Compared to conventional ethylene carbonate (EC), DFEC-based electrolytes show a six-fold increase in the rate of desolvation at –20 °C. Remarkably, LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811)||Li cells using the DFEC electrolyte retained 91% capacity after 300 cycles at 25 °C, and 51% of their room temperature capacity at –30 °C. This work establishes fluorination engineering as a critical paradigm for designing advanced cryogenic electrolytes, enabling high-energy-density battery operation under extreme thermal constraints.⁶⁷

2. Siloxane solvent

Siloxane-based solvents are expected to be electrolyte compositions for lithium-based batteries operating under extreme conditions, including wide temperature ranges (–40 °C to >60 °C)^{69,70} and extended voltage windows (>4.5 V vs. Li⁺/Li) (Fig. 4a) (Table 3).⁷¹ This potential stems from their intrinsic molecular properties: the robust Si–O bonding (energy of ~452 kJ mol^{–1}) confers excellent thermal stability,⁷² effectively mitigating high-temperature decomposition and thermal runaway, while the low highest occupied molecular orbital

(HOMO) energy level confers excellent anodic stability (Fig. 4b), suppressing oxidative decomposition at the cathode–electrolyte interface under high-voltage charging.⁷³ Furthermore, their characteristically low viscosity,⁷⁴ low melting point,⁷⁵ and weak solvation capability ensure efficient ion transport and rapid interfacial kinetics even at ultra-low temperatures, resulting in significantly improved rate capabilities.⁷⁶ Crucially, siloxane solvents facilitate the formation of an inorganic-rich solid electrolyte interphase (SEI) on high-energy-density anodes, such as lithium metal (Fig. 4c). With enhanced thermal and chemical stability, this SEI effectively inhibits detrimental side reactions and dendrite growth under harsh operating stresses, including severe thermal cycling, high current densities, and large voltage differentials, resulting in significant improvements in cycle life, Coulombic efficiency,⁷⁷ and safety under extreme conditions.⁷⁸ These combined properties make siloxane-based electrolyte solvents a key enabler for the development of next-generation lithium (metal) batteries that offer high safety, extended operational temperature and voltage ranges, and high energy density.⁷⁹

At the molecular level, siloxane molecules form lithium-centered, anion-rich clusters *via* Si–O elimination reactions, resulting in fluorine (F) and oxygen (O)-rich interphases. This process enhances the stability of electrolyte interfaces with lithium metal anodes and high-voltage cathodes. This property is ascribed to the high bond energy of Si–O bonds (452 kJ mol^{–1}), which is significantly higher than that of C–O bonds (352 kJ mol^{–1}), thereby rendering siloxane solvents more stable in chemical and electrochemical reactions.

Fan *et al.* developed a siloxane-based electrolyte utilizing the Si–O bond strategy with 1,2-dimethoxyethane (DME) and ethylene carbonate (EC) as representative ether and ester solvents, respectively. DME forms a bidentate coordination with Li⁺ due to its distinctive structure, which leads to a high desolvation energy (Fig. 4d). Additionally, the desolvation energy can be reduced by adjusting the length of the alkyl chain between the ether groups. The high desolvation energy of EC is attributed to the high polarity of its rigid cyclic structure. In contrast, linear carbonates (*e.g.*, DMC) have lower desolvation energy because their open structure leads to molecular dipole cancellation, which enhances the dynamic behavior of the electrode–electrolyte interface. Molecular orbital theory simulations further suggested substituting the central alkyl chain of DME with silicon, leading to the design of a novel siloxane solvent (Fig. 4e). With a wider electrochemical window and better chemical stability, this new solvent can significantly improve the overall performance of the electrolyte. In thin Li||NCM811, thin Li||LCO batteries, and 1.4 A h pouch cells, the siloxane-based electrolyte performed well, demonstrating its wide

Table 3 Siloxane solvent classes and the battery performance

Solvents	Cell configuration	Protocol	Discharge capacity	Ref.
TMMS	Li NCM811	~60 °C, >4.4 V (vs. Li ⁺ /Li)	200 cycles, 93%	80
DMMS	Li NCM811	~60 °C, >4.4 V (vs. Li ⁺ /Li)	350 cycles, 80%	72
TFTMS	Li NCM811	~60 °C, >4.2 V (vs. Li ⁺ /Li)	200 cycles, 62.8%	71
MTOS	Graphite NCM811	–40 to 25 °C, >4.4 V (vs. Li ⁺ /Li)	100 cycles, 88.8%	81
DMSP	Li NCM811	~60 °C, >4.5 V (vs. Li ⁺ /Li)	200 cycles, 77%	82



