The Fluorine Toolbox: from Molecular Design to Advanced Batteries

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Abstract

The increasing demand for high-performance rechargeable batteries, particularly in energy storage applications such as electric vehicles, has driven the development of advanced battery technologies with improved energy density, safety, and cycling stability. In this regard, fluorine has emerged as a crucial element in achieving these goals with fluorinated materials being employed in a wide range of battery applications, including solid and liquid electrolytes, electrolyte additives, solvents, binders, and protective layers for electrodes. This review explores the design and utilization of fluorine-containing materials in advanced batteries, focusing on the significance of controlling their chemical structure and understanding their impact on battery performance. A key aspect is the role of fluorinated materials in facilitating the formation of a thin, protective film of corrosion products at the metal-electrolyte interface, which serves as a barrier against further chemical reactions with the electrolyte. The electron-withdrawing property of fluorine endows these fluorinated materials with high oxidative stability at high voltages. Moreover, the non-flammable nature of fluorinated compounds contributes to the design of batteries with enhanced safety and prolonged lifespan. Additionally, we discuss the current challenges and future directions in harnessing the battery-related aspects of fluorinated materials, with a focus on the regulatory landscape surrounding the use of fluorinated compounds.

Introduction

The increasing demand for renewable energy resources, such as solar and wind power, is driving the need for large-scale energy storage technologies based on batteries, which are essential for integrating renewable energy sources into the electrical grid and enabling off-grid energy access. However, grand challenges are present in developing reliable and efficient battery technologies for improved energy density, cycle life, safety, and sustainability[1-3]. One of the main challenges is controlling side reactions between electrodes and electrolytes, which can lead to the formation of a chemically unstable and mechanically fragile electrode-electrolyte interphase. The formation of dendrites, degradation of battery components, and short circuits due to the growth of these interphases can cause battery failure, combustion, or explosions.

Due to their unique chemical and physical properties[4,5], the incorporation of fluorinated materials has great potential for overcoming the above challenges and enabling the development of next generation batteries[6]. Fluorine-containing compounds have been widely used in various battery components, including as ion-conducting salts, electrolyte solvents, all-solid-state electrolytes, functional additives, separators, as well as electrode materials like binders and coatings (**FIG. 1**)[6-8]. The electronegative nature of fluorine endows these fluorinated materials with high thermal and oxidative stability, chemical inertness and non-flammability[5].

A major benefit of using fluorine materials in batteries is the ability to facilitate the formation of rigid and stable fluoride-rich protection layers on the surface of anodes (i.e. solid electrolyte interface (SEI)) and cathodes (i.e. cathode SEI or cathode electrolyte interphase (CEI)). These layers play a critical role in preventing metal dissolution, improving electrochemical cycling stability, and ultimately enhancing battery performance[9]. Additionally, the high oxidation stability of fluorinated compounds makes them ideal candidates for use in high-voltage batteries with a broad electrochemical stability window and associated chemical inertness[10]. Moreover, the introduction of fluorine increases electronegativity, thereby modifying the local environment surrounding the ion-conducting salts. These modifications facilitate improved dissociation between cationic and anionic species, leading to enhanced ion transport properties. Finally, the use of fluorinated systems gives rise to good thermal properties, which is essential for preventing thermal runaway and improving battery safety[11]. **FIG. 1** summarizes the applications and benefits of using fluorinated materials in advanced batteries.

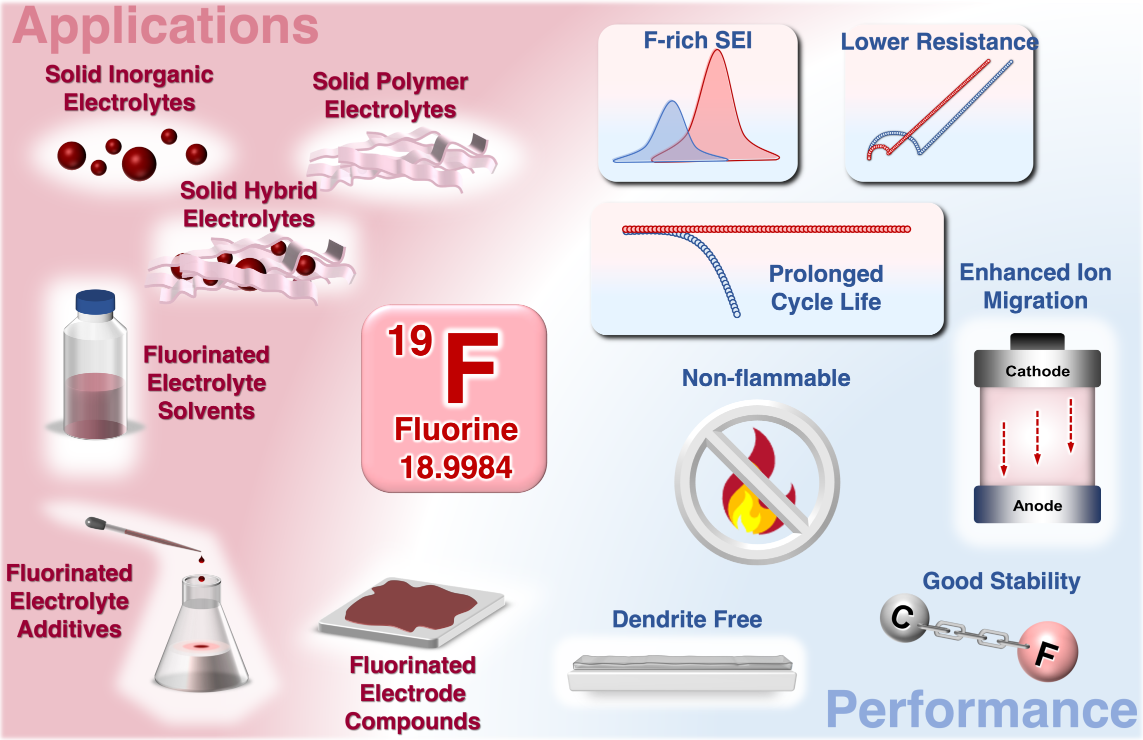

Fig. 1 | **Applications and benefits of fluorinated compounds for enhanced battery performance.** The review mainly covers applications of fluorinated compounds in solid inorganic, polymer and hybrid electrolytes, electrolyte additives, solvents, and electrode protection. The incorporation of fluorine improves battery performance in a range of aspects including facilitated ion transport, enhanced interfacial stability, improved electrochemical stability, excellent fire resistance and finally prolonged battery cycling stability and lifespan.

The growing demand for advanced batteries necessitates the development of innovative fluorinated materials that leverage our understanding of structure-property relationships. In this review, we discuss the recent advances in the utilization of fluorinated materials in the design of advanced battery components. We summarize the fundamental role of fluorine in driving achievements in battery chemistries, delve into the latest design principles, and elucidate the fluorination strategies involved in this process. The review is divided into two main categories: electrolyte materials, including Sections 2, 3 and 4 *Fluorinated All-Solid-State Electrolytes*, *Fluorinated Electrolyte Solvents* and *Fluorinated Electrolyte Additives*; and electrode compounds, including Section 5 *Fluorinated Electrode Compounds*. The review covers particularly the role of fluorine in battery research and how these concepts drive the design of new fluorinated materials for advanced batteries. The main requirements, limitations, and environmental concerns of utilizing fluorine in battery design are also discussed to provide a realistic outlook in the final section.

Fluorinated All-Solid-State Electrolytes

All-solid-state batteries (ASSBs) show great promise as next-generation large-scale sustainable energy storage systems. ASSBs are potentially low cost, have high energy density, wide operating temperatures, and an excellent safety profile[12]. Solid-state electrolytes are a critical component of ASSBs, as both the medium for transport of ions and as a replacement for commonly used volatile liquid electrolytes to eliminate safety risks associated with leakage and ignition. One of the challenges with developing solid-state electrolytes is to achieve the optimal balance of properties such as high ionic conductivity, good mechanical performance, stable electrolyte-electrode interfaces even at high voltages, and long cycling performance. Incorporating fluorine into the structure of electrolytes in ASSBs has been shown to be an advantageous strategy for achieving this balance of properties. Key goals include improved electrochemical stability at high voltages, enhanced conductivity, more effective formation of fluoride-rich surface protection electrolyte-electrode layers (e.g. SEI/CEI), and improved long cycling performance of the ASSBs.

