

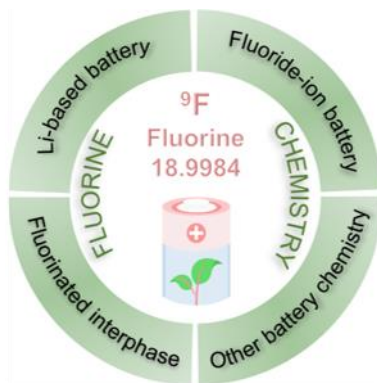
Fluorine Chemistry in Rechargeable Batteries: Challenges, Progress and Perspectives

Yao Wang[†], Xu Yang[†], Yuefeng Meng[†], Zuxin Wen, Ran Han, Xia Hu, Bing Sun, Feiyu Kang, Baohua Li^{*}, Dong Zhou^{*}, Chunsheng Wang^{*}, Guoxiu Wang^{*}

Abstract

The renewable energy industry demands rechargeable batteries that can be manufactured at low cost using abundant resources, while offering high energy density, good safety, wide operating temperature windows, and long lifespans. Utilizing fluorine chemistry to re-design battery configurations/components is considered a critical strategy to fulfil these requirements due to the natural abundance, robust bond strength and extraordinary electronegativity of fluorine, and the high free energy of fluoride formation, which enables the fluorinated components with cost-effectiveness, non-flammability and intrinsic stability. In particular, fluorinated materials and electrode|electrolyte interphases have been demonstrated to significantly affect reaction reversibility/kinetics, safety and temperature tolerance of rechargeable batteries. However, the underlining principles governing material design and the mechanistic insights of interphases at the atomic level have been largely overlooked. This review covers a wide range of topics including the exploration of fluorine-containing electrodes, fluorinated electrolyte constituents and other fluorinated battery components for metal ion-shuttle batteries, to constructing fluoride-ion batteries, dual-ion batteries and other new chemistries. In doing so, this review aims to provide a comprehensive understanding of the structure-property interactions, the features of fluorinated interphases, and of cutting-edge techniques for elucidating the role of fluorine chemistry in rechargeable batteries. Further, we present current challenges and promising strategies for employing fluorine chemistry, aiming to advance the electrochemical performance, wide-temperature operation, and safety attributes of rechargeable batteries.

Table of Contents (TOC)



Contents

1. Introduction

- 1.1. Brief Background on Rechargeable Li-Based Batteries and Beyond
- 1.2. Role of Fluorine Chemistry in Rechargeable Batteries

2. Fluorine Chemistry in Li-Based Batteries

2.1. Fluorine-Containing Electrode Materials

- 2.1.1. Metal Fluorides
- 2.1.2. Metal Hydroxy Fluorides and Oxyfluorides
- 2.1.3. Fluorine-Substitution Electrode Materials
- 2.1.4. Fluorinated Surface Modification

2.2. Fluorinated Electrolytes

- 2.2.1. Fluorinated Salts
- 2.2.2. Fluorinated Solvents and Co-solvents
- 2.2.3. Fluorinated Additives
- 2.2.4. Fluorinated Solid/Quasi-Solid-State Electrolytes

2.3. Other Fluorinated Battery Components

- 2.3.1. Fluorinated Separators
- 2.3.2. Fluorinated Binders and Current Collectors

3. Understanding Fluorinated Interphases in Li-Based Batteries

3.1. Fluorinated Solid Electrolyte Interphases on Anodes

- 3.1.1. Components of SEI
- 3.1.2. Formation of Fluorinated SEI
- 3.1.3. Distribution and Impacts of Fluorides on SEI

3.2. Fluorinated Cathode Electrolyte Interphases

- 3.2.1. Formation of Fluorinated CEI
- 3.2.2. The Impact of Fluorinated CEI on Battery Performance

3.3. Critical Role of Fluorinated Interphases for Extreme Li-Based Batteries

3.4. Techniques to Probe Fluorinated Interphases

- 3.4.1. Cryo-EM
- 3.4.2. Quantifying Techniques
- 3.4.3. Composition Analysis Techniques
- 3.4.4. Functional Features Analysis Techniques

4. Fluorine Chemistry in Rechargeable Fluoride-Ion Batteries

4.1. Fluoride Electrode Materials

4.1.1. Conversion-Type Electrode Materials

4.1.2. Intercalation-Type Electrode Materials

4.2. Fluoride Electrolytes

4.2.1. Solid-State Electrolytes

4.2.2. Non-Aqueous Liquid Electrolytes

4.2.3. Aqueous Electrolytes

5. Fluorine Chemistry in Other Rechargeable Batteries

5.1. Na- and K-Based Batteries

5.1.1. Fluorine-Containing Electrode Materials in Na-Based Batteries

5.1.2. Fluorinated Electrolytes in Na-Based Batteries

5.1.3. Fluorine-Containing Electrode Materials in K-Based Batteries

5.1.4. Fluorinated Electrolytes in K-Based Batteries

5.2. Multivalent Metal-Based Batteries

5.2.1. Aqueous Multivalent Metal-Based Batteries

5.2.2. Non-Aqueous Multivalent Metal-Based Batteries

5.3. Dual-Ion Batteries and Beyond

5. Conclusions and Outlook

1. Introduction

To satisfy the ever-growing demand for energy storage, the development of next-generation rechargeable batteries hinges on advanced materials that possess low cost, abundant resources, long lifespan and high safety, especially when considering high energy/power density, wide temperature range and high voltage operation applications.¹⁻⁴ Significant advancements in fulfilling these requirements have been successfully achieved by utilizing fluorine chemistry to re-design the battery configurations/components, toward specific targeted applications. It is known that fluorine chemistry research can be traced to 1886 when Henri Moissan first isolated the elemental fluorine.^{5,6} Over the past century, fluorine chemistry has significantly contributes to technological innovations, which began with the creation of Freons for refrigeration applications in the 1930s.^{7,8} Currently, fluorine chemistry has been successfully utilized in various fields, including pharmaceutical/agrochemical industries and fluoropolymer industry. The extraordinary electronegativity of fluorine and the high free energy of fluoride formation endow the fluorides with intrinsic high stability along with non-/low flammability (**Figure 1a**). In addition, as the 13th most abundant

element in the Earth's crust (~ 585 ppm),^{9, 10} fluorine (mined as CaF_2) demonstrates an advantage in terms of raw material cost (**Figure 1b**).¹¹ However, the availability of resources remains a significant concern for essential elements employed in Li-based electrodes (*e.g.*, Co and Ni are ~ 25 and ~ 84 ppm in Earth's crust, respectively).¹⁰ In this context, the integration of fluorine chemistry into battery components and novel configurations is thus a promising avenue for advancing battery technology, which has garnered growing interest among the research community. The rapid development of employing fluorine chemistry in various types of rechargeable batteries necessitates a comprehensive review. However, unlocking fluorine chemistry at the atomic scale presents a big challenge. More importantly, the design principles of fluorinated materials and the mechanistic understandings of fluorinated electrode|electrolyte interphases, as well as their effects on the ionic conductivity and reaction kinetics/stability of charge carriers under extreme conditions (*e.g.*, fast cycling rate, wide temperature range and high working voltage) have been long overlooked.