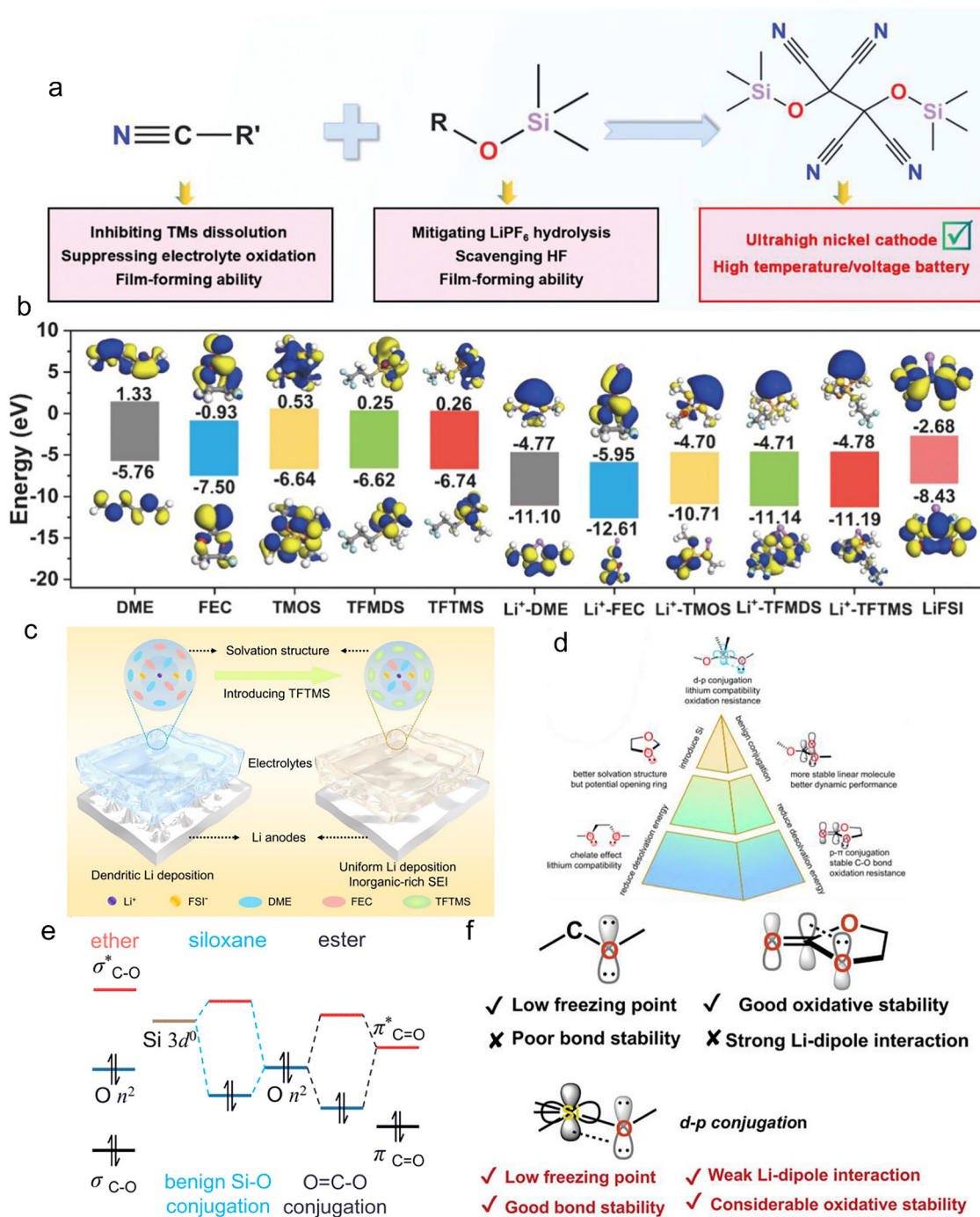


Fig. 4 (a) Schematic illustration of the delicate design of TDSTCN. (Reproduced from ref. 76 with permission from John Wiley and Sons, copyright 2023.)⁷⁶ (b) HOMO and LUMO energy levels of different molecules and clusters. (Reproduced from ref. 71 with permission from American Chemical Society, copyright 2024.)⁷¹ (c) Schematic illustration of the solvation structure from the E-DME/FEC and E-TFTMS electrolyte. (Reproduced from ref. 71 with permission from American Chemical Society, copyright 2024.)⁷¹ (d) 1,2-Dimethoxyethane (DME) and ethylene carbonate (EC) are respectively typical representatives of ether and ester solvents.⁷² (e) Schematic illustration of the approximated molecular orbitals of ether, siloxane and ester. Among them, siloxane and ester have conjugated effects.⁷² (f) The structures and properties of typical carbonate and ether solvents, and the bonding structures and properties of siloxane solvents. (Reproduced from ref. 81 with permission from John Wiley and Sons, copyright 2025.)⁸¹

applicability by showing ultra-long cycle life and high energy density.⁷²

Siloxane electrolyte solvents also exhibit remarkable low-temperature performance advantages. Their low viscosity and

high ion mobility allow them to maintain good conductivity and interfacial compatibility under low-temperature conditions. Wang's team designed a novel low-temperature electrolyte based on siloxane, which reduces the interaction between Li⁺ and



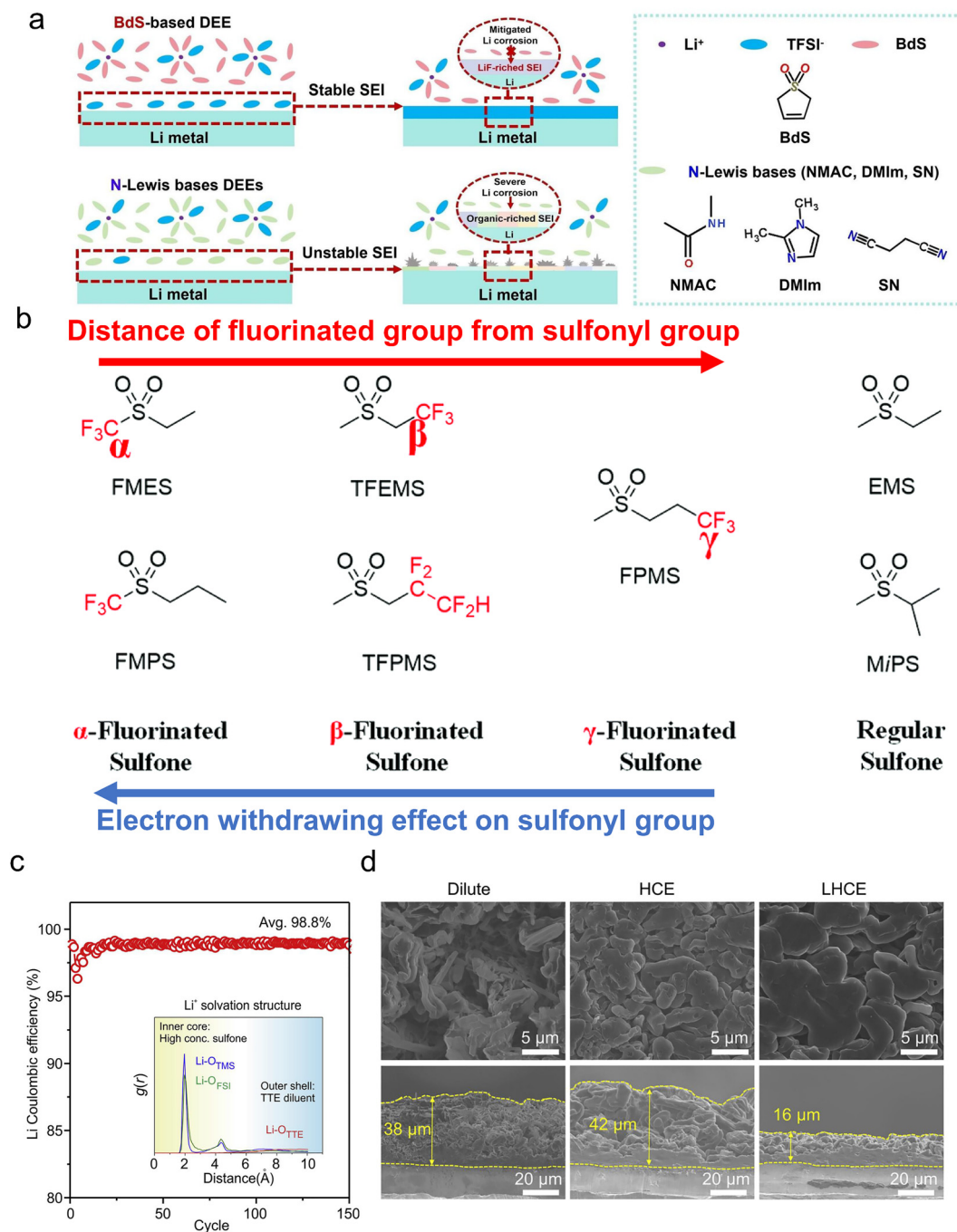


Fig. 5 (a) Schematic demonstration of the Li compatibility with LTB-3.0 or typical N-containing Lewis bases-based DEEs. (Reproduced from ref. 91 with permission from John Wiley and Sons, copyright 2024.)⁹¹ (b) Sulfones with fluorinated groups in different positions.⁸⁸ (c) Achievement of a high Coulombic efficiency of nearly 99% through the incorporation of a non-solvating co-solvent in a sulfone-based localized high-concentration electrolyte.⁹⁰ (Reproduced from ref. 90 with permission from Elsevier, copyright 2018.) (d) Scanning electron microscopy (SEM) images depicting the lithium deposition morphologies in various sulfone-based electrolytes. (Reproduced from ref. 90 with permission from Elsevier, copyright 2018.)⁹⁰