Solid Polymer Electrolytes

Poly(ethylene oxide) (PEO) based electrolytes are one of the most promising solid polymer electrolytes (SPEs) due to their simple preparation and ability to solvate ion conducting salts. However, PEO is semi-crystalline, leading to low ionic conductivity at room temperature ($\approx 10^{-6}$ to 10^{-7} S cm^{-1}), which limits its use in practical applications[13-15]. Its poor oxidative stability (e.g. < 4 V versus Li/Li^{+}) also hinders their use in high voltage cathodes with a reduction in the ability to transfer target cations. Additionally, the resulting SEI is non-uniform and brittle, leading to charge polarization and volumetric changes during electrodeposition, which contributes to dendrite growth[16,17]. A wide range of fluorinated polymers have been used as SPEs, including fluorinated PEO, e.g. P(PEGMA-*co*-HFBMA)[18], PEGA-*b*-PFPE[19]; thermoplastic PVDF[20] and PVDF-*co*-HFP[21]; PFEC[22]; as well as fluorinated cross-linked electrolyte P(OFHDODA-*co*-VEC[23]. Chemical structures of several typical fluorinated SPEs are shown in **FIG. 2a**.

Enhanced interfacial stability. It has been widely reported that fluorination increases the electronegativity of electrolytes, facilitating formation of an electronically insulating and ionically conductive SEI thin layer at the electrode-electrolyte interface[24]. Moreover, fluorination can suppress the growth of dendrites, a major cause of short circuits and battery failure, by forming an SEI layer that inhibits the penetration of metal ions into the electrolyte and prevents dendrite formation. Transmission electron microscope (TEM), scanning electron microscope (SEM) and X-ray tomography are commonly used to visualize electrode surfaces and provide high-resolution images to highlight dendrite suppression when fluorinated polymer electrolytes are employed. These results clearly suggest that fluorination improves the homogenous interface between fluorinated SPEs and the surface of metal anodes. This improvement effectively changes the large electric field distribution, promoting uniform ion plating/stripping and mechanical suppression of dendrite growth. In addition, it prevents further decomposition of the electrolyte and reduces the consumption of lithium ions during cycling, resulting in improved cycling stability of the battery[25,26]. Consequently, fluorinated SPEs show remarkable cycling stability in both Li and Na ASSBs with an average coulombic efficiency of 99% for a wide range of cathodes, including $LiFePO_4$ (LFP) and nickel manganese cobalt oxide (NMC) systems[25,27,28]. Fluorination can also increase the thermal stability of solid polymer electrolytes, contributing to improving overall battery stability.

Improved electrochemical stability. Polymer electrolytes with an increased electrochemical window aid battery operation at high voltages, playing an important role in achieving high-energy-density batteries[29]. To achieve this goal, there are many challenges to developing a practical polymer electrolyte having high voltage resistance and electrochemically stability during cycling. An underlying feature is that the electrochemical oxidation potential of the electrolyte is closely related to its highest occupied molecular orbital (HOMO) level. Several important considerations are needed to achieve reliable high-voltage SPEs: (i) polymer electrolytes should be stable against oxidation on cathodes at high potential to avoid the decomposition of electrolyte, (ii) a stable SEI must be formed when the electrolyte is reduced on the electrode surface, and (iii) nonflammable polymer electrolytes are desired for achieving batteries with enhanced safety features. Generally, incorporation of electron-withdrawing fluorine decreases HOMO-LUMO energies, facilitating the formation of thin and stable inorganic SEI layers, increasing oxidative stability, and finally improving battery safety and performance[30,31]. As shown in **FIG. 2b**, a series of fluorinated polymer electrolytes have been reported to improve the electrochemical stability window, such as trifluoroacetyl-terminated polycarbonate, polyoxalate and polymalonate (>4.4 V)[32], PFEC (>5.5 V)[22], P(PEGMA-*co*-HFBMA) (~5.0 V)[18], PVDF (>4.60 V)[20], P(VEC-*co*-TFEMA) (>5.0 V)[33], β-

CD-*g*-PTFEMA (~4.7 V)[34], P(OFHDODA-*co*-VEC) (5.08 V)[23] for Li/Li$^+$; P(PEGA-*co*-PFPE) (~4.5 V)[19], *β*-CD-*g*-PTFEMA (~5.0 V)[34] for Na/Na$^+$. Significantly, all these fluorinated SPEs exhibit improved electrochemical stability compared with non-fluorinated PEO-based polymer electrolytes.

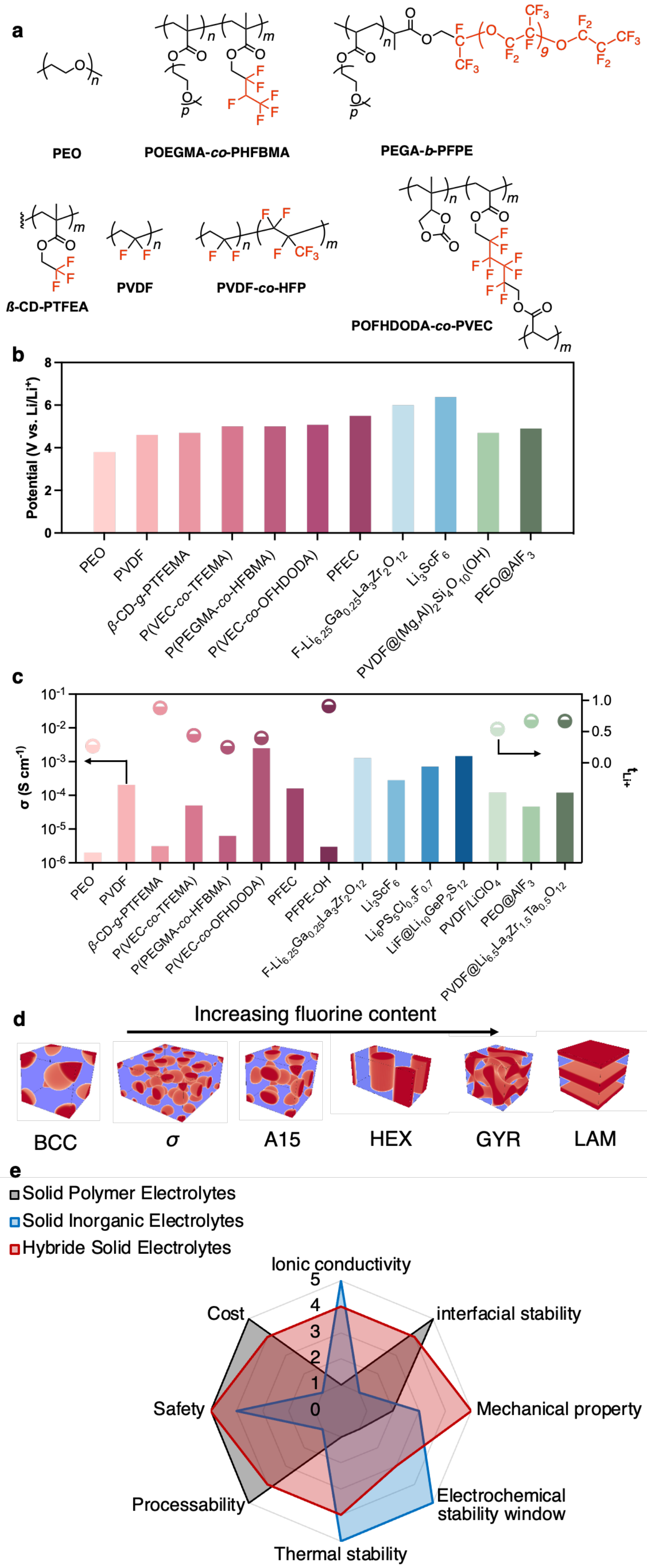
a
PEO
POEGMA-co-PHFBMA
PEGA-b-PFPE
β-CD-PTFEA
PVDF
PVDF-co-HFP
POFHDODA-co-PVEC
b
Potential (V vs. Li/Li+)
0
2
4
6
8
PEO
PVDF
β-CD-g-PTFEMA
P(VEC-co-TFEMA)
P(PEGMA-co-HFBMA)
P(VEC-co-OFHDODA)
PFEC
F-Li6.25Ga0.25La3Zr2O12
Li3ScF6
PVDF@(Mg,Al)2Si4O10(OH)
PEO@AlF3
c
σ (S cm-1)
10-1
10-2
10-3
10-4
10-5
10-6
1.0
0.5
0.0
tLi+
PEO
PVDF
β-CD-g-PTFEMA
P(VEC-co-TFEMA)
P(PEGMA-co-HFBMA)
P(VEC-co-OFHDODA)
PFEC
PFPE-OH
F-Li6.25Ga0.25La3Zr2O12
Li3ScF6
Li6PS5Cl0.3F0.7
LiF@Li10GeP2S12
PVDF/LiClO4
PEO@AlF3
PVDF@Li6.5La3Zr1.5Ta0.5O12
d
Increasing fluorine content
BCC
σ
A15
HEX
GYR
LAM
e
Solid Polymer Electrolytes
Solid Inorganic Electrolytes
Hybride Solid Electrolytes
Ionic conductivity
interfacial stability
Mechanical property
Electrochemical stability window
Thermal stability
Processability
Safety
Cost
0
1
2
3
4
5