In this review, we begin by providing a short overview of operating mechanisms, characteristics, and current limitations of Li-based batteries, along with beyond Li battery chemistry based on either low-cost metal ions or fluorine-containing charge carriers, prior to moving into an in-depth and specific discussion of fluorine chemistry in rechargeable battery systems. From the physicochemical and electrochemical properties to the safety aspects related to the battery operation, key research progresses and technical achievements for the application of fluorine chemistry in battery materials are summarized, spanning from designing fluorine-containing electrodes, fluorinated electrolyte constituents (*e.g.*, conducting salt, co-/solvent, additive) and other fluorinated battery components for metal ion-shuttle batteries (*e.g.*, Li-based batteries), to constructing rechargeable fluoride-ion batteries (FIBs), dual-ion batteries (DIBs) and beyond chemistries. We highlight the relationship between fluorinated materials and battery performance, the characteristics of fluorinated interphases, along with the cutting-edge characterization techniques available for elucidating fluorine chemistry. We also identified the current major restrictions, and the design strategies for utilizing fluorine chemistry toward improving performances of rechargeable batteries (**Figure 1c**).

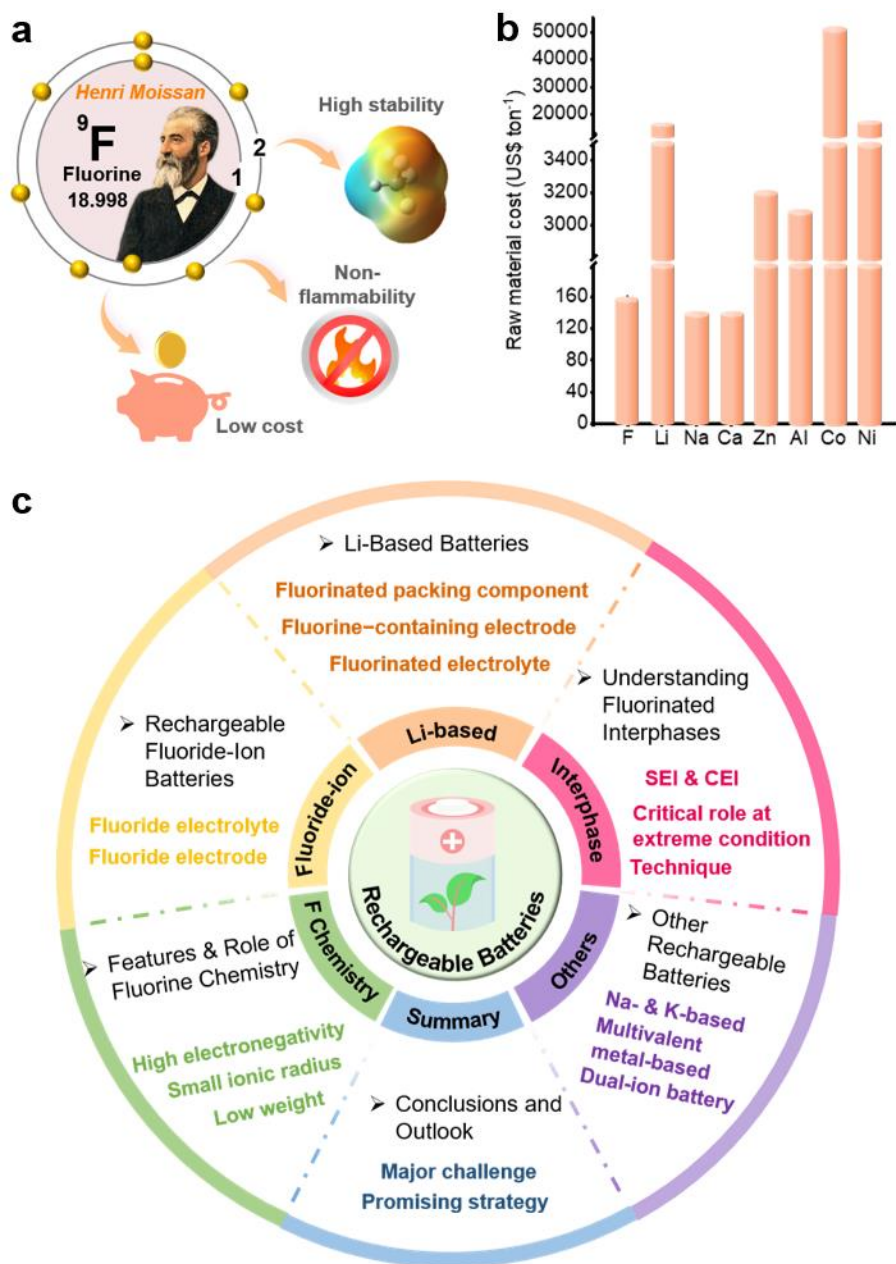


Figure 1. Features and interest of fluorine chemistry for utilizing in rechargeable batteries. (a) Discovery and features of fluorine chemistry. (b) Comparisons of raw material costs of F (mined as CaF_2), Li (Li_2CO_3), Na (Na_2CO_3), Ca (CaO), Zn, Al, Co and Ni in 2021. Data extracted from ref 11. (c) Schematic diagram of the main aspects covered in this review.

1.1. Brief Background on Rechargeable Li-Based Batteries and Beyond

Since the inception of lithium-ion batteries (LIBs) in the 1970s, extensive work has been conducted on the quest for higher energy density and longer lifespan, solidifying LIBs as the most promising candidate for many applications. Typically, LIBs rely on the insertion of Li^+ into host structures, with a variety of layered oxides (*e.g.*, LiCoO_2 , LiFePO_4 , and LiMn_2O_4) and graphite as the cathode and anode material, respectively. They were developed by John B. Goodenough and other researchers over the past four decades.¹² Nevertheless, the energy density of LIBs is expected to reach its intrinsic limits within a few years (around

300 Wh kg⁻¹), which is incapable of satisfying the escalating demands for high energy density.¹³ To further increase the energy density, the cathode and the anode must offer high specific capacities and a substantial voltage gap between them. For instance, cathode materials with higher capacity and voltage platforms have been developed, such as Li-rich Mn-based materials ($x\text{Li}_2\text{MnO}_3(1-x)\text{LiTMO}_2$ (TM = Ni, Mn, Co, *etc.*; $0 < x < 1$)) and Ni-rich $\text{LiNi}_x\text{MnyCo}_{1-x-y}\text{O}_2$ (NMC, $x \geq 0.5$, $x + y < 1$),¹⁴⁻¹⁸ in addition to advanced anodes (*e.g.*, Li metal or Si/C anode) with low reaction potential and ultra-high specific capacity.¹⁹⁻³⁰ Unfortunately, these electrode materials usually experience severe capacity fading especially in extreme conditions due to structure deterioration and side reactions. More significantly, safety issues and low Coulombic efficiency (CE) resulting from notorious Li dendrites (in the case of Li metal anode) or Li deposition on the non-Li metal anodes have not been fully addressed. Meanwhile, it is imperative to re-design electrolyte systems that exhibit sufficient anti-oxidative stability (typically > 4.5 V *vs.* Li/Li⁺), high compatibility towards both electrodes (*i.e.*, robust electrode|electrolyte interphases), excellent temperature tolerance (-60 °C to $+60$ °C), and high safety characteristics (*e.g.*, the risk of fire and explosion), which are critical for adapting to high-energy-density Li-based batteries.³¹

Alternative rechargeable batteries based on more abundant elements promise higher energy density and improved safety features. Among them, sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs), utilizing the Earth's crust 6th and 7th most abundant elements, are considered as outstanding complementary technologies to Li-based batteries.³² Although operate with similar chemistry with Li-based batteries, SIBs and PIBs are facing several challenges due to their larger ionic radii (Shannon ionic radii: 1.02 Å, 1.38 Å and 0.76 Å for Na⁺, K⁺ and Li⁺, respectively), higher redox potentials (-2.71 V for Na, -2.936 V for K, compared with -3.04 V for Li, *vs.* standard hydrogen electrode (SHE)), greater atomic masses (23 g mol⁻¹, 39 g mol⁻¹ and 7 g mol⁻¹ for Na, K and Li, respectively), resulting in low specific capacity, poor rate capability, reduced lifespan and low theoretical energy density.³³⁻³⁵ In contrast, multivalent-metal-based (*e.g.*, Mg²⁺, Ca²⁺, Zn²⁺, Al³⁺) batteries offer high energy density and low cost, benefiting from their multielectron redox capability and Earth's crust abundance. However, their larger ionic radii and greater charge density pose great challenges in ion transport, polarization and reversibility.^{36, 37}