Table 4 Sulfone solvent classes and the battery performance

Solvents	Cell configuration	Protocol	Discharge capacity	Ref.
FPMS	Graphite NCM532	~80 °C, > 6.0 V (vs. Li ⁺ /Li)	500 cycles, 84%	87
FMES	Graphite NCM532	~80 °C, > 6.0 V (vs. Li ⁺ /Li)	500 cycles, 80%	88
EMS	Graphite NCM622	~60 °C, > 6.0 V (vs. Li ⁺ /Li)	400 cycles, 50%	88
TFPMS	Graphite NCM622	~60 °C, > 6.0 V (vs. Li ⁺ /Li)	400 cycles, 85%	88



design and optimizing the formation of interphase membranes; incorporating high-performance additives to regulate interfacial chemical reactions; developing cost-effective and efficient synthesis techniques; and investigating blended systems of sulfone solvents with other solvents to further enhance their overall performance.⁷⁴

In conclusion, sulfone solvents have high oxidative decomposition voltage, significant thermal stability and inherent flame-retardant properties, showing great potential for application in high-voltage and high-energy-density lithium-ion batteries. Through molecular design, co-solvent incorporation, and advances in interfacial engineering, sulfone solvents are anticipated to play a pivotal role in the development of high-safety and high-performance lithium-ion batteries.⁷⁵ Additionally, they provide essential technical support to meet the demands of electric vehicles, energy storage systems and other applications in advanced fields.^{77,79} Future research is expected to further facilitate the practical application of sulfone solvents, making a significant contribution to the realization of more efficient and safer lithium-ion battery systems.⁷⁰

4.1 Ether solvents. Ether-based solvents (*e.g.*, DME, THF)^{92–94} are uniquely advantageous in wide temperature range

lithium-ion batteries by utilizing the inherent conformational flexibility and weak intermolecular forces of their C–O–C backbone.^{95,96} The exceptionally low rotational energy barrier ($< 5 \text{ kJ mol}^{-1}$) of ether linkages imparts pronounced conformational freedom to molecular chains, enabling ultra-low viscosity to be maintained under extreme cryogenic conditions (Fig. 6a).⁹⁷ Concurrently, their moderate donor number (DN: 16–20) facilitates the formation of stable solvation sheaths,⁹⁸ promoting uniform lithium-ion deposition. However, deployment in high-voltage applications is constrained by a narrow electrochemical stability window ($< 4.0 \text{ V vs. Li}^+/\text{Li}$). This limitation stems from the fact that ether α -hydrogen is susceptible to dehydrogenation and oxidation at potentials greater than 4.0 V ,^{99,100} thereby initiating a radical-mediated chain decomposition reaction at the cathode interface (Table 5).

REN *et al.* explored the molecular structure optimization of ether solvents (DME, DMP, DMB) and found that the six-membered ring coordination structures, exemplified by 1,2-dimethoxypropane (DMP), exhibits stronger lithium-ion coordination abilities and can effectively inhibit the decomposition of free solvents. At the high-voltage cathode surface (4.7 V),¹⁰¹ DMP preferentially undergoes hydrogen transfer reactions,

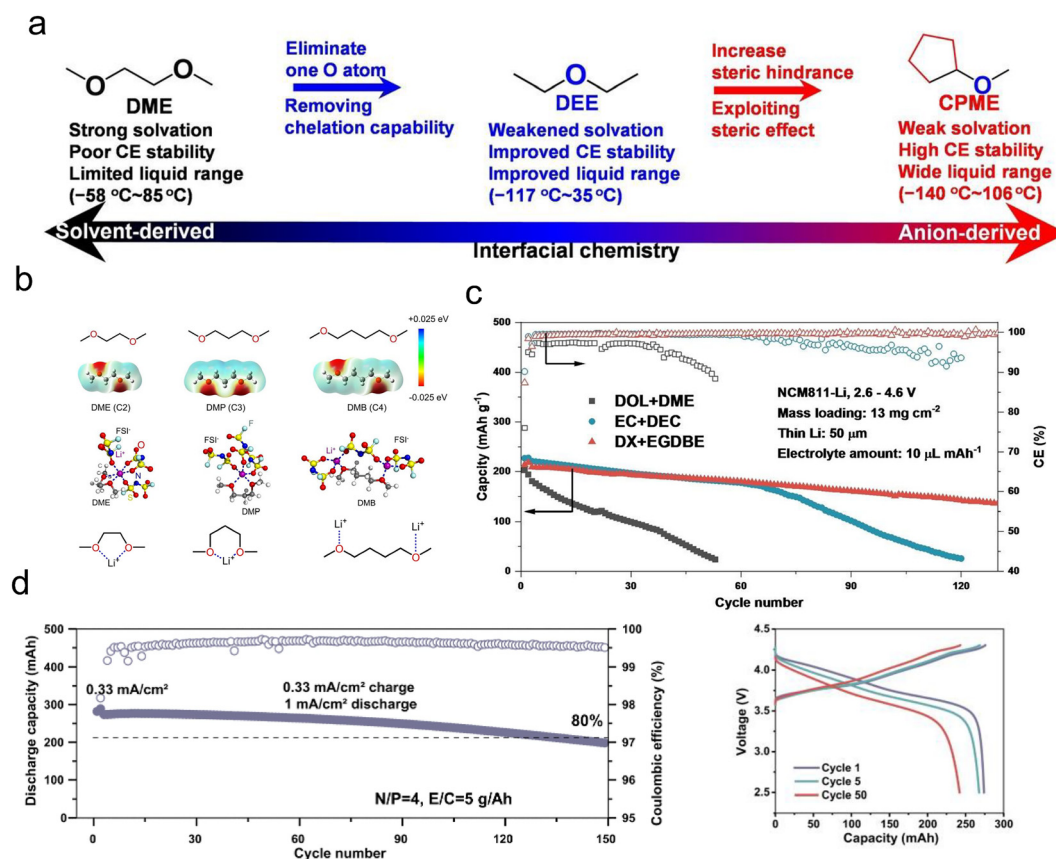


Fig. 6 (a) Step-by-step molecular design to tune solvation properties of solvents. (Reproduced from ref. 105 with permission from John Wiley and Sons, copyright 2023.)¹⁰⁵ (b) Characterization of solvation structures for DME, DMP, and DMB electrolytes, including their molecular structures and electrostatic potential maps. (Reproduced from ref. 106 with permission from John Wiley and Sons, copyright 2023.)¹⁰⁶ (c) Performance of NCM811||Li batteries under harsh conditions within the voltage window of 2.6–4.6 V.¹⁰⁷ (d) Long-term cycling performance and cycling profiles of a 300 mA h double-sided pouch cell utilizing a DPE-based electrolyte.¹⁰²



Table 5 Ether solvent classes and the battery performance

Solvents	Cell configuration	Protocol	Discharge capacity	Ref.
DME	Li NCM811	−58 to 85 °C, ~4.2 V (vs. Li ⁺ /Li)	94 cycles, 80%	119
DEE	Li NCM811	−117 to 35 °C, ~4.4 V (vs. Li ⁺ /Li)	182 cycles, 80%	119
CPME	LFP Gr	−140 to 106 °C, ~4.4 V (vs. Li ⁺ /Li)	1000 cycles, 80%	120
DMP	Li NCM811	−117 to 83 °C, ~4.3 V (vs. Li ⁺ /Li)	180 cycles, 86%	121
EGDBE	Li NCM811	−74 to 121 °C, ~4.5 V (vs. Li ⁺ /Li)	130 cycles, 80%	122
FDMB	Li NCM532	>60 °C, >6.0 V (vs. Li ⁺ /Li)	420 cycles, 90%	123
FXDEE	Li NCM811	−40 to 50 °C, >5.0 V (vs. Li ⁺ /Li)	200 cycles, 80%	59

leading to the formation of a stable LiF-rich cathode electrolyte interphase (CEI), which significantly improves the cycling stability of the battery (Fig. 6b).⁹²