Fig. 2 | **Advanced all-solid-state electrolyte chemistries and performance. a |** Chemical structures of representative fluorinated all-solid-state polymer electrolytes. **b |** Electrochemical stability window of fluorinated polymer, inorganic and hybrid electrolytes. **c |** A comparison of the room-temperature σ and t^+ of fluorinated polymer, inorganic and hybrid electrolytes. **d |** Self-assembly of fluorinated polymer electrolytes to form well-defined ion transport channels (blue). The fluorinated domain is shown in red. **e |** Radar plots of the performance properties of solid polymer, inorganic and hybrid electrolytes. Poly(polyethylene glycol methyl ether acrylate-*co*-2,2,3,4,4,4-hexafluorobutyl methacrylate (P(PEGMA-*co*-HFBMA))[18]; poly(PEGA-*b*-perfluoropolyether (P(PEGA-*co*-PFPE))[19]; β-cyclodextrin-poly(trifluoroethyl methacrylate) (β-CD-*g*-PTFEMA)[34]; polyvinylidene fluoride (PVDF)[20]; PVDF-*co*-hexafluoropropylene (PVDF-*co*-HFP); poly(vinyl ethylene carbonate-*co*-2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol diacrylate) P(VEC-*co*-OFHDODA)[23]; poly(fluoroethylene carbonate) (PFEC)[22]; poly(vinyl ethylene carbonate-*co*-trifluoroethyl methacrylate) (P(VEC-*co*-TFEMA))[33]; F-$Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$[35]; $LiScF_6$[36]; $Li_6PS_5Cl_{0.3}F_{0.7}$[37]; LiF@$Li_{10}GeP_2S_{12}$[38]; PVDF/$LiClO_4$[39]; PEO@AlF_3[40]; PVDF@$Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$[41].

Improved ion transport. Fluorination can increase the polarity and ionic conductivity of solid electrolytes by altering the local environment around the ionic species, resulting in improved ion transport properties. Additionally, the fluorine atoms can form strong hydrogen bonds with the polymer backbone of the electrolyte, enhancing the polymer's rigidity and preventing crystallization, leading to increased mobility of the ionic species. As a result, the use of fluorinated solid electrolytes in battery systems can enhance overall performance by improving ion conductivity, cycling stability, and overall safety.

Previously, fluorinated electrolytes have been utilized in both Li and Na devices and exhibit higher ionic conductivity (σ) when compared to the corresponding non-fluorinated counterparts. This is due to the creation of additional ion conduction pathways through the polar C-F···Li^+ (Na^+) units, enhancing traditional pathways (e.g. the ethylene oxide group in PEO) and resulting in more extensive dissociation of ion-conducting salts (e.g. Li^+ and $TFSI^-$)[23]. This further leads to an overall improvement in ionic conductivity. For example, fluorinated PEO electrolytes exhibit significant improvement in σ at a temperature of 80 °C (e.g. 6.43×10^{-4} vs. 0.4×10^{-4} S cm^{-1} in a Li battery and 8.43×10^{-4} S cm^{-1} vs. 0.7×10^{-4} S cm^{-1} in a Na battery)[34].

Additionally, the transference number of cation metal ions (t_+) in fluorinated solid electrolytes is significantly increased compared with non-fluorinated systems. There are a few possible explanations for this improvement. Firstly, the rich diversity of metal ion coordination facilitates cation transport, providing additional migration routes for cations. Secondly, the presence of hydrogen bonds and fluorous interactions significantly hinders the migration of fluorinated anions such as FSI^- or $TFSI^-$[19,42]. Literature data shows approximately four times higher t_+ values for Li or Na transport in fluorinated polymer electrolytes compared with non-fluorinated derivatives ($t_{Li+} = 0.88$ vs. 0.21 and $t_{Na+} = 0.71$ vs. 0.20, respectively). The improved σ and t_+ for a series of fluorinated polymer electrolytes are summarized and shown in **FIG. 2c**. The superior conductivity and Li^+ transport numbers for fluorinated polymer electrolytes will also benefit from the high capacity and superior rate performance of ASSBs.

Well-defined ion transport channels. Fluorinated segments in polymer chains have a high tendency to self-assemble in hydrocarbon matrices due to the large Flory–Huggins interaction parameter (χ). The self-assembly of fluorinated segments can lead to the formation of various morphologies, such as body-centred cubic spheres (BCC), Frank–Kasper σ, A15, hexagonally packed cylinders (HEX), gyroid (GYR) and lamellar (LAM) morphologies (**FIG. 2d**), depending on χ, total volumetric degree of polymerization (N) and relative block volume fractions (f)[43-47]. Such self-assembled morphologies create well-defined ion transport channels at various temperatures, which leads to improved ion conductivity and mechanical properties[48-

[51]. Previously, it was reported in our group that the addition of a perfluoropolyether (PFPE) segment to PEO-based electrolytes results in the creation of self-assembled BCC structures, and significantly improves the mechanical property of the block copolymer matrix, even at elevated temperatures around 100 °C[19]. This self-assembled nanostructure creates 3D interconnected ionic transport pathways leading to increased ionic conductivity compared to the non-fluorinated PEO polymer electrolyte, with t_{Na+} being observed to increase from 0.33 to 0.46 when NaFSI was introduced to the electrolyte system. These findings suggest the introduction of fluorinated blocks can facilitate the self-assembly of block copolymer electrolytes leading to formation of well-defined ion-conducting channel for improved conductivity and battery performance. It is worthwhile to note that different morphologies may have varied enhancements in ion transport. For example, the development of A15 structures was found to provide more efficient ion transport compared with the HEX- and LAM-forming samples[48]. However, there are several challenges in developing advanced fluorinated polymer electrolytes with efficient ionic conductivity and mechanical properties. Firstly, it has been difficult to access or stabilize well-defined network morphologies, especially those with complex σ and A15 phases, over a wide temperature range. This poses a challenge in achieving optimal battery performance. Secondly, identifying promising fluorinated polymer electrolytes that can maintain high cycling stability and battery performance while also exhibiting the desired self-assembled morphology is a significant challenge.

Solid Inorganic Electrolytes

Solid inorganic electrolytes, such as $Li_{6.4}La_3Zr_{1.7}Ta_{0.3}O_{12}$ (LLZTO)[52], $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$ (LATP)[53], and $Li_{10}GeP_2S_{12}$[54], exhibit superior mechanical properties, higher ionic conductivity (over 0.1 mS/cm at room temperature) and wider electrochemical stability windows compared to solid polymer electrolytes[8,37,38]. However, a drawback is that many inorganic solid electrolytes tend to be brittle and pose challenges in processing, resulting in poor contacts with electrodes[3]. This can lead to high interfacial resistance, limiting their practical implementation[17,55,56].

Fluorination of inorganic solid electrolyte presents an efficient approach to enhance the interfacial stability between the electrolyte and electrode. Fluorine doping into traditional oxide and sulfide solid electrolytes can stabilize the electrode interface and reduce the voltage polarization of corresponding batteries, such as for argyrodite and LLZO-based systems. Two strategies have been reported to achieve efficient fluorination of inorganic compounds. The first approach involves direct fluorine doping into inorganic structures using conventional solid-state reactions, such as ball milling with LiF or NH_4F as the fluorine source[37]. The second method involves coating the surface of the inorganic material with a layer of fluoride-rich compound, for example accomplished through gas-solid reactions using NH_4F as the fluorine source[38].