Anions, as charge carriers, typically offer faster mobilities due to their less effective nuclear charge and corresponding reduced solvation compared to cations with similar absolute charge. This feature has prompted the development of anion shuttle batteries, exemplified by FIBs employing F⁻ anion as the charge carrier, which utilize abundant materials to achieve high theoretical energy density.^{9, 38-42} Specifically, F⁻ ions are released from the cathode material and transfer to the anode side during discharging, whereas the process occurs in reverse upon charging.⁹ The high electronegativity of fluorine imparts F⁻ anion with high oxidative stability, facilitating high-voltage redox reactions. The utilization of F⁻ also contributes to high theoretical energy densities from multiple-electron electrochemical processes,^{9, 39, 43-45} along with dendrite-

free anode reactions due to the absence of the metal plating process, highly enhancing safety over alkali metal batteries. Nevertheless, FIBs present several unique challenges, including significant volume changes in electrode materials during fluoridation and defluoridation, contact loss, and interphase degradation. In addition, the electrode dissolution in electrolytes exacerbates self-discharge and capacity decay. More importantly, development of chemically/electrochemically stable electrolytes possessing high room-temperature (RT) conductivity is crucial for FIB commercialization, which is still at an incipient stage.⁹

Combining the cation and anion storage, DIBs provide advantages of low cost, material availability, safety, and high voltage. They operate by simultaneously incorporating anions into the cathode and cations into the anode upon charging, with both ions being released back into the electrolyte during discharging.^{46, 47} Particularly, the de-/insertion of anions occurring at high voltage is beneficial for enhancing the energy density. However, the insufficient oxidative stability and poor electrode compatibility of conventional organic electrolytes, and the scarcity of electrode materials with high storage capacity and structural stability present substantial obstacles. Furthermore, emerging battery chemistries such as reverse dual-ion batteries (RDIBs) face significant challenges due to the lack of suitable electrolytes, impeding their practical advancement.

1.2. Role of Fluorine Chemistry in Rechargeable Batteries

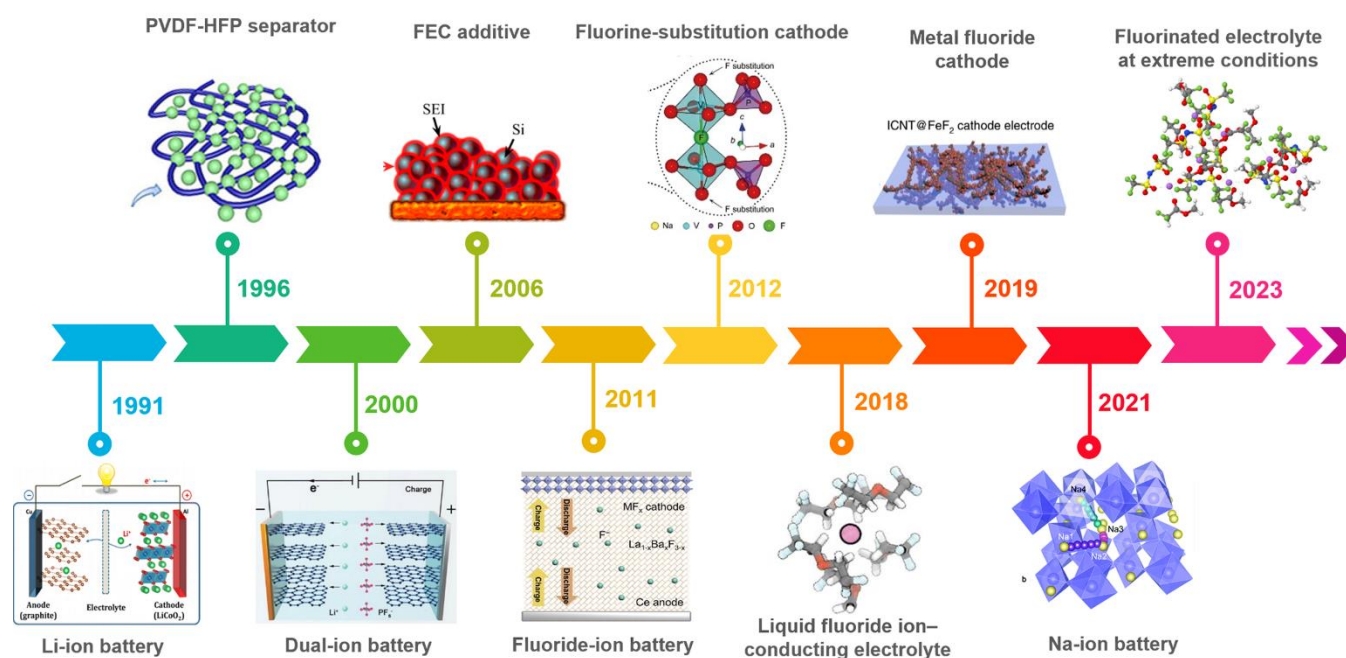


Figure 2. Timeline of the application of fluorine chemistry in rechargeable batteries. Reproduced with permission from ref ⁴⁸. Copyright 2013 American Chemical Society. Reproduced with permission from ref ⁴⁹. Copyright 1996 Elsevier. Reproduced with permission from ref ⁴⁷. Copyright 2021 Wiley-VCH. Reproduced with permission from ref ³⁸. Copyright 2021 Elsevier. Reproduced with permission from ref ⁵⁰. Copyright 2012 Elsevier. Reproduced with permission from ref ⁵¹. Copyright 2006 Elsevier. Reproduced with permission from ref ⁵². Copyright 2018 American Association for the

Fluorine, as the most electronegative element with a comparably low atomic weight, small ionic size (1.33 Å) and natural abundance,⁵⁶ drives new levels of performance and safety in rechargeable batteries. To elucidate the role of fluorine chemistry in rechargeable batteries, the key progress and brief development history are presented, as outlined in **Figure 2**.

Owing to the electron-withdrawing properties of F atoms and the delocalized charge of anions, F-containing Li salts (*e.g.*, lithium hexafluorophosphate, LiPF₆) are generally highly soluble in dipolar aprotic solvents with good electrochemical stability at high voltage. The development of these salts for commercial LIBs dates back to the early 1990s,⁵⁷⁻⁶⁰ but their chemical and thermal instability has prompted the search for alternative conducting salts, usually at the expense of other performance attributes. The utilization of fluorine has been extended to advanced battery components (*e.g.*, separators, binders, current collectors) for Li-based batteries. Efforts can be traced to 1996, when Tarascon *et al.* developed the fluorinated polymer (*i.e.*, poly(vinylidene fluoride-hexafluoropropylene), PVDF-HFP) separator for the first time.⁴⁹ After that, fluorinated copolymers and grafted commercial separators by F-containing groups have been intensively utilized, enhancing oxidation stability, thermal stability, ionic conductivity and safety for battery operations. Moreover, due to the electron-withdrawing inductive effect, the substitution of fluorine to hydrogen of electrolyte co-/solvents and additives typically decreases the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels simultaneously, leading to higher resistance towards oxidation while poorer resistance to reduction.⁶¹⁻⁶⁷ Specifically, the prior reduction of fluorinated additives benefits the anode by generating an effective solid electrolyte interphase (SEI),⁶⁸⁻⁷⁰ among which fluoroethylene carbonate (FEC) stands out as the most popular additive with excellent film-forming ability on various electrodes.⁵¹ Besides the film-forming ability, the introduction of fluorine demonstrates unique physicochemical and electrochemical properties, including high oxidative stability, wide temperature range and nonflammability. In particular, fluorinated interphase are pivotal for Li-based batteries under extreme conditions such as wide temperature range, extended cycling, fast cycling rate and high voltage operation. A significant progress was reported recently by Wang *et al.*, designing a fluorinated electrolyte that yielded LiF-rich interphases on both the cathode and the anode, which enhanced the battery performance across temperature range from -60 °C to +60 °C with high voltage and fast-charging characteristics.⁵⁵ Despite advances, electrode materials remain a major bottleneck for energy density enhancement. The highly ionic character of the metal-fluorine bond and the light atom mass of F element endow fluorinated cathodes with higher voltage and/or higher capacity.⁵³ Additionally, F-related chemistry involved in the modification strategy can improve the interphasial stability and rate capability of electrodes.