Experimental results demonstrate that DMP-based electrolytes maintain stable operation over a wide temperature range (−20 °C to 50 °C) and achieve a capacity retention of 91.4% after 100 cycles under high-voltage conditions, offering a novel design direction for the development of high-energy-density lithium–metal batteries. Zhang *et al.* extended the alkyl chains of ether molecules using molecular engineering principles to optimize their structure, lower the energy barrier for the hydrogen transfer reaction, and adjust the covalency of Ni–O bonds. They developed a hybrid electrolyte system that includes 1,3-dioxane (DX) and dibutyl ethylene glycol ether (EGDBE) (Fig. 6c).⁹⁹

The results indicated that this system effectively suppressed the oxidative decomposition of the electrolyte, the formation of rock-salt NiO phases, and gas evolution. Furthermore, it facilitated the formation of a thin and stable solid electrolyte interphase (SEI) on the lithium–metal anode surface. Compared to conventional carbonate and ether electrolyte solvents, this novel system extended battery lifespans by 100% to 500%, with 80% capacity retention and 99.85% Coulombic efficiency at a high voltage of 4.6 V. These findings underscore the pivotal role of molecular engineering in optimizing the performance of ether solvents.

To mitigate the oxidative decomposition at the cathode interface in ether electrolyte solvents, Li *et al.* introduced a non-polar ether electrolyte system consisting of dipropyl ether (DPE) and highly concentrated lithium salt (LiFSI). By regulating the solvation structure and controlling the decomposition sequence, they achieved the long-term stable operation of lithium–metal batteries at a high voltage of 4.3 V. This system reduced the coordination strength between solvent molecules and lithium ions, thereby enhancing anion aggregation effects. This system facilitated the formation of an inorganic-rich CEI film that preferentially decomposed on the cathode surface, effectively suppressing free solvent decomposition and generating a solvent-depleted layer in the interfacial region, which significantly improved the stability of the battery interface.

Experimental results showed that the DPE-based electrolyte enabled Li||NCM811 coin cells to retain 82% of their capacity after 220 cycles at a current density of 1 mA cm^{−2}. Furthermore, a 300 mA h pouch cell exhibited a capacity retention of 74.1% after 150 cycles (Fig. 6d).¹⁰² This study offers an effective strategy for the practical application of ether solvents in high-voltage lithium–metal batteries.

Despite the significant potential of ether solvents in lithium-ion batteries, challenges such as their narrow electrochemical window and susceptibility to high-voltage decomposition remain to be resolved.¹⁰³ Future research should prioritize the optimization of ether solvent performance through molecular structure design, incorporation of multifunctional additives, and development of mixed electrolyte systems.¹⁰⁴ By tailoring molecular structures, refining interfacial film compositions, and regulating solvation capacity and interfacial chemical reactions, ether solvents are anticipated to play a pivotal role in high-energy-density lithium–metal batteries and batteries designed for extreme conditions. These advancements could provide essential support for technological breakthroughs in electric vehicles and energy storage systems.¹⁰²

4.2 Fluorinated ether. The superior performance of fluorinated ether-based electrolytes stems fundamentally from the strategic incorporation of the fluorine (F) atoms. Of all the elements, the fluorine atom has the highest electronegativity and therefore provides a strong electron-withdrawal effect in solvent molecules (Fig. 7a and b). This greatly improves the oxidative stability of the solvent due to the elevated energy level of the highest occupied molecular orbital (HOMO), which creates a higher energy barrier for electron removal and subsequent oxidative decomposition. This effect directly expands the upper limit of the electrochemical stability window (ESW), enabling compatibility with high-voltage cathode materials (*e.g.*, lithium-rich manganese-based, high-nickel layered oxides).

Meanwhile, during electrochemical reduction at the anode (*e.g.*, graphite, silicon-based, or lithium–metal), the fluorinated ether molecules preferentially cleave the C–F or C–O bonds to produce fluorinated reduction products, such as lithium fluoride (LiF) and lithium alkoxides (ROLi). This property leads to the formation of a LiF-rich solid electrolyte phase (SEI) on the anode surface. LiF is known for its low electronic conductivity, high ionic conductivity (facilitating facile Li⁺ transport with a low activation barrier),^{110,111} and exceptional chemical/electrochemical stability (Fig. 7c), which results in a SEI layer with superior ionic conductivity and remarkable mechanical/chemical robustness.¹¹² This stabilized SEI effectively broadens the lower limit of ESW, and improves compatibility with highly active anode materials (*e.g.*, silicon, lithium metal) that operate at low potentials, kinetically suppressing deleterious side reactions and dendrite growth. Furthermore, the unique molecular structure of fluorinated ethers, characterized by flexible ether bonds (−C–O–C−) and sterically demanding fluorine atoms/fluorinated groups, gives the electrolyte low viscosity and a



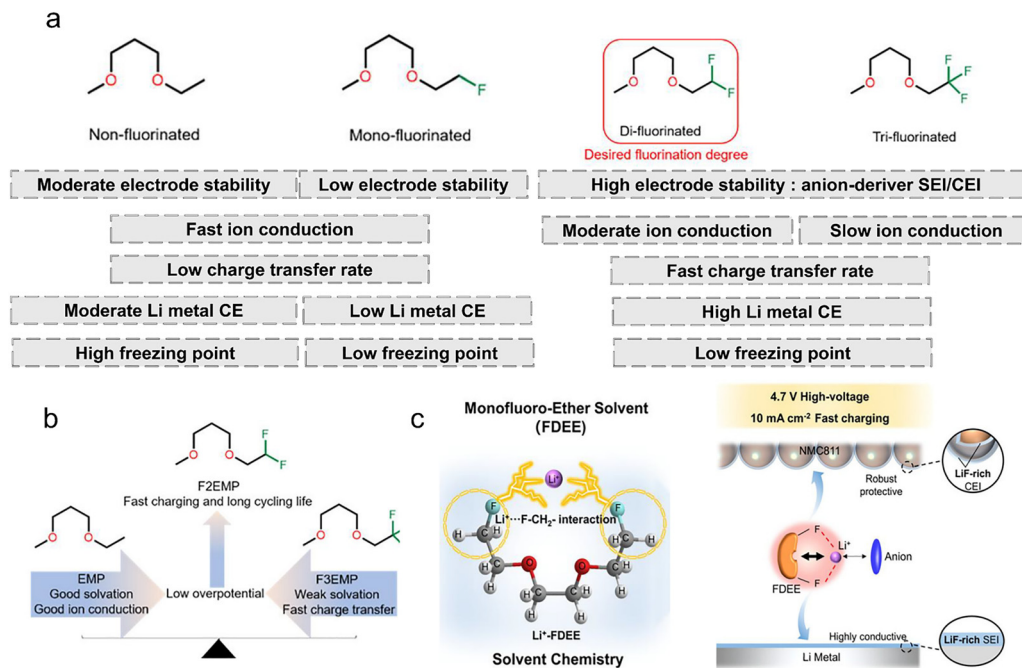


Fig. 7 (a) Overview on EMP and fluorinated-EMP electrolytes. EMP and F1EMP with good solvation favor the ionic conductivity, and F2EMP and F3EMP with weak solvation contribute to the fast charge transfer process. The modification by the F atom also reduces the freezing point of electrolyte by increasing the molecule polarization and increases the electrode/electrolyte interfacial stability (excluding F1EMP). (Reproduced from ref. 108 with permission from American Chemical Society, copyright 2024.)¹⁰⁸ (b) Considering the cycling life and rate performance, F2EMP is considered as the optimized electrolyte solvent for LMBs. (Reproduced from ref. 108 with permission from American Chemical Society, copyright 2024.)¹⁰⁸ (c) Comparison of anion chemistry and solvent chemistry in tailoring electrochemical interphases for high-voltage and fast-charging LMBs.¹⁰⁹