Several fluorinated inorganic electrolytes have been designed and reported, such as Li_3MF_6 (M = Al, Sc, Ti, V, Cr, Ga, In)[36], F-$Li_{6.25}Ga_{0.25}La_3Zr_2O_{12}$ (F-LGLZO)[35], $Li_6PS_5Cl_{0.3}F_{0.7}$[37] and LiF@$Li_{10}GeP_2S_{12}$[38]. All these compounds demonstrate the ability for *in-situ* formation of a stable and high concentration of fluoride-rich interface (e.g. LiF) between electrode and electrolyte. As discussed in the section of solid polymer electrolytes, this interface effectively suppresses dendrite growth and inhibits side reactions against battery components, resulting in enhanced battery cycling stability and rate performance. In addition, fluorinated inorganic electrolytes exhibit a wide and stable electrochemical window (**FIG. 2b**), making them beneficial for achieving high-energy-density batteries.

Solid Hybrid Electrolytes

Fluorinated hybrid electrolytes, combining polymers, inorganic components, and fluorine elements, present several notable advantages in battery applications. By incorporating fluorine, they exhibit enhanced ionic conductivity, surpassing pure polymeric or inorganic electrolytes, leading to improved battery performance and power output[57,58]. Fluorinated hybrid electrolytes also demonstrate improved stability, mitigating undesirable side reactions and ensuring long-term cycling performance. Additionally, fluorination in hybrid electrolytes promotes better interfacial compatibility with electrodes, resulting in reduced resistance and improved charge transfer kinetics. Overall, hybrid electrolytes leverage the strengths of polymers, inorganic materials and fluorine elements, offering a promising approach for advanced battery systems.

Two strategies can be employed to prepare fluorinated hybrid electrolytes, providing flexibility in tailoring their composition and properties. The first approach involves incorporating fluorinated inorganic compounds into non-fluorinated polymers like PEO[59]. This can be achieved by introducing fluorinated inorganics, such as fluorinated metal salts or fluorinated metal oxides, into the polymer matrix. A recent study demonstrates that introduction of mesoporous α-aluminum fluoride (AlF_3) nanoparticles with a high specific surface area into a PEO matrix favors the formation of ionically conductive components in the SEI (i.e. Li_2O and LiF), while also hindering dendritic growth. The strong adsorption of TFSI on the surface of AlF_3 leads to a high t_{Li^+} at 0.67 for this fluorinated solid electrolyte[40] (**FIG. 2c**). Another study highlights that the F-doped $Li_{0.33}La_{0.557}TiO_3$ (F-LLTO) can serve as filler for the PEO system to enhance the effect of Li dendrite suppression through the formation of a LiF protection layer at the electrode surface[60]. The second strategy to prepare hybrid electrolytes involves mixing inorganic materials with fluorinated polymers. In this approach, fluorinated polymers, which possess unique properties such as enhanced processing, are combined with inorganic components. As a commonly used fluorinated polymer, PVDF has been widely reported to mix with inorganic compounds, e.g. LLZO-based $Li_{6.75}La_3Zr_{1.75}Ta_{0.25}O_{12}$[61], $Li_{6.5}La_3Zr_{1.5}Ta_{0.5}O_{12}$[41], $Li_7La_3Zr_2O_{12}$[62], argyrodite $LiClO_4$[39], and Li_6PS_5Cl[63], to form hybrid electrolytes for improved battery performance.

These strategies enable the design and preparation of fluorinated hybrid electrolytes with tailored properties suitable for specific battery applications (**FIG. 2e**). The combination of fluorinated inorganic compounds with non-fluorinated polymers or the integration of inorganic materials with fluorinated polymers allows for the optimization of key electrolyte characteristics, including processing feasibility, ionic conductivity, mechanical strength, electrochemical stability, and interface compatibility. By utilizing these strategies, researchers can explore a wide range of fluorinated hybrid electrolyte systems for advanced battery technologies.

Fluorinated Electrolyte Solvents

Liquid electrolytes are widely used in batteries to offer benefits such as high ionic conductivity, cost effectiveness, and flexibility[64-67] with carbonates and ethers being the two main classes of electrolyte solvents that have been extensively used in the current battery market. Carbonates, such as ethylene carbonate (EC) and ethyl methyl carbonate (EMC), are commonly employed in metal-ion batteries due to their high ionic conductivities, and the ability to form a robust SEI on the anode. However, when carbonates are used in batteries with metal anodes, the resulting SEI tends to be porous, exacerbating side reactions with metal anodes and resulting in low Coulombic efficiencies. The use of ether-based solvents, such as 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME), have been reported to exhibit high ionic conductivities and promote high Coulombic efficiencies during metal deposition and stripping[64]. However, the use of ether solvents is not compatible with high-voltage cathodes like Ni-rich NMC 811 due to their limited oxidative stability (below 4 V vs Li/Li^+)[68,69].

Fluorination of current commercially available carbonates and ethers is a promising solvent engineering strategy[70]. As shown in **FIG. 3a**, researchers have designed and prepared a series of fluorinated electrolyte solvents, including the DME derivatives 1,1,1-trifluoro-2,3-dimethoxypropane (TFDMP)[71] and perfluoro 1,4-dimethoxylbutane (FDMB)[72]; fluorinated

1,2-diethoxyethane derivatives (F3DEE, F4DEE, F5DEE, F6DEE)[73] which are further developed from FDMB; 2,2-dimethoxy-4-(trifluoromethyl)-1,3-dioxolane (DTDL)[31]; cosolvents consisting of 1,1,1,3,3,3-hexafluoropropan-2-yl N,N-dimethyl-carbamate (F-C2), 1,1,1,3,3,3-hexafluoropropan-2-yl N,N-diethylcarbamate (F-C4)[74], fluoroethylene carbonate (FEC)[75], 1,1,1,3,3,3-hexafluoroisopropylmethyl ether (HFPM)[76], 1H,1H,5H-octafluoropentyl-1,1,2,2-tetrafluoroethyl ether (OFE)[77], bis(2,2,2-trifluoroethyl) carbonate (FDEC)[75]. The general design principle is to enlarge the oxidation window and enhance metal compatibility by the introduction of fluorine, while still maintaining the ability to solvate ion-conducting salts and conduct ions.

The position of fluorine substitution within the molecular framework is an important consideration. Consider the fluorination of DME ester as an example. Increasing the length of the central alkyl units to give 1,4-dimethoxylbutane (DMB) or 1,2-dimethyoxypropane (DMP)[64,78] allows the introduction of fluorine without significantly impacting the stability of the ether linkages while also maintaining the solvation capacity for ionic salts[78,79]. Hence only the central part of the DMB backbone is replaced with $–CF_2–$ or $–CF_3$ while the –O– is still linked to $CH_3–$ and $–CH_2–$ groups. As a result, the obtained FDMB molecule is expected to be stable to both metal anodes and high-voltage cathodes, and has increased oxidation stability due to the electron-withdrawing inductive effect[80,81].

Interfacial analysis and solvation structure studies have also demonstrated the significant role of fluorination in enhancing dendrite suppression and ion transport properties. TEM images presented in **FIG. 3b,c** reveal that the SEI formed using fluorinated solvents exhibits reduced dendritic growth, smoother morphology, and reduced thicknesses (~6 nm) when compared to non-fluorinated counterparts (~10 nm)[72]. Moreover, unlike the wrinkled and non-uniform SEI observed with non-fluorinated or conventional electrolyte solvents, the SEI formed in fluorinated solvents demonstrates remarkable uniformity, as confirmed by fast

Fourier transform analysis (insets in **FIG. 3b, c**). These distinctive characteristics effectively minimizes the consumption of electrolyte and anode materials during SEI formation in each cycle, leading to improved CE.