Apart from Li-based batteries, fluorine chemistry is integral to other univalent metal-based batteries such as SIBs and PIBs, where the increase of ionic M-X bonds in fluorides promotes redox reactions of transition metal cations instead of oxygen anions at high voltage. The lower molecular weight of fluorine cation compared to polyanions enhances the specific capacity. Additionally, F-based compounds are considered to be more stable against oxidation, making metal fluorinated materials highly appealing. The diversity in compositions, structures and properties of fluorinated electrode materials offers vast opportunities for cathode design. On the anode side, F-doping improves the surface disorder of carbonaceous materials, creating large amounts of defects for facilitating K^+ adsorption.⁷¹ In aqueous multivalent metal-based systems (*i.e.*, Zn-ion batteries, ZIBs), fluorine chemistry enables the formation of fluoride-rich interphases for dendrite suppression and electrolyte stability. In non-aqueous systems, fluorinated materials accelerate plating kinetics in Mg-ion and Ca-ion batteries, thus expediting their practical applications.

Since the first proof-of-concept rechargeable FIB demonstrated by Fichtner *et al.* in 2011,⁴³ fluorine chemistry has been utilized in FIB developments, spanning from electrode materials to electrolyte formulations. The F^- anion displays exceptional anti-oxidation stability, enabling the utilization of high-voltage redox couples. Besides, the F^- storage is typically involved in multiple-electron reactions and metal fluoride formation reactions, which are characterized by substantial Gibbs free energy change, realizing high voltages. As the charge carrier, F^- anion possesses a smaller ionic radius and lower weight compared than Cl^- , thus assisting fast ionic transport and high theoretical energy density of 5000 Wh L^{-1} .^{9, 39, 43, 52, 72-75} FIBs are experiencing many challenges with electrodes and electrolytes, among which suitable electrolytes with sufficient F^- conductivity being crucial. A significant advancement by Jones *et al.* in 2018 designed a novel fluoride salt possessing high RT ionic conductivity, broad electrochemical stability window and sufficient chemical stability in ether solvents, enabling a reversible/stable FIB at RT.⁵² Ongoing efforts should be devoted to developing diverse conversion and intercalation-based electrode materials and fast F^- conducting electrolytes to make FIBs a promising option for commercial-grade batteries.⁷⁶

As for DIBs, Dahn *et al.* studied the intercalation mechanism of the PF_6^- anion into graphite cathodes in 2000 for the first time, proving staged phases of graphite via the *in situ* X-ray diffraction (XRD).⁷⁷ Various anions with F-containing groups such as PF_6^- ,⁷⁸⁻⁸¹ bis(trifluoromethanesulfonyl)imide ($TFSI^-$),^{82, 83} bis(fluorosulfonyl)imide (FSI^-),⁸³⁻⁸⁶ fluorosulfonyl-(trifluoromethanesulfonyl)imide ($FTFSI^-$),^{87, 88} tetrafluoroborate (BF_4^-),^{89, 90} difluoro(oxalato)borate ($DFOB^-$),⁹¹ trifluoromethanesulfonic ($CF_3SO_3^-$)⁹² and tetrafluoroaluminate (AlF_4^-)⁹³ have been extensively explored for their unique characteristics and electrochemical behaviors. Besides, fluorination of other electrolyte components in DIBs imparts advantages such as wide voltage window, broad temperature range, non-flammability and enhanced

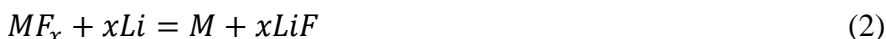
electrode|electrolyte compatibility, enhancing the reversibility/kinetics of anion insertion. Fluorine can also be introduced to cathode materials for boosting and stabilizing properties of anion intercalation.

2. Fluorine Chemistry in Li-Based Batteries

2.1. Fluorine-Containing Electrode Materials

The increasing demands for high energy density batteries with long lifespan and low cost have prompted the research of advanced electrode materials, especially the fluorine-containing materials. This is because fluorine elements are widely distributed on earth and the strong electronegativity of fluorine endows the fluorine-containing materials with high free energy of formation, generally leading to high electrochemical energy density and stability. Here, we represent a comprehensive review to reveal the roles of F-chemistry playing in the advanced fluorides electrodes and fluorine-doping materials.

2.1.1. Metal Fluorides. Metal fluoride cathodes for LIBs have been widely investigated as a promising next-generation rechargeable battery with high theoretical voltage and energy density, owing to the highly ionic metal-fluorine bonding and low atom mass of F element,⁹⁴ as well as the multielectron transfer characteristics of transition metal (M) in metal fluoride cathodes. The battery reaction of metal fluorides-based LIBs follows the following reaction:



Abundant types of metal fluorides, including copper fluorides (CuF₂),⁹⁵ iron fluorides (FeF₃/FeF₂),^{53, 96, 97} nickel fluorides (NiF₂),⁹⁸ cobalt fluorides (CoF₃/CoF₂),^{99,100} manganese fluorides (MnF₂),¹⁰¹ and multi metal fluoride solid-solutions, were investigated and verified their attractive merits in terms of specific capacity, cycling stability, and rate performance (**Table 1**).

Table 1. Comparisons of the electrochemical performance of F-based electrodes for LIBs.

Electrode materials	Discharge voltage vs. Li/Li ⁺ (V)	Current density (mA g ⁻¹)	Initial discharge capacity (mAh g ⁻¹)	Retained discharge capacity (mAh g ⁻¹)	Capacity retention	Cycle number	Ref.
CuF	2.7	0.106	523	80	15.3%	5	95
FeF ₂	2.2	0.3	700	525	75%	50	96
Cu _{0.5} Fe _{0.5} F ₂	2.5	9.2	580	475	81.9%	5	102
FeF ₂	2	50	650	450	69.2%	100	53
FeF ₃	3	2000	92	90	97.8	100	97
Cu _{0.25} Ni _{0.75} F ₂	2	0.055	550	210	38.2%	6	98

CoF ₂	2	100	360	335	93%	200	99
CoF ₃	1.5	5	1000	400	40%	14	100
MnF ₂	0.5	6000	300	270	90%	4000	101
VO ₂ F	3	13.1	200	150	75%	50	103
BiOF	2.5	30	343	148	43.1%	40	104
FeOF	2	10	500	355	71%	30	105
TiOF ₂	2	0.26	200	180	90%	30	106
NbO ₂ F	1.3	30	650	180	27.7%	20	107

Iron(II) fluoride is one of the typical metal fluoride cathodes for LIBs owing to its high theoretical specific capacity and abundant raw material resources⁹⁶. However, the performance of the as-reported iron(II) fluoride cathode is not satisfactory for practical application, and the failure mechanism remains blurred. In 2020, Mauro Pasta and colleagues reported a single-crystalline, monodisperse FeF₂ nanorod synthesized by a facile colloidal method⁹⁶. As shown in **Figure 3a**, the as-obtained 20 nm-wide nanorods were single-crystalline, monodisperse and faceted. This FeF₂ cathode can deliver a high specific capacity (close to the theoretical value of 570 mA h g⁻¹) and cycling stability (capacity retention > 90%) for more than 200 cycles at higher rates (0.5 C, 1 C = 570 mA g⁻¹) and temperatures (50 °C) within an ionic liquid electrolyte. Based on the complex morphological features, lattice orientation relationships, and oxidation state changes from high-resolution transmission electron microscopy (HRTEM) analysis, the transformation mechanism of FeF₂ nanorod was comprehensively estimated. This mechanism provided a new expiation that the phase evolution, diffusion kinetics, and cell failure were all critically affected by surface-specific reactions of FeF₂ nanorod. Topotactic cation diffusion through an invariant lattice of F⁻ ions and the nucleation of metallic particles on semi-coherent interphases synergistically affected the reversibility of FeF₂ cathode.