low freezing point.⁶⁰ This maintains high ionic mobility, which ensures excellent low-temperature performance.¹¹³ Due to the low polarizability of fluorine, intermolecular interactions (e.g., van der Waals forces) are weakened, while inherent molecular flexibility is maintained, collectively lowering viscosity and inhibiting crystallization at subambient temperatures. Critically, the carbon-fluorine (C-F) bond exhibits exceptionally high bond dissociation energy (approximately 485 kJ mol⁻¹, which greatly exceeds that of the C-H bonds (~414 kJ mol⁻¹) and C-C bonds (~347 kJ mol⁻¹). As a result, the thermal decomposition of fluorinated ether molecules requires a higher energy input, which greatly improves the thermal stability of the electrolyte at elevated temperatures. Concomitantly, fluorine acts as an effective radical scavenger, which interrupts the radical chain reactions fundamental to combustion processes, thereby endowing the electrolyte with intrinsic flame-retardant properties and substantially improving the safety profile of the battery system. In summary, fluoroether-based electrolytes leverage fluorine's unique physico-chemical properties of high electronegativity, large atomic radius, and high bond strength to synergistically optimize oxidative stability,¹¹⁴ SEI composition and properties, rheological behavior, and thermal/chemical resilience.¹¹⁵ These combined properties enable lithium-ion batteries to operate reliably and safely over a wider temperature range (from cryogenic to elevated temperatures) and over a broader voltage window, making fluoroethers a critical material in the development of next-generation high-performance batteries.

Ali Coskun and colleagues have designed a novel fluorinated ether solvent, 2,2-dimethoxy-4-(trifluoromethyl)-1,3-dioxolane (DTDL), that integrates cyclic fluorinated ether groups with linear ether segments. This molecular design enhances high-voltage stability and tunable Li⁺ solvation capability¹¹⁴ (Fig. 8a and b).

In high-voltage lithium metal batteries (LMBs), especially with high nickel content LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ (NCM811) cathodes and ultrathin Li-metal anodes (20 μm), 1 M lithium bis(fluorosulfonyl)imide (LiFSI) in the DTDL electrolyte demonstrates exceptional oxidative stability up to 5.5 V (vs. Li⁺/Li) (Fig. 8c) and achieves a Li⁺ transference number (t⁺Li) of 0.75 (Fig. 8e). This value greatly exceeds the conventional 1 M LiFSI in 1,2-dimethoxyethane (DME) electrolyte. Crucially, the DTDL-based electrolyte facilitates the formation of solid electrolyte interphase (SEI) enriched with LiF and sulfur-fluorine (S-F) moieties on the Li-metal anode. This robust SEI effectively suppresses the growth of Li dendrites, resulting in improved Coulombic efficiency (CE) and cycling stability. Remarkably, full cells consisting of an NCM811 cathode and a 20-μm Li-metal anode using a 2 M LiFSI-DTDL electrolyte retain 84% of their initial capacity after 200 cycles at 0.5C, demonstrating outstanding long-term cyclability and high energy density. Concurrently, fluorinated ethers exhibit superior low-temperature functionality, manifesting enhanced ionic conductivity and accelerated interfacial kinetics at subzero conditions, which is primarily attributed to their weakened solvation strength and reduced electrolyte viscosity (Fig. 8d).¹¹⁴