The solvation structures of metal ions are strongly impacted when fluorinated electrolyte solvents are used. Taking the comparison between DME and DTDL solvents as an example[31]. When mixing LiTFSI with non-fluorinated DME solvent, free FSI anion and Li^+-DME coordination clusters can be observed (**FIG. 3d**). In contrast, significantly fewer free FSI anions and the appearance of contact ion pairs (CIP, free FSI^- coordinating to a single Li^+) and aggregates (AGG, free FSI^- coordinating to two or more Li^+) can be seen when the fluorinated DTDL solvent was used (**FIG. 3e**). The formation of CIP and AGG solvation structures decreases the LUMO energy of the anion, promoting FSI decomposition earlier than electrolyte solvent, forming an anion-derived inorganic SEI for improved battery cycling stability and performance[82,83].

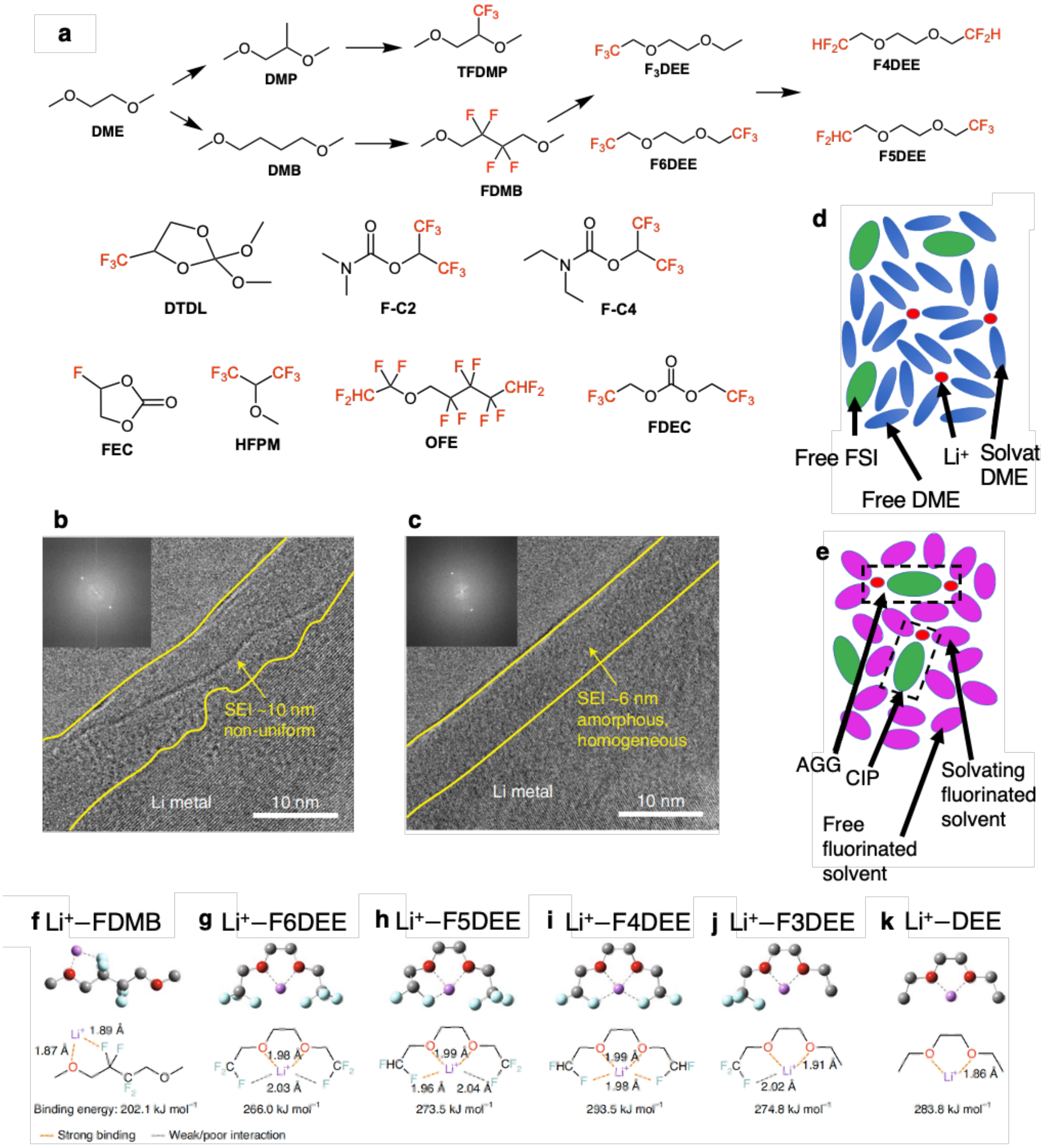

Fig. 3 | **Design and performance of fluorinated electrolyte solvents in batteries**. **a |** Chemical structures of typical fluorinated electrolyte solvents. **b,c |** Cryo-TEM showing SEI in LiFSI-DME and LiFSI-FDMB, respectively[72]. **d,e |** Schematic diagram of lithium solvation structure without and with fluorinated solvent additives[31]. **f-k |** Coordination structures and binding energies between one Li^+ ion and different solvent molecules calculated using density functional theory (DFT). 1,1,1-trifluoro-2,3-dimethoxypropane (TFDMP)[71]; perfluoro 1,4-dimethoxylbutane (FDMB)[72]; fluorinated 1,2-diethoxyethane (F3DEE, F4DEE, F5DEE, F6DEE)[73]; 2,2-dimethoxy-4-(trifluoromethyl)-1,3-dioxolane (DTDL)[31]; 1,1,1,3,3,3-

hexafluoropropan-2-yl N,N-dimethyl-carbamate (F-C2); 1,1,1,3,3,3-hexafluoropropan-2-yl N,N-diethylcarbamate (F-C4)[74]; fluoroethylene carbonate (FEC)[75]; 1,1,1,3,3,3-hexafluoroisopropylmethyl ether (HFPM)[76]; 1H,1H,5H-octafluoropentyl-1,1,2,2-tetrafluoroethyl ether (OFE)[77]; bis(2,2,2-trifluoroethyl) carbonate (FDEC)[75]. Panel **b,c** images are from REF. [72]; Panel **d,e** are from REF. [31]; Panel **f-k** data are from REF. [73]. Reproduced by permission of Springer Nature Limited.

The number of fluorine atoms per solvent molecule is also important to determine battery parameters[73,84]. It was reported that partially fluorinated, locally polar –CHF_2 units lead to improved performance when compared to fully fluorinated –CF_3 units that are found in commercial systems. Solvents containing –CHF_2 group(s) have been shown to have high ionic conductivity, low and stable overpotential, excellent Coulombic efficiency as well as fast activation. This is largely due to the stronger intermolecular interactions in –CHF_2 solvents (i.e. F4DEE and F5DEE, **FIG. 3h, i**) and better Li^+ solvation than for all-fluorinated and symmetric counterparts (i.e. F3DEE and F6DEE, **FIG. 3g, j**). This can also be supported by the DFT calculations showing that the Li–F distance is shorter with –CHF_2 than –CF_3 (e.g. 1.96 Å versus 2.04 Å, respectively, **FIG. 3h**). As a result, the extent of improvement in battery performance varies among the different fluorination strategies employed in the design of electrolyte solvents. Future research innovations in fluorinated solvents may focus on partially fluorinated and asymmetric electrolyte solvents, and hold promise for enhancing battery performance.

Fluorinated Electrolyte Additives

Addition of electrolyte additives is an innovative approach that has been widely applied in the field of energy storage, including in batteries. This approach allows flexible tuning of structure, composition as well as function without major adjustment to the battery manufactory process[85]. These factors address many critical issues such as electrolyte decomposition, anode dendrites, and cathode dissolution by incorporating small amounts (usually ≤ 10 %, by weight or volume) of these additives into the electrolyte[86].

The utilization of fluorinated electrolyte additives has been considered particularly promising due to the unique nature of fluorine substiution[87-89]. Fluorinated additives with relatively high reduction potential can be preferentially reduced over major electrolyte components during initial cycles to form a thin, uniform and fluoride-rich layer on the surface of electrodes (SEI/CEI, **FIG. 4a**). The stable fluoride-rich layer can reduce the formation of metal dendrites on the anode, suppressing the continuous consumption of battery components during the electrochemical process, preventing severe side reactions between the electrode and the electrolyte, thereby preserving more electrolyte and reducing electrode dissolution[90]. Additionally, fluorinated additives contribute to improved safety by enhancing the thermal stability of electrolytes and reducing the flammability of battery components. Ultimately, enhanced cycle stability and extended cycle life of rechargeable batteries can be achieved through this facile method of incorporating fluorine into electrolyte formulations[85,91].