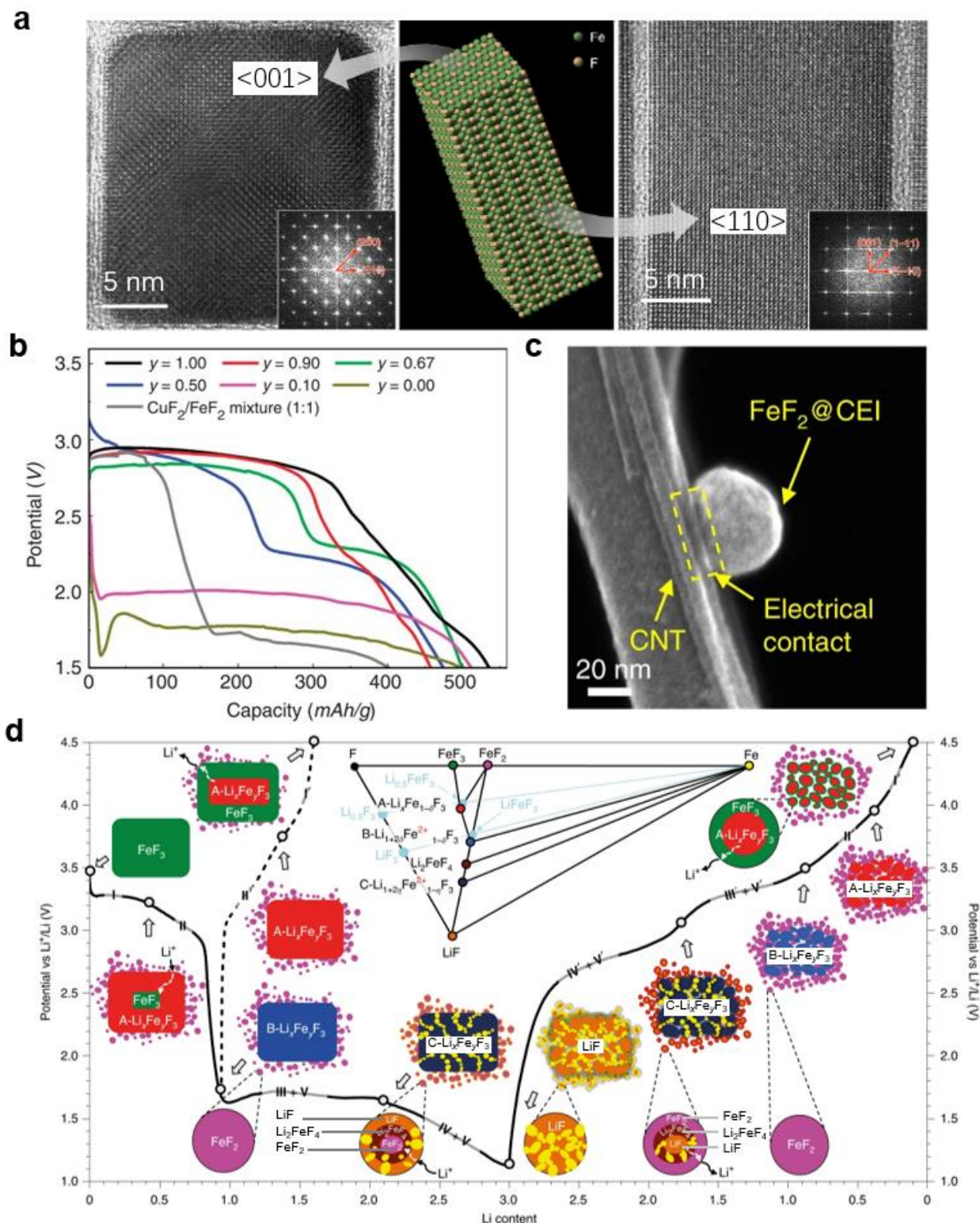


Figure 3. Metal fluorides as electrode materials for LIBs. (a) HRTEM images of a single FeF₂ nanorod and space-filling model of a single nanorod derived from the standard CIF file of FeF₂. Reproduced with permission from ref ⁹⁶. Copyright 2020 Springer Nature. (b) Voltage profiles (first discharge at a current 5 mA g⁻¹) of the Cu_yFe_{1-y}F₂ series along with a simple mixture of CuF₂ and FeF₂. Reproduced with permission from ref ¹⁰². Copyright 2015 Springer Nature. (c) Scanning transmission electron microscope (STEM) image of an FeF₂ particle on a single CNT. Reproduced with permission from ref ⁵³. Copyright 2019 Springer Nature. (d) Simplified Li-Fe-F ternary phase diagram and illustration of reaction pathways of the FeF₃-FeF₂ system (with voltage curves for insertion charge and full reaction cycle respectively, denoted using dashed and solid lines). The reference phases in the phase diagram are labelled and indicated by light blue circles to show the positions of the A- and B-Li_xFe_yF₃, whose Fe concentration is off-stoichiometric. The color of each phase in the phase

diagram is consistent with those in the pathway illustration. Impeded external and internal Li transport is indicated by black solid and white dashed arrows, respectively. Reproduced with permission from ref ¹⁰⁸. Copyright 2021 Springer Nature.

Feng and colleagues developed a ternary metal fluoride ($\text{Cu}_y\text{Fe}_{1-y}\text{F}_2$ solid solution) *via* a mechanochemical reactions method.¹⁰² Synchrotron XRD and TEM characterization verified the distorted rutile structure of $\text{Cu}_y\text{Fe}_{1-y}\text{F}_2$ solid solution in the form of complex agglomerates composed of small nanocrystallites under different Cu/Fe ratios ($y = 0, 0.1, 0.33, 0.5, 0.67, 0.9, 1$). In the corresponding discharge voltage profiles in **Figure 3b**, no typical voltage dip of pure FeF_2 was found. This indicated that the electrochemical properties of $\text{Cu}_y\text{Fe}_{1-y}\text{F}_2$ solid solution was significantly affected by the cooperative redox of Cu and Fe sitting on the same lattice. This ternary metal fluoride $\text{Cu}_y\text{Fe}_{1-y}\text{F}_2$ achieved the reversible Cu redox reaction ($\text{Cu}^{2+/0}$) with a low voltage hysteresis (<148 mV), which was uncommon in binary fluorides. Thermodynamics and kinetics of the lithium (re)conversion reactions following two-stage (de-)lithiation path of $\text{Cu}_y\text{Fe}_{1-y}\text{F}_2$ were supported by measurements of X-ray absorption spectroscopy (XAS) and TEM-electron energy loss spectrometer (EELS) characterizations. Initially, Cu^{2+} reduces into metallic Cu^0 with the concomitant formation of disordered FeF_2 , followed by $\text{Fe}^{2+/0}$ reduction. In contrast, the de-lithiation path undergoes a different process, where Fe^0 is partially oxidized up to Fe^{3+} as rutile framework, followed by the reconversion of Cu^{2+} to form disordered rutile-like Cu-Fe-F final phase. This work promotes the development of Cu-based ternary metal fluorides as promising cathode candidates for LIBs. However, the reversible specific capacity of Cu conversion faded rapidly, which can be ascribed to the Cu^+ dissolution on the cathode electrolyte interphase (CEI). Thus, the construction of a stable CEI layer is one of the strategies to improve the cycling stability of metal fluoride cathodes in LIBs. Accordingly, Yushin and co-workers introduced solid polymer electrolytes (SPEs) to pair with carbon nanotubes (CNT)@ FeF_2 composites cathode.⁵³ The obtained solid-state cells delivered a high specific capacity of more than 450 mAh g^{-1} and a long cycle stability of over 300 cycles at 50 mA g^{-1} and 50°C . The introduction of SPE not only prompted the formation of an elastic, thin and stable CEI on the FeF_2 surface (**Figure 3c**), but also reduced the electrolyte decomposition and maintained the cathode structural stability due to the enhanced mechanical properties. This work intrigues the research on the CEI, which will guarantee an improved lifespan of the metal fluoride cathode with merits of low-cost and high energy density.