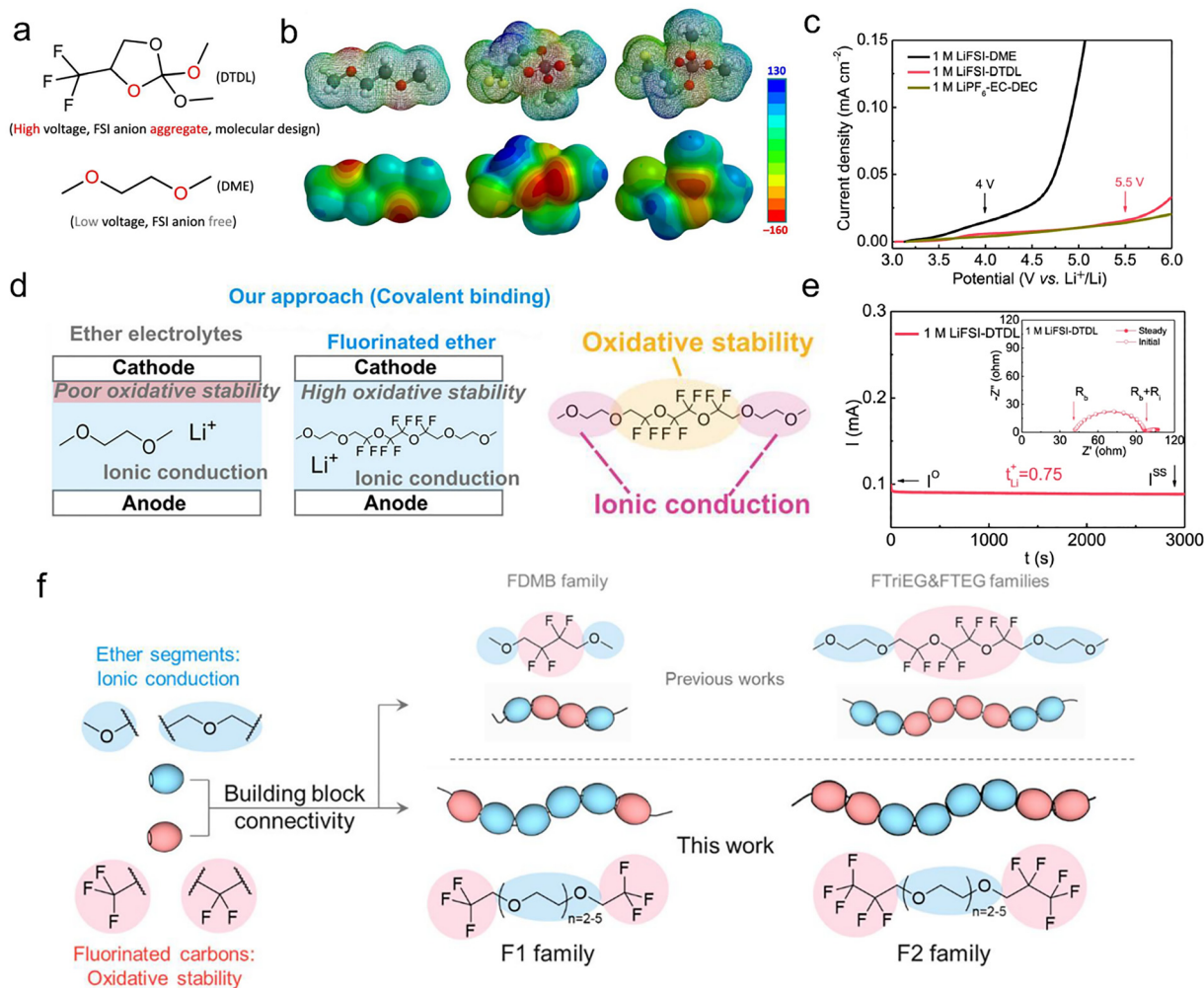


Fig. 8 (a) The comparison of molecular structures of DTDL and DME. (b) Electrostatic potential maps (ESP) of DME and DTDL with front and back views, color scheme: yellow, F; red, O; gray, C; white, H.¹¹⁶ (c) Oxidation stability of three electrolytes in Li||Al half cells tested by linear sweep voltammetry (LSV).¹¹⁶ (d) Motivation and synthetic scheme. Illustration of typical challenges with common electrolytes. (Reproduced from ref. 117 with permission from American Chemical Society, copyright 2020.)¹¹⁷ (e) Li^+ transference numbers and the chronoamperometry profiles of Li||Li symmetrical cells in 1 M LiFSI-DTDL.¹¹⁶ (f) Molecular design. Using ether segments (blue bead) and fluorinated carbons (red bead) as building blocks, previous work has built several centrally fluorinated ethers (FDMB, FTriEG, and FTEG families).¹¹⁸

Amanchukwu's team has achieved three critical breakthroughs in lithium–metal battery systems through the innovative structural tuning of fluoroether molecules with an ether chain core and fluorinated terminal groups, accompanied by the precise tuning of ionic solvation effects. First, they realized high ionic conductivity (1.3 mS cm^{-1} at 30°C) with exceptional low-temperature performance, retaining functionality even at -60°C . Second, contrary to conventional wisdom, reducing fluorine content (e.g., from E6F1 to E3F1) significantly improved the oxidative stability of the electrolyte to 5.2 V (vs. Li/Li^+) (Fig. 8f). Raman spectroscopy revealed that higher fluorine content weakens solvation capability, increasing the population of free solvent molecules that are susceptible to oxidation. Finally, they achieved unprecedented long-term cycling stability, with lithium metal deposition overpotentials remaining below 20 mV and average Coulombic efficiencies of 98.9%. The $\text{Li}/\text{LiFePO}_4$ (LFP) full cells can sustain more than

250 cycles, while the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO)/ $\text{LiNi}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ (NMC111) cells significantly outperforms those using conventional ether-based electrolytes. This work establishes a new molecular design strategy for high-energy-density battery electrolytes that synergistically optimizes molecular connectivity, solvation structure, and electrochemical properties.¹¹⁸

5. Ionic liquid

The molecular design of ionic liquid electrolyte solvents is guided by three fundamental principles: weak coordination, large steric bulk, and targeted functionalization. These materials offer a structurally rigid yet synthetically tunable backbone, allowing the incorporation of polar side chains such as ether, cyano, or carbonate groups to reduce viscosity while maintaining thermal integrity. Their broad liquidus range prevents decomposition at elevated temperatures, facilitates lithium salt dissociation, and promotes the formation of stable electrode–electrolyte



interphases, thus supporting operation over an extensive temperature window. Through rational selection of cation–anion pairs, electrochemical stability windows exceeding 5 V can be achieved. Molecular simulation-guided optimization further enables the development of ionic liquids combining low viscosity, high ionic conductivity, and excellent interfacial film-forming abilities. Such tailored electrolyte solvents exhibit enhanced compatibility with high-performance electrode

materials, positioning them as promising candidates for next-generation high-energy-density and safe energy storage systems. Imidazolium-based ionic liquids (ILs), for instance, demonstrate considerable promise as electrolyte solvents for high-voltage lithium-ion batteries (Fig. 9a).¹²⁴ Structural asymmetry introduced at the N1/N3 positions—such as through ethyl-methyl substitution—disrupts cationic symmetry and reduces packing efficiency, markedly depressing both the melting point (T_m)