Anode SEI-Forming Additives

Fluorinated electrolyte additives play a vital role as SEI-forming agents in battery systems. Numerous fluorine-containing compounds have been reported to be promising in improving electrochemical performance as effective SEI-forming additives, including fluoroethylene carbonate (FEC), 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (HFE), heptafluorobutyric anhydride (HFA) and trimethylethyl ammonium trifluoromethanesulfonate ($Me_3EtNOTF$) (**FIG. 4a**). Fluorinated additives generally have a lower level of the lowest unoccupied molecular orbital LUMO (e.g. −0.87, −0.38, 0 eV for FEC, EC and DEC, respectively, **FIG. 4b**)[92], which leads to an easier reduction on the surface of electrodes during cell cycling, facilitating the formation of a protective SEI layer with desirable characteristics (**FIG. 4c**). This fluoride-rich SEI layer acts as a barrier, preventing unwanted side reactions between the electrode and electrolyte. This improves the stability of the electrode-electrolyte interface, reducing the consumption of electrolyte components and inhibiting the degradation of electrode materials[93,94]. The fluorinated SEI layer also enhances ion transport kinetics, promoting more efficient charge and discharge processes. Moreover, the fluorine-containing SEI exhibits good mechanical stability, preventing the formation of dendrites and suppressing undesired reactions at the electrode surface[90,95]. The impact of fluorinated electrolyte additives on the morphology of SEI can be observed clearly through TEM images. Without the presence of fluorinated electrolyte additives, the SEI appears thicker and rough (**FIG. 4d, e**), whereas with the addition of fluorinated additives, the SEI becomes smoother and thinner (**FIG. 4f, g**).

As a well-established SEI film-engineering additive, the addition of a small-amount of FEC to electrolyte mixtures enables the rapid formation of a thin and compact fluoride-rich SEI layer. These fluorinated layers possess high mechanical strength and are particularly beneficial for silicon or graphite electrodes[90,95]. The cracking of silicon anodes causing by the volume expansion of lithiation during cycling and the resulting capacity loss as well as electrode deactivation can be effectively restrained by adding FEC film-forming additive, thereby preventing the continuous production of SEI on the exposed anode surface and electrolyte decomposition. Additionally, the passivation layer formed by the reductive degradation of fluorinated additives during the electrochemical process can significantly improve the cycle life of batteries. Qiao and co-workers presented evidence that the addition of fluorinated ether HFE additive dramatically increase battery cycling life to 14,000 h in Li||Li symmetric cells[96]. Meanwhile, the CE of Li||Cu batteries with HFE still maintains an outstanding retention rate of 99.3% after 600 cycles, demonstrating the effectiveness of fluorinated film formers for maintaining the reversibility and cycle stability of plating/dissolving Li.

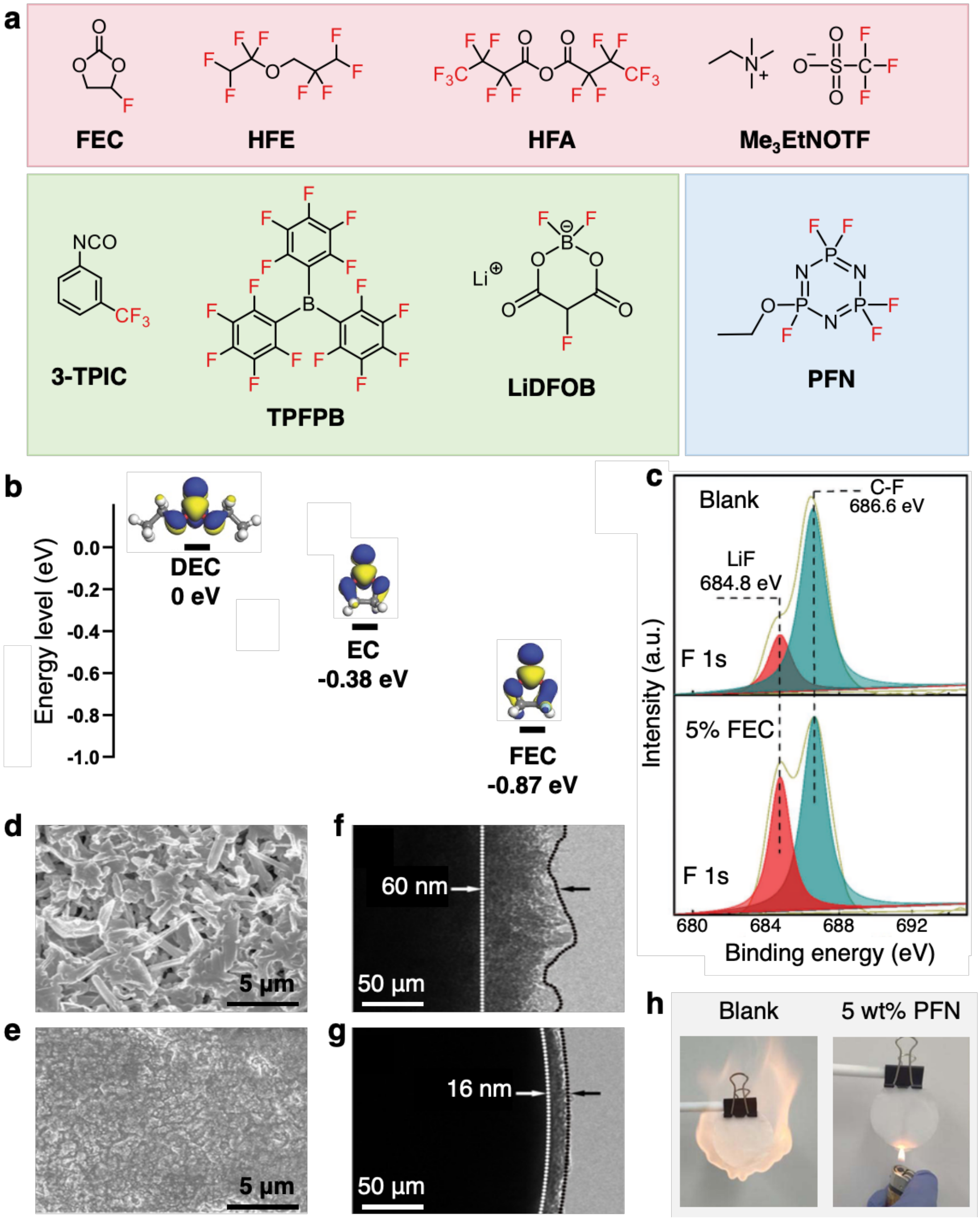

Fig. 4 | **Fluorinated electrolyte additives in batteries. a |** Chemical structures of typical fluorinated electrolyte additives. SEI-forming additives (pink): fluoroethylene carbonate (FEC)[90,92-95], 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (HFE)[96], heptafluorobutyric anhydride (HFA)[97] and trimethylethyl ammonium trifluoromethanesulfonate ($Me_3EtNOTF$)[98]; CEI-forming additives (green): meta trifluoromethyl phenyl isocyanate (3-TPIC)[99], tris(pentafluorophenyl)borane (TPFPB)[100] and lithium difluoro(oxalate)borate (LiDFOB)[101-106]; safety-enhancing additives (blue): ethoxy-(pentafluoro)-cyclotriphosphazene (PFN)[107]. **b |** Calculated LUMO energy level of DEC, EC and FEC. **c |** F 1s XPS spectra of the SEI layer induced by 0% and 5% FEC after lithium stripping on Cu substrate for 10 cycles. **d,e |** SEM images of the metallic lithium anode after 50 cycles in electrolyte (1 M $LiPF_6$ in EC/DMC, 1:1) without (d) and with (e) 1 wt % HFA additives. **f,g |** The TEM image of NCM622 cathode after 10 cycles in the blank and 1 wt % HFA-containing electrolyte. **h |** Photographs of the flammability testing of electrolytes without and with 5 wt% PFN additives. Blank electrolyte (1 M LiPF6/EC+DEC+DMC (1:1:1, v/v/v)). Panel **c** is adapted from REF. [92], reproduced by permission of the Wiley-VCH GmbH; panel d-g are adapted from REF. [97] with permission of the Wiley-VCH GmbH; panel **h** is adapted with permission from the Elsevier, REF. [107].