Although it has been widely accepted that metal fluorides are conversion-type cathodes for LIBs, Grey and colleagues demonstrated a different viewpoint of reaction mechanisms in metal fluoride cathodes.¹⁰⁸ The material structure was well measured by X-ray total scattering and electron diffraction techniques over multiple length scales and analyzed by density functional theory (DFT) calculations. The results indicated that the mobility difference of displaced species affected the diffusion rate during the (de)lithiation of metal fluorides. The illustration of reaction pathways of the FeF_3 system are demonstrated in **Figure 3d**. During

a typical lithiation process, FeF_3 initially transforms into FeF_2 and a cation-ordered and stacking-disordered phase ($\text{A-Li}_x\text{Fe}_y\text{F}_3$) on the surface of cathode particles, then the transition phase product successively converts into B-, C- $\text{Li}_x\text{Fe}_y\text{F}_3$ and end in LiF and Fe as the final discharge products. The subsequent delithiation process follows a reversible pathway. This new mechanistic principle provides a reference model to develop more isomorphic metal fluorides as cathodes for high-energy-density LIBs.

2.1.2. Metal Hydroxy Fluorides and Oxyfluorides. Metal fluoride hydrates have also been investigated as cathode materials for LIBs. In 2013, Wang and co-workers synthesized a series of iron fluoride hydrates with different hydration water content *via* the liquid-phase method.¹⁰⁹ Pure crystalline $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, and FeF_3 were obtained during the dehydration process at increasing calcination temperature, verified by the XRD patterns and their Rietveld refinements. When applied in liquid LIBs, the orthorhombic $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ cathode delivered the highest discharge specific capacity of 88.0 mAh g^{-1} and the lowest polarization among all three samples (**Figure 4a**). Authors attributed this better electrochemical performance of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ to its huge hexagonal cavity for faster Li^+ transfer. These iron fluoride hydrates were simply ball milled with acetylene black to form high electronic conductive composite cathodes, and the initial discharge specific capacity of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ cathode was improved to 177.6 mAh g^{-1} at 0.1 C ($1 \text{ C} = 237 \text{ mA g}^{-1}$) with a high retention of 83.8% after 100 cycles. This reveals that the optimization of crystal structure is important in the development of high-performance metal fluoride hydrates cathodes for LIBs.

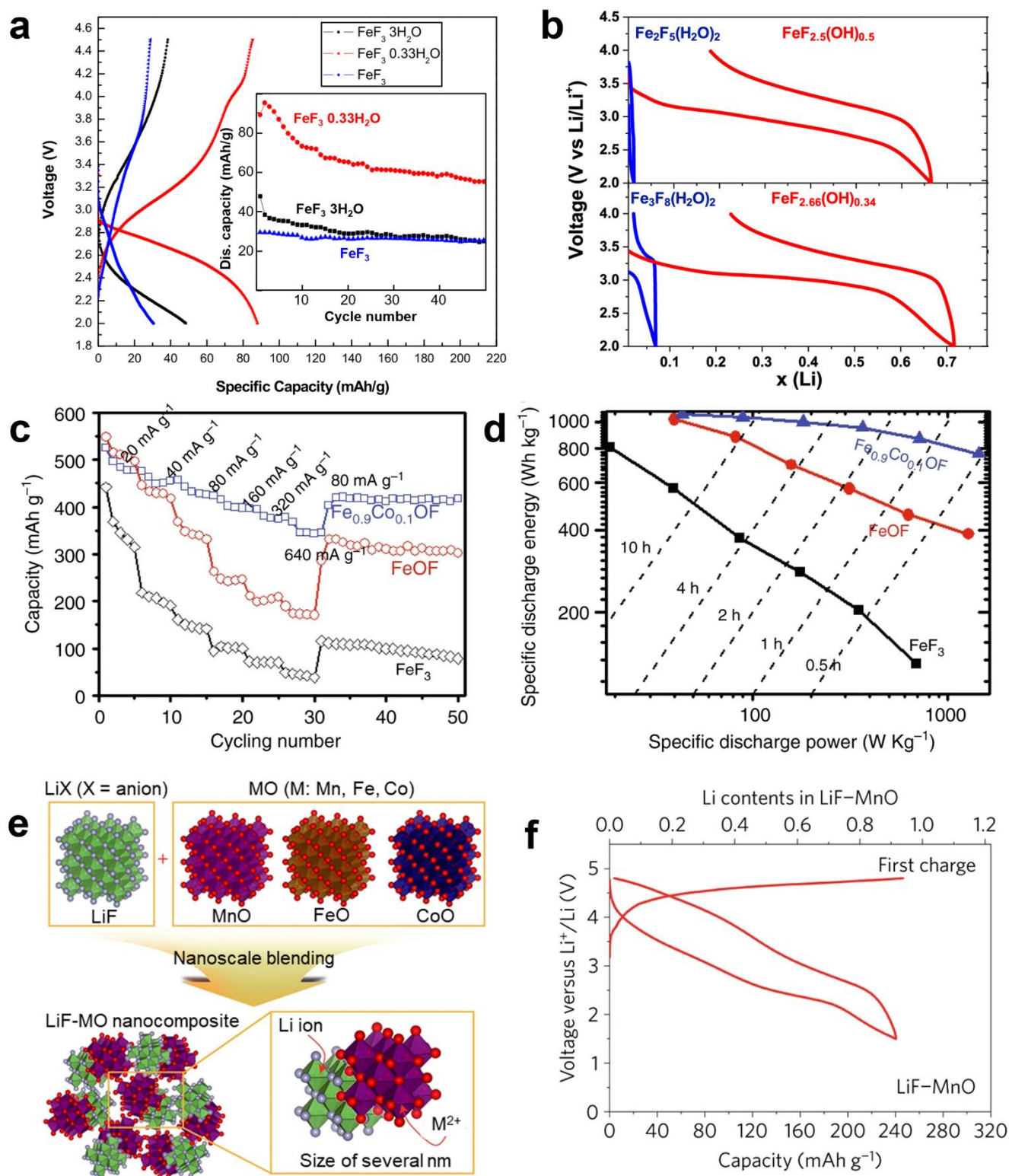
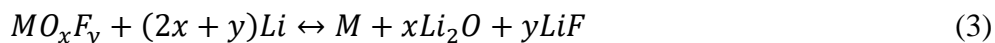