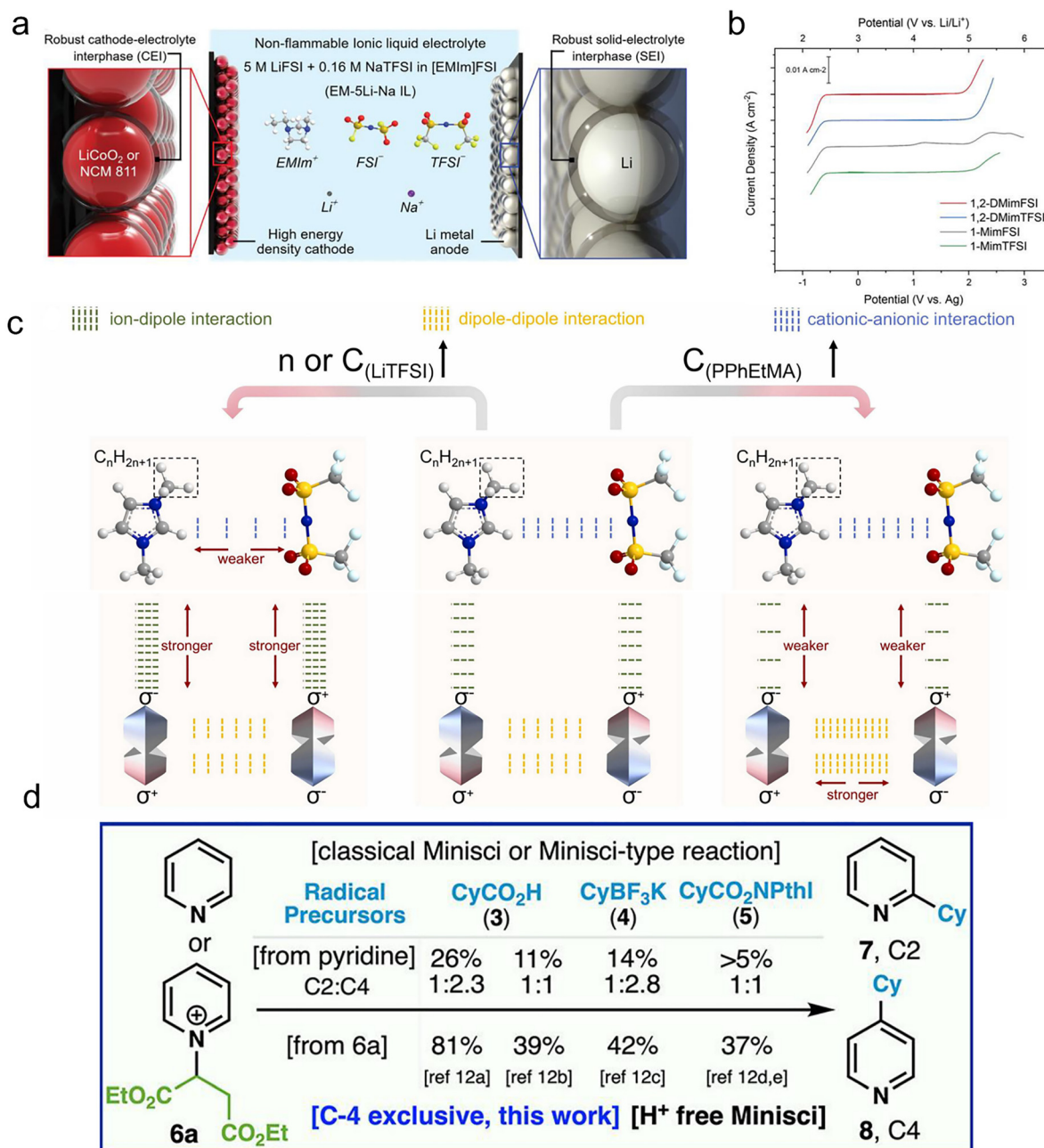


Fig. 9 (a) Schematic illustration of the battery configuration and electrolyte composition of the EM-5Li-Na IL electrolyte. (Reproduced from ref. 124 with permission from John Wiley and Sons, copyright 2020.)¹²⁴ (b) Electrochemical stability window of the pure synthesized PILs at 60 °C. (Reproduced from ref. 125 with permission from John Wiley and Sons, copyright 2018.)¹²⁵ (c) Schematic illustration for the interactions between PPhEtMA polymer and [Cnmim][TFSI] ionic liquids and the variation of these interactions with electrolyte composition. (Reproduced from ref. 126 with permission from Elsevier, copyright 2025.)¹²⁶ (d) Comparison experiment with pyridine. (Reproduced from ref. 127 with permission from American Chemical Society, copyright 2021.)¹²⁷



and glass transition temperature (T_g) to maintain a liquid state below -40 °C. Concurrently, the combination of short or branched alkyl chains with compact C2 substituents (*e.g.*, methyl) weakens intermolecular interactions, leading to reduced viscosity and improved low-temperature ionic conductivity. A key challenge with imidazolium-based ionic liquids lies in the inherent acidity of the C2-position hydrogen ($pK_a \approx 23$), which limits their oxidative stability. Strategic substitution at this site with electron-withdrawing groups ($-\text{CN}$, $-\text{CF}_3$) or alkyl moieties ($-\text{CH}_3$) stabilizes the π -conjugated cationic structure and raises the highest occupied molecular orbital (HOMO) energy level, resulting in significantly enhanced oxidation resistance exceeding 5.0 V *versus* Li^+/Li . This molecular-level tailoring enables full compatibility with high-voltage cathodes such as LiCoO_2 , NMC811, and LNMO (Fig. 9b and c).^{125,126} Pyridinium-based ionic liquids exhibit exceptional promise as electrolyte solvents for lithium batteries capable of operating under demanding conditions, spanning wide temperature ranges (-40 to 150 °C) and high-voltage windows (>5.0 V). A key molecular engineering strategy involves N1-position asymmetric alkylation such as a combination of a long-chain C_8H_{17} group and a branched isopropyl substituent which disrupts molecular packing to significantly depress melting

and glass transition temperatures. Furthermore, incorporating ether-functionalized side chains ($-\text{OCH}_2\text{CH}_2-$) enhances conformational flexibility, enabling high ionic conductivity at subzero temperatures. The inherent structural robustness of the pyridinium ring lacking an acidic proton at the C2 position confers a high intrinsic oxidation potential (~ 5.2 V *vs.* Li^+/Li). This stability can be further extended by introducing electron-donating groups (*e.g.*, $-\text{OCH}_3$) at the C4 position, raising the anodic stability limit to 5.5 V (Fig. 9d).¹²⁷ Such targeted molecular modifications underscore the versatility of pyridinium ionic liquids in meeting the stringent requirements of next-generation high-voltage lithium batteries.

Pyrrolidinium-based ionic liquids (Pyr-ILs), constructed from a saturated five-membered nitrogenous heterocycle, represent a promising class of electrolyte solvents for high-voltage lithium-ion batteries due to their combination of wide electrochemical windows, high ionic conductivity, and exceptional thermal/interface stability (Fig. 10a).¹²⁸ Their ability to withstand extreme potentials exceeding 5.8 V stems from deliberate molecular engineering. For instance, in the C_3mpyr^+ cation, asymmetric *N*-alkyl substitution enhances conformational flexibility and substantially lowers the glass transition temperature (T_g). Concurrent saturation fluorination at the C3 position

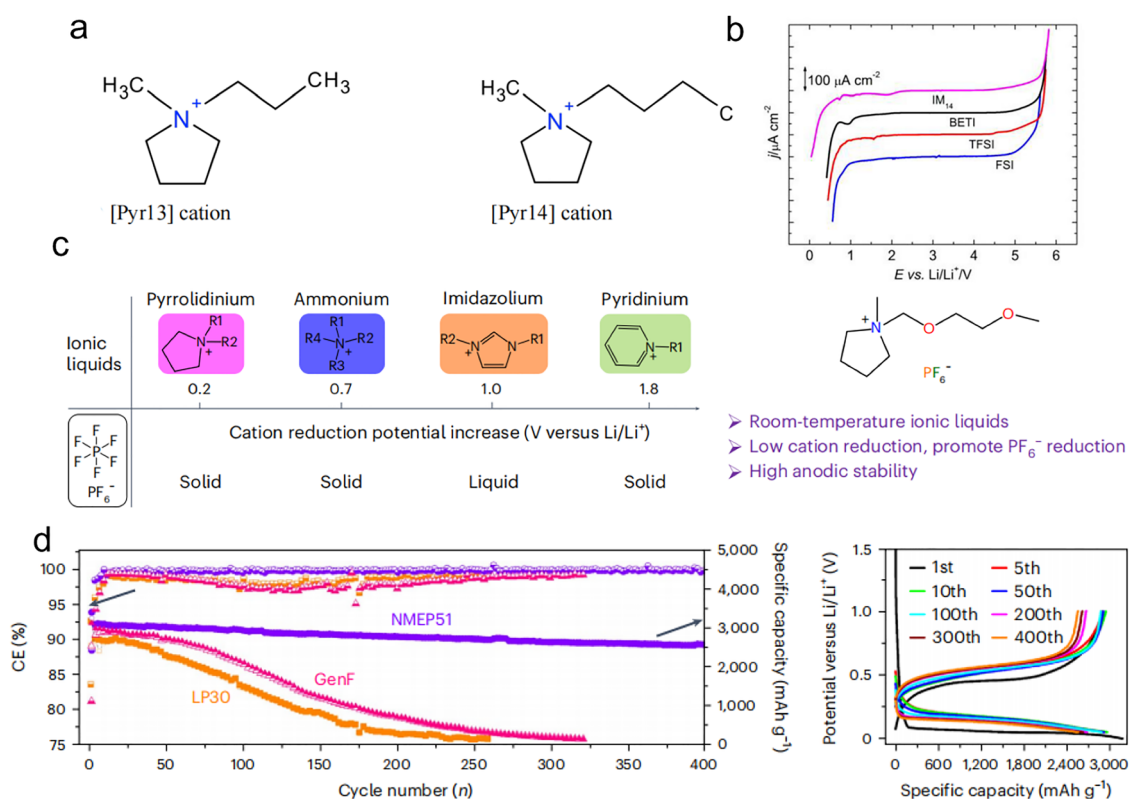


Fig. 10 (a) Schematic representation of the utilized IL constituents. (Reproduced from ref. 128 with permission from John Wiley and Sons, copyright 2017.)¹²⁸ (b) Linear sweep voltammograms of PYR_{1201} -based ionic liquids measured with the scan rate of 1 mVs^{-1} at 20 °C (working and counter electrodes were platinum, and the reference was lithium metal). (Reproduced from ref. 129 with permission from Elsevier, copyright 2013.)¹²⁹ (c) The $[\text{PF}_6^-]$ -based room-temperature ionic liquid design strategy for micro-sized alloying anodes. (Reproduced from ref. 130 with permission from Springer Nature, copyright 2024.)¹³⁰ (d) Cycling stability and CEs of μSi electrodes at $\text{C}/8$ (447 mA g^{-1}) in NMEP51 (violet), LP30 (orange) and GenF (1.2 M $\text{LiPF}_6\text{-EC/EMC}$ (3/7 w/w) + 10 wt% FEC) (pink) electrolytes. The μSi electrodes were activated at a rate of $\text{C}/20$ (179 mA g^{-1}) for one cycle and then cycled at $\text{C}/8$ (447 mA g^{-1}). (Reproduced from ref. 130 with permission from Springer Nature, copyright 2024.)¹³⁰