Cathode SEI-Forming Additives

High energy density is a key objective in the development of advanced batteries, however the dissolution of cathode materials and the electrochemical instability of conventional carbonate-based electrolytes at high voltages hinder commercialization. Fluorinated electrolyte additives play a crucial role as cathode SEI-forming agents in the formation of a protective layer on the surface of cathode materials. This stable and robust SEI layer acts as a barrier, preventing the dissolution of cathode materials into the electrolyte, therefore contributing to the improved performance and cycling efficiency of batteries. A series of fluorinated cathode SEI -forming additives has been discovered, such as meta trifluoromethyl phenyl isocyanate (3-TPIC)[99], tris(pentafluorophenyl)borane (TPFPB)[100], pentafluoropyridine (PFP)[108], ethoxy(pentafluoro) cyclotriphosphazene (PFN)[109] and lithium difluoro(fluoromalonato)borate (LiDFOB)[101-106]. These fluorinated compounds have shown remarkable potential in forming a thin and stable fluoride-rich SEI layer on the surface of cathodes. They have been tested with different cathode types in both Li-ion and Na-ion batteries, including $LiCoO_2$[99], $LiFePO_4$[110], $Na_3V_2(PO_4)_3$[111], $LiNi_{0.9}Co_{0.05}Mn_{0.05}O_2$ (NCM90)[108] and $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811)[109].

Safety-Enhancing Additives

Fluorinated electrolyte additives play a crucial role in enhancing battery safety and mitigating the risk of fire. These additives possess non-flammable properties, thereby reducing the likelihood of thermal runaway and combustion. As discussed in the sections above, fluorinated compounds can effectively suppress the formation and growth of dendrites and reduce the reactivity between electrodes and electrolytes by forming protection layers on the surface of electrodes, which are a major cause of short circuits and thermal instability in batteries. By incorporating fluorinated electrolyte additives, battery systems can achieve higher levels of safety and minimize the risk of fire hazards. Fluorophosphate compounds, such as ethoxy(pentafluoro)cyclotriphosphazene (PFPN), have been extensively researched as flame retardant additives[112,113]. Incorporating PFPN at a concentration of 5 wt% effectively eliminates the flammability of commonly used organic electrolytes[107]. This flame-retardant property arises from the non-flammability of phosphates in combination with the electrochemical stability of fluorine. The presence of fluorine radicals in fluorinated compounds can effectively suppress free radical reactions and impede flame propagation by reacting with hydrogen radicals[114]. By introducing fluorine additives, not only can the performance of high-voltage cathode materials be enhanced, but the thermal stability of the electrolyte can also be ensured. This promising approach paves the way for further development and commercialization of high-voltage batteries.

As highlighted earlier, fluorinated electrolyte additives offer a convenient and flexible means of enhancing the performance of rechargeable batteries without the need for major modifications to the core components of a battery. This approach presents a notable advantage for commercialization, as it imposes lower requirements on industrial production lines. The exceptional benefits provided by fluorinated electrolyte additives should lead to further research to establish standardized guidelines for their design and selection. Such guidelines would greatly contribute to the development of advanced energy storage devices, enabling their widespread adoption and commercial viability.

Fluorinated Electrode Compounds

Fluorine plays a crucial role in protecting the electrode surface in various battery systems. By incorporating fluorine onto the battery electrode surface, several benefits can be achieved. Firstly, fluorine-based materials have a high capacity for forming stable and protective layers on the electrode surface, known as the SEI, inhibiting the growth of dendrites, reducing the occurrence of side reactions, and preventing metal ion dissolution. Secondly, the fluorinated layers act as a physical barrier, preventing direct contact between the electrode and the electrolyte, thereby minimizing unwanted chemical reactions and enhancing the stability of the electrode-electrolyte interface. Overall, the use of fluorine-based materials provides an effective strategy for protecting the electrode surface, enhancing battery stability, and enabling improved performance and safety.

Compounds for Anode Protection

The surface of metal anodes in batteries is susceptible to a range of challenges, including uncontrollable electro-decomposition during repeated stripping and plating cycles, random dendrite growth and aggregation, significant volume variations, and increased polarization[115]. Additionally, the naturally formed SEI on the anode surface is fragile and prone to extrusion and cracking, particularly due to uneven dendrite growth. This leads to the exposure of fresh metal surfaces, which accelerates electrolyte decomposition and promotes dendrite accumulation, ultimately resulting in battery failure and potential short circuits. To address these issues, the incorporation of fluorine has emerged as a promising approach. By introducing fluorine to the anode system, the formation of a stable and protective fluorinated SEI can be achieved, mitigating dendrite growth, suppressing side reactions, and enhancing the overall stability of the anode-electrolyte interface. This fluorination strategy is not only useful in organic electrolyte systems (e.g. LIBs, SIBs) but also in the aqueous based batteries (e.g. Zn batteries)[119].

Two distinct methods have been employed for the fluorination of the anode system: *ex-situ* and *in-situ* formation of a fluoride-rich SEI. In the *ex-situ* approach, fluorinated chemicals, such as F_2[116], NF_3[117], SnF_2[118], are utilized to create a fluoride-rich surface on the anode before battery assembly (**FIG. 5a**). This pre-fluorination step ensures the formation of a protective fluorinated SEI, which acts as a barrier against dendrite growth and side reactions. As shown in **FIG. 5b,c**, F_2 gas reacts with reactive Li metal surface to form a thin LiF protection layer of ~100 nm thick[116]. The LiF coating serves as a chemically stable and mechanically strong interfacial layer for Li metal anodes by minimizing corrosion reactions with carbonate electrolytes and suppressing the dendrite formation. This strategy is generally applicable to other metal, such as Na, Zn, Al, or graphite anodes[119].

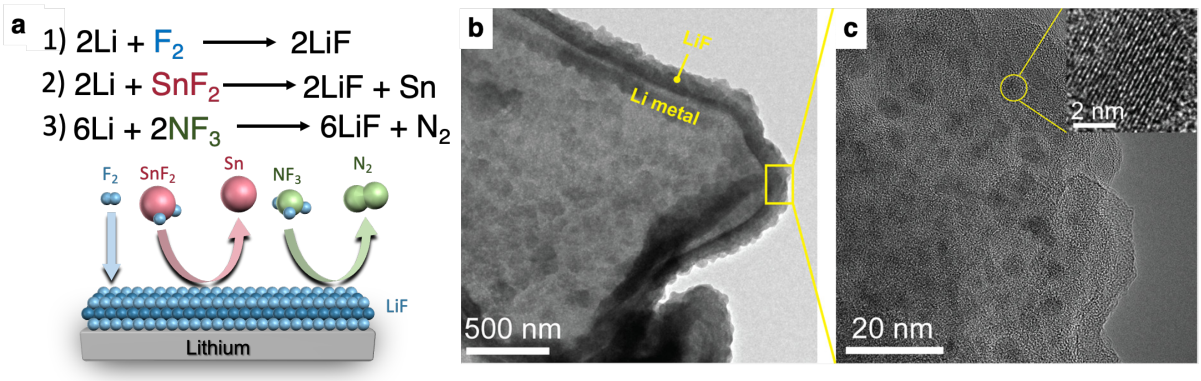

Fig. 5. | ***Ex-situ* formation of fluoride-rich protection layer on the surface of anodes. a |** Several reaction equations and schematic illustration of the use of fluorinated chemicals to react with Li metal to form a uniform and compact LiF coating. **b |** TEM image of Li metal after LiF coating. **c |** A magnified TEM image shows a dense coating layer composed of ultrafine crystallites in the range of 5−10 nm. Inset: High-resolution TEM image reveals the

(111) lattice plane of a LiF nanocrystal with plane spacing of 0.234 nm. Panel **b,c** are adapted from REF. [116], reproduced by permission of the American Chemical Society.

The *in-situ* formation of a fluoride-rich SEI is another promising method, involving the generation of a protection layer during battery cycling itself. This process occurs as a result of the reaction between the anode material and fluorine-containing species during battery cycling process. Several fluorinated species for *in-situ* formation of fluoride-rich SEI have been reported, including anode surface coating with perfluoropolyether[120,121], polymethyldifluoroacetate[122], methyldifluoroacetate[123], LiTFSI[124] or PVDF[125], and fluorinated solvents using fluoroethylene carbonate or hydrofluoroethers[117,126]. The *in-situ* formation of a fluoride-rich SEI offers the advantage of continuous improvement and stabilization of the SEI layer throughout battery operation.

Both *ex-situ* and *in-situ* fluorination methods have shown promise in enhancing anode performance and enabling improved battery cycling stability. However, as highlighted in **FIG. 6a**, the two methods have different working mechanisms in metal ion deposition and protection efficiencies[117]. To be more specific, the *ex-situ* formed SEI exhibits breakdown behavior from the onset of cycling due to the "roughened deposition". It fails to intrinsically protect the exposed anode and leads to the reaction between anodes and electrolytes. In contrast, the *in-situ* method can form an elastomeric and fluoride-rich layer that continuously repairs the broken SEI because of the "smooth deposition". It should be also noted that the *in-situ* formed SEI suffers from the same breakdown process and cannot protect new metal ion deposits once the fluorinated source is removed. Therefore, the *in-situ* formation of a thin, compact fluoride-rich layer to quickly protect the anode surface may be more critical than the properties of metal fluoride itself for battery performance (**FIG. 6b**).

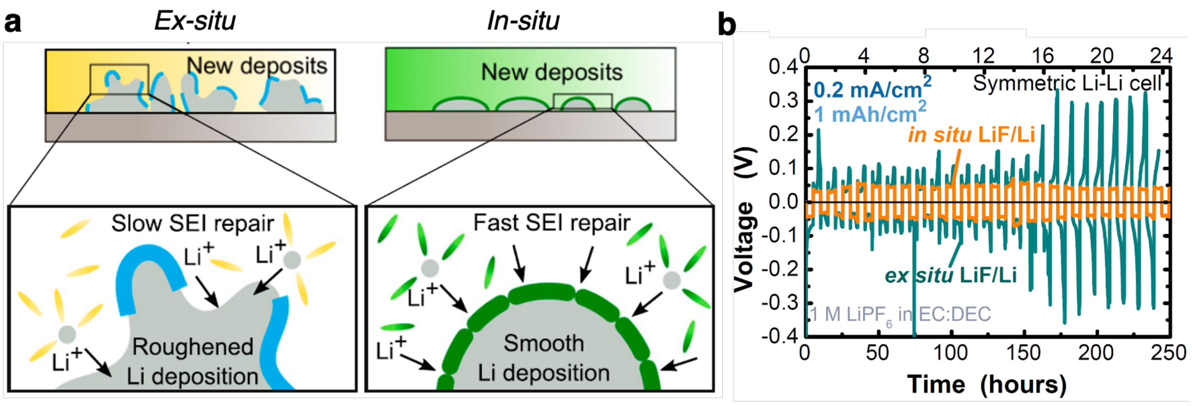

Fig. 5. | **Working mechanism of *ex situ* and *in situ* formation of F-rich layers on the Li anode. a |** where the *ex-situ* layers are referred to the coating layer formed before cycling and the in-situ layers are regarded as the coating layer generated during the cycling. **b |** The battery performance of symmetric Li|Li cells with the protection of *ex situ* and *in situ* F-rich layers. Panel **a** and **b** are adapted with permission from REF. [117], National Academy of Sciences.

Compounds for Cathode Protection

Fluorine has emerged as a promising element for protecting cathodes in battery systems[127,128]. Its unique properties enable the formation of a stable and protective layer on the cathode surface, mitigating undesired side reactions and enhancing the overall performance and lifespan of the battery. By introducing fluorine into the cathode materials, the fluorine-rich interface acts as a barrier, inhibiting the penetration of electrolyte components and reducing the detrimental effects of undesired reactions. Unlike the anode surface, where dendrite aggregation poses a challenge to battery performance, the critical issues on the cathode surface involve the loss of active materials due to side reactions with charged/discharged intermediates and electrolytes. Thus, the role of fluorinated coating is crucial in protecting the cathode materials against dissolution and preserving their integrity.

Surface coating of fluorides, such as LiF[127], MgF_2[129], AlF_3[130], LaF_3[131], etc., has been reported to improve electrochemical performance due to improved stabilization of cathode–electrolyte interface and reduced rock-salt phase[132]. The effect of coating can vary depending on thickness and uniformity. Typically, a low concentration of fluorine at approximate 1 mol% is sufficient to provide cathode protection without a significant increase in surface resistivity[128]. For instance, NH_4F has been proposed as a fluorine source, reacting with residual lithium species (such as LiOH, Li_2CO_3, and $LiHCO_3$) present on the high-nickel $Li[Ni_{0.95}Mn_{0.015}Co_{0.02}Al_{0.01}Mg_{0.005}]O_2$ (NMCAM) cathode surface to form a LiF coating layer[128]. This fluorinated coating effectively suppresses surficial phase transformation to the rock-salt phase and mitigates nickel dissolution. Another approach involves the use of atomic layer deposition (ALD), where hexafluoroacetylacetone (Hfac) and TiF_4 serve as the fluorine sources to deposit LiF protective coatings on high manganese cathode $LiMn_{1.5}Ni_{0.5}O_4$ powder[127]. Both coating strategies presented a reduced Mn dissolution, and subsequent improvement in cycling stability and battery performance.

Conclusion and outlook

We have discussed the importance of fluorination in the design of compounds for battery applications, introducing the molecular design and utility of fluorinated materials in a variety of battery components, including solid-state electrolytes, electrolyte solvents and additives, as well as electrode protection layers. There are several important roles of fluorine in advancing battery performance. Firstly, it facilitates the formation of fluoride-rich surface protection electrolyte-electrode layers to suppress undesirable reactions between electrolytes and electrodes, leading to the formation of a dendrite-free and compact interconnected network morphology. Secondly, fluorination enables high electronegativity that alters the local environment around the ion-conducting salts, resulting in better dissociation between cationic and anionic species for improved ion transport properties. Thirdly, the C–F is one of the strongest single chemical bonds and thus offers both thermal and electrochemical stability benefits to batteries. It provides resistance against chemical and thermal degradation to reduce the risk of thermal runaway and safety hazards, allowing for prolonged battery cycle life. Additionally, fluorination enables high-voltage battery performance through the increase of resistance to oxidation when operating at high voltages, leading to improved energy density of batteries.

In February 2023, the European Chemicals Agency (ECHA) published a proposal to ban around 10,000 'forever' fluorinated chemicals called per- and polyfluoroalkyl substances (PFAS). Fluorinated compounds containing at least one fully fluorinated methyl ($-CF_3$) or methylene ($-CF_2-$) carbon atom (without any H/Cl/Br/I attached to it) are proposed to be banned. Such an extensive restriction of fluorinated compounds may significantly hinder the innovation of next-generation advanced battery systems. Nevertheless, the restriction of fluorinated compounds also presents an opportunity for innovation and exploration of alternative materials and approaches.

Looking to the future, with the increasing deployment of renewable energy sources, a growing market share for electric vehicles, and the continuous advancement of portable electronics, the demand for efficient battery technologies will only intensify. To fully capitalize on the advantages of fluorine in battery research, it is imperative to adopt responsible strategies for the use of fluorinated compounds. Firstly, the development and implementation of efficient recycling processes is important to ensure the recovery and reuse of fluorinated compounds to minimize environmental contamination. These recycling methods may focus on efficiently recovering and reusing valuable materials from spent batteries, including fluorinated compounds, while minimizing the release of harmful substances into the environment. Through this approach, the recovered fluorinated compounds can be treated and recycled for reuse in battery production. Additionally, developing sustainable and environmentally friendly alternative materials, such as new non-fluorinated electrolyte systems, solvents, and protective coatings, that offer comparable or even superior performance to fluorinated compounds, will certainly be a promising direction[133]. This may involve exploring new synthesis methods, utilizing novel materials, and optimizing existing technologies to meet the evolving regulatory landscape. In summary, fluorinated materials have been extensively utilized in various battery components, offering unique properties and benefits, such as improved stability, enhanced performance, and increased safety. However, due to environmental concerns and regulatory measures, the use of fluorinated compounds is being subjected to restrictions and regulations, which may pose challenges to this research direction.

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Author contributions

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Competing interests

The authors declare no competing interests.