Figure 4. Metal hydroxy fluorides and oxyfluorides for LIBs. (a) Discharge and charge profiles of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, and anhydrous FeF_3 at 0.5 C. Inset: cycling stability curves of $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, and FeF_3 at 0.5 C in the voltage of 2.0–4.5 V. Reproduced with permission from ref ¹⁰⁹. Copyright 2013 Elsevier. (b) First cycle voltage-composition curves for Li/iron fluoride cells in the LP30 electrolyte at 0.05 C. Upper panel: comparison of $\text{Fe}_2\text{F}_5(\text{H}_2\text{O})_2$ and $\text{FeF}_{2.5}(\text{OH})_{0.5}$. Lower panel: comparison of $\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$ and $\text{FeF}_{2.66}(\text{OH})_{0.34}$. Reproduced with permission from ref ¹¹⁰. Copyright 2019 American Chemical Society. (c) Rate capability for $\text{Fe}_{0.9}\text{Co}_{0.1}\text{OF}$, FeOF , and FeF_3 cathode materials, respectively. (d) The Ragone plot of FeF_3 , FeOF , and $\text{Fe}_{0.9}\text{Co}_{0.1}\text{OF}$ (based on active mass). Reproduced with permission from ref ¹¹¹. Copyright 2018 Springer Nature. (e) Schematic of the positive electrode material design strategy using metal monoxide (MO). Metal monoxides that had electrochemical activity only as the negative electrode were designed as

positive electrode material by forming mixtures with LiF in nanoscale under high-energy ball milling. After mechanochemical mixing, LiF and MO exist without chemical reaction in the several nanometer scale. The crystal structure of all compounds is described by a polyhedral image. Red, O; grey, F; green, Li; purple, Mn; brown, Fe; blue, Co. (f) First discharge and second charge profiles of LiF-MnO nanocomposites after the initial activating charge protocol as a positive electrode (1.5–4.8 V) in 1 M LiPF₆ in ethyl carbonate/dimethyl carbonate (EC/DMC, 1:1 by vol.) electrolyte at a 20 mA g⁻¹ (0.03 mA cm⁻²) constant current rate. Reproduced with permission from ref ¹¹². Copyright 2017 Springer Nature.

Later, in 2019, Lhoste and colleagues further investigated the structural effects of iron hydroxy fluorides as cathodes in LIBs.¹¹⁰ First, two anion-deficient iron fluoride hydrates Fe₂F₅(H₂O)₂ and Fe₃F₈(H₂O)₂ were synthesized by a facile microwave synthesis method, which were unstable under the ambient atmosphere. After special heating treatments, two stable iron hydroxy fluorides FeF_{2.5}(OH)_{0.5} (pyrochlore structure) and FeF_{2.66}(OH)_{0.34} (hexagonal tungsten bronze structure) were obtained. When applied as cathodes in LIBs, the dehydrated iron hydroxy fluorides delivered higher reversible specific capacity than their hydrated opponents (**Figure 4b**). The structure analysis of XRD and Mössbauer spectrometry proved that the removal of structural water molecules within the hexagonal cavities opened the Li diffusion channels for the battery cycling process.

Metal oxyfluorides, such as VO₂F¹⁰³, BiOF¹⁰⁴, FeOF^{105, 111}, TiOF₂¹⁰⁶, and NbO₂F¹⁰⁷ (**Tabel 1**), have shown great potential as cathode for LIBs owing to high specific capacity, high voltage, good conductivity and good cycling stability.¹¹³ The battery reaction of metal oxyfluorides (MO_xF_y)-based LIBs follows the following reaction:



In 2018, Wang and co-authors reported a cobalt doping iron oxyfluoride (Fe_{0.9}Co_{0.1}OF) synthesized by a solvothermal method.¹¹¹ The specific capacity of Fe_{0.9}Co_{0.1}OF was much higher than the pristine FeOF and FeF₃ (**Figure 4c**), achieving a high energy density of ~1000 Wh kg⁻¹ (**Figure 4d**). This Fe_{0.9}Co_{0.1}OF cathode delivered a high specific capacity of 350 mAh g⁻¹ for 1000 cycles at 500 mA g⁻¹ and the voltage hysteresis was reduced to 0.27 V. Combined with TEM techniques, pair distribution function (PDF) analysis, and first-principles calculations, the author verified that the reaction kinetics of Fe_{0.9}Co_{0.1}OF was enhanced by the co-substituted anion (O) and cation (Co) in Fe_{0.9}Co_{0.1}OF. In this case, the less reversible conversion reaction was replaced by a highly reversible intercalation-extrusion reaction due to the decrease in particle size and abundance of metallic Fe(Co). Hence, this co-substitution strategy inspires the development of other conversion-type electrode materials with similar reversibility problems.

Unlike the crystalline oxyfluorides, Kang and colleagues reported a special LiF-metal monoxide (MO, M = Mn, Fe, Co) nanocomposite as Li-free cathode for LIBs,¹¹² which was synthesized by blending the transition metal monoxides and nanosized lithium fluoride in high-energy ball miller under an argon atmosphere (**Figure 4e**). This cathode material delivered high specific capacity after the first charging step with a high voltage (*e.g.*, average voltage of 3.1 V for LiF-MnO, **Figure 4f**). In contrast with the

conventional Li intercalation, the reaction mechanism of LiF-MO nanocomposite cathode can be ascribed to a surface conversion reaction as follows:



Moreover, the performance of LiF-MO nanocomposite cathode can be further improved by decreasing the particle size of metal compounds. This novel mechanism is expected to be expanded to other transition metal compounds and Li salts couples for advanced cathode materials in LIBs.

2.1.3. Fluorine-Substitution Electrode Materials. To achieve higher electrochemical performance, fluorides are added to electrodes to improve the properties of original cathode materials. Silver vanadium oxide ($Ag_2O \cdot xV_2O_5$) has been commercialized as cathode material in primary Li batteries for high-rate applications. The increase of Ag: V ratio can extend the high-voltage plateau but is accompanied by the poor kinetics and low conductivity. In 2005, Poeppelmeier and colleagues reported the synthesis of single crystals of $Ag_4V_2O_6F_2$ ($Ag_2O \cdot V_2O_5 \cdot 2AgF$) *via* a low-temperature hydrothermal technique.¹¹⁴ The introduction of AgF phase increased the Ag: V ratio and reaction potential of the cathode. At the same time, the dimensionality of the vanadium oxide framework was partially reserved (**Figure 5a**), which served as the Li-ion conduction pathways between vanadium centers. Therefore, $Ag_4V_2O_6F_2$ cathode delivered enhanced initial discharge plateau and higher specific capacity above 3 V (3.52 V and 148 mAh g⁻¹), compared to the undoped silver vanadium oxides (3.22 V and 100 mAh g⁻¹, **Figure 5b**).

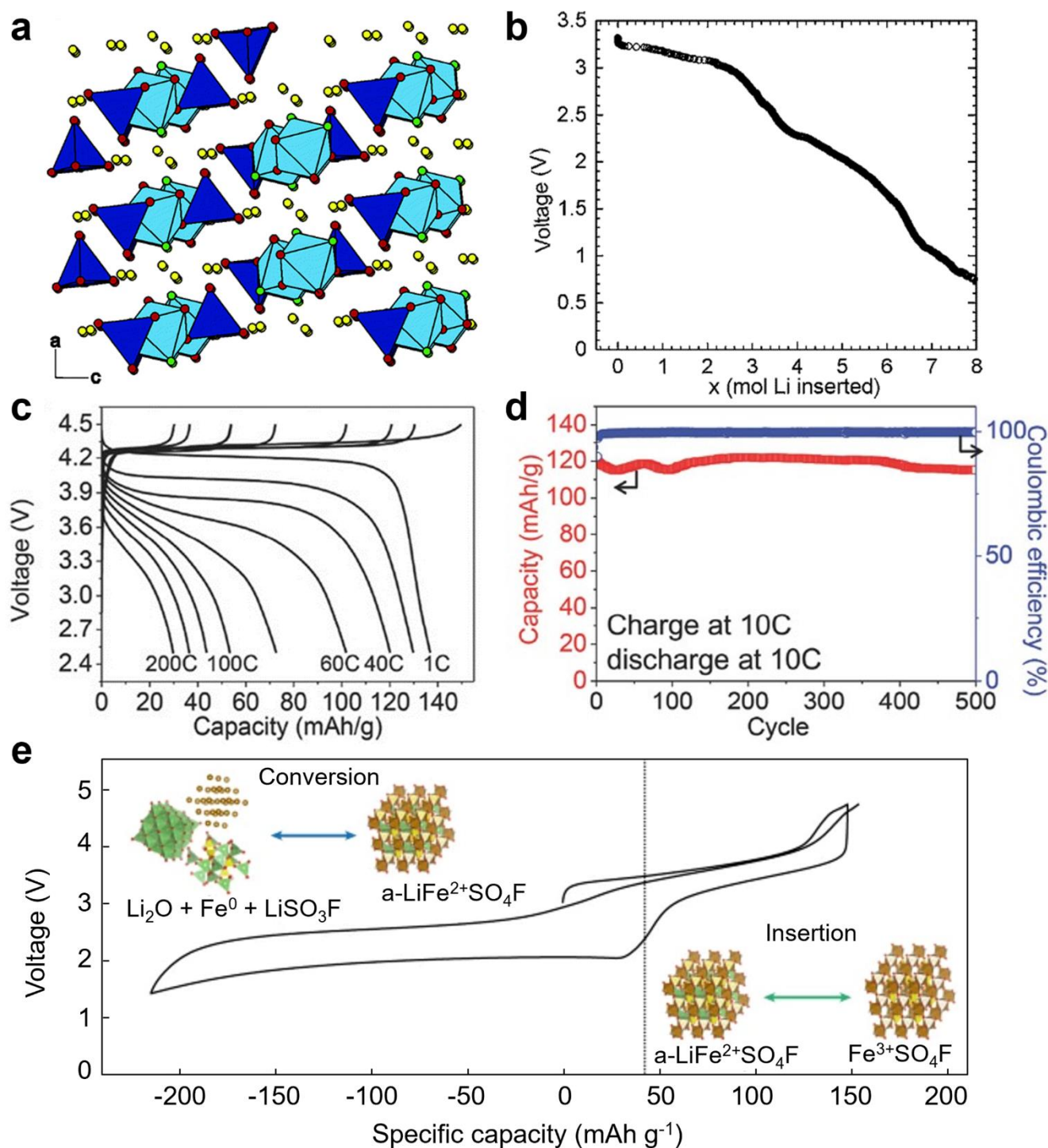


Figure 5. Fluoride-contained electrode materials. (a) Three-dimensional packing diagrams of $\text{Ag}_4\text{V}_2\text{O}_6\text{F}_2$. Yellow spheres represent silver atoms, vanadium oxide fluoride octahedra are in light blue, and vanadium oxide tetrahedra are in dark blue. (b) Constant current discharge curve of $\text{Ag}_4\text{V}_2\text{O}_6\text{F}_2$. Reproduced with permission from ref ¹¹⁴. Copyright 2005 American Chemical Society. (c) Charge and discharge voltage profiles of C-coated LiVPO_4F at various rates (right to left: discharging at 1 C, 20 C, 40 C, 60 C, 80 C, 100 C, 120 C, 150 C, and 200 C and charging at 1 C without a voltage hold). (d) Capacity retentions at 10 C charge/10 C discharge for 500 cycles. The cutoff voltage was 2.5–5 V (only for cycle retention). Reproduced with permission from ref ¹¹⁵. Copyright 2015 Wiley-VCH. (e) Charge/discharge profile with schematic of two-step reaction mechanism of $\text{a-LiFeSO}_4\text{F}$ as insertion and conversion reactions. Reproduced with permission from ref ¹¹⁶. Copyright 2022 Springer Nature.

The strategy of fluoride doping can also multiply the rate energy density and performance of cathode material. The low electronic conductivity and limited specific capacity are the main drawbacks of conventional polyanion compound cathode,¹¹⁷ including LiFePO₄ phosphates, LiMBO₃ borates Li₂MSiO₄ silicates, and Li₂Fe(SO₄)₂. In 2015, Kang and co-workers reported fluorinated polyanion compound cathode (LiVPO₄F) for LIBs,¹¹⁵ which was synthesized by scalable single-step solid-state reaction. As shown in **Figure 5c**, the Li||LiVPO₄F cell achieved superior rate capability up to 200 C with low polarization and maintained a high specific capacity of ~ 120 mAh g⁻¹ at 10 C for 500 cycles with > 95% retention efficiency (**Figure 5d**). Owing to its higher operating voltage (> 3.45 V), LiVPO₄F can achieve higher energy density (~ 521 Wh g⁻¹ at 20 C, 1 C=158 mA g⁻¹) than LiFePO₄. The smaller particle size, negligible number of antisite defects, and minimal surface oxidation endowed this LiVPO₄F cathode material with remarkable rate capability and energy density, overwhelming the commercial LiFePO₄ cathode materials.

Moreover, fluorosulfate such as LiFeSO₄F¹¹⁸ and Li(Fe_{1- δ} Mn _{δ})SO₄F¹¹⁹ has been investigated as cathode materials for LIBs for decades owing to the low-cost and the abundant distribution of these transition metal elements on earth. However, the low gravimetric specific capacity of the heavy polyanion group in the cathode materials restricts its commercial application. In 2022, Kang and colleagues reported an amorphous iron fluorosulfate (a-LiFeSO₄F) synthesized by a simple ball milling process of LiF and FeSO₄.¹¹⁶ This fluoride-doping polyanion cathode demonstrated a high specific capacity of 360 mAh g⁻¹ with ~ 98.6% specific capacity retention after 200 cycles even at 60 °C. With an average discharge voltage of ~ 2.52 V, a high energy density of 906 Wh kg⁻¹ was achieved by a-LiFeSO₄F cathode. Different from the conventional crystalline polymorphic LiFeSO₄F, the a-LiFeSO₄F with a unique inherent amorphous structure underwent a three-electron redox reaction based on combined intercalation and conversion (**Figure 5e**), which maintained an intact structural integrity for reversible cycle stability. This multi-mechanistic lithiation process of amorphous intercalation material is promising for the development of high-capacity and low-cost cathodes for LIBs.

2.1.4. Fluorinated Surface Modification. F-modification technologies such as fluoride-coating and fluorine-substitution are widely used to improve the performance of conventional oxide-based cathodes for LIBs. The high electronic and ionic resistance caused by unstable CEI limits the rate capability and cycle life of Co-free layered oxide cathode materials¹²⁰. In 2012, Clare and co-authors investigated the coating strategy of layered Li[Li_{1/9}Ni_{1/3}Mn_{5/9}]O₂ cathode processed by the commercial aluminum fluoride (AlF₃) aqueous suspension and followed by a heating treatment¹²¹. As shown in **Figure 6a**, the XRD, TEM, energy-dispersive X-ray (EDX) and ²⁷Al Nuclear magnetic resonance (NMR) proved that a uniform layer of fluorinated amorphous aluminum oxide (Al₂O₃) was successfully coated on the surface of the cathode

material. The $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$ cathode with a low coating layer (1 mol% Al/F) delivered a specific capacity of 215 mA h g^{-1} with a cut-off charging voltage of 4.6 V. Zhang and