(e.g., with $-\text{CF}_3$) reinforces C–H bond strength, raising the oxidation potential to 6.0 V compared to non-fluorinated analogues and thus providing superior voltage endurance (Fig. 10b).¹²⁹ Further demonstrating the structural modularity of this platform, Wang and colleagues developed NMEP51, a pyrrolidinium-based cation incorporating an integrated dimethoxyethane (DME) motif within its molecular framework. This design generates an asymmetric coordination environment that circumvents the inherent incompatibility between LiPF_6 and conventional ether solvents while retaining the beneficial low reduction potential of ether groups. The resulting electrolyte enables highly reversible Li^+ deposition/stripping on micron-scale alloy anodes, as evidenced by a ~ 325 mesh silicon-based anode maintaining $>87\%$ capacity retention and $>99.9\%$ Coulombic efficiency over 400 cycles at C/8 (447 mA g^{-1}) (Fig. 10c and d).¹³⁰

6. Hybrid solvents

The pursuit of lithium-ion batteries with higher energy densities and broader operational windows has exposed the limitations of single-solvent electrolyte systems, which are often inadequate in

meeting the multifaceted and stringent performance requirements. A fundamental challenge lies in the intrinsic trade-off between essential physicochemical properties: solvents possessing high dielectric constants, which promote lithium salt dissociation, are typically plagued by high viscosity, impairing low-temperature performance. Conversely, low-viscosity solvents that enable high ionic conductivity generally suffer from narrow electrochemical stability windows, rendering them unsuitable for high-voltage applications. To circumvent these constraints, research efforts have shifted towards molecularly engineered hybrid solvent strategies. This paradigm transcends mere physical blending by harnessing synergistic inter-component interactions to achieve a “1 + 1 > 2” enhancement in overall performance, thereby establishing itself as a cornerstone approach for developing electrolytes capable of operating under wide temperature and high voltage conditions.⁵²

Guided by the principle of synergistic dual-solvent regulation of lithium-ion solvation structures, Cui *et al.* developed an advanced electrolyte composed of fluorinated 1,6-dimethoxyhexane (FDMH) a solvent with an extended fluorinated

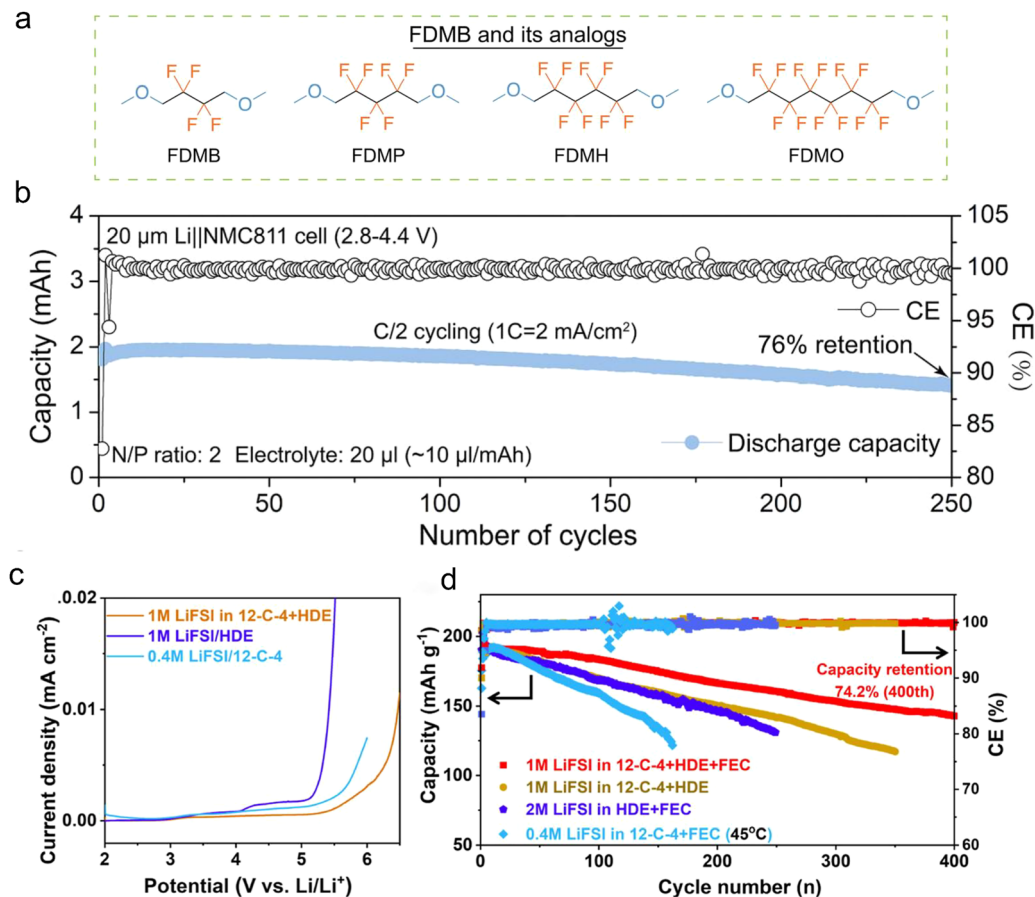


Fig. 11 (a) Molecular structures of FDMB and its analog molecules FDMP, FDMH, and FDMO. (Reproduced from ref. 131 with permission from John Wiley and Sons, copyright 2021.)¹³¹ (b) A $20 \mu\text{m Li||NMC811}$ coin cells achieve 250 cycles before reaching 76% of initial discharging capacity. (Reproduced from ref. 131 with permission from John Wiley and Sons, copyright 2021.)¹³¹ (c) LSV curves of 1 M LiFSI in 12-C-4 and HDE (W12-C-4/WHDE = 20 : 80 and nLiFSI/n12-C-4/nHDE = 1 : 1 : 5), 1 M LiFSI/HDE, and 0.4 M LiFSI/12-C-4 (nLiFSI/n12-C-4 = 1 : 15.45). (Reproduced from ref. 132 with permission from American Chemical Society, copyright 2025.)¹³² (d) Cycling performances of the Li||NCM85 cells with different electrolytes. The charge–discharge processes were conducted at 0.1C in the initial three cycles and then 0.3C in the following cycles (cycling temperature: 45°C for 0.4 M LiFSI in 12-C-4 + FEC, 25°C for all the other cells). (Reproduced from ref. 132 with permission from American Chemical Society, copyright 2025.)¹³²



cited in the reference list. The original data can be accessed by obtaining the full-text articles using the provided PubMed IDs (PMIDs) or Digital Object Identifiers (DOIs).

Acknowledgements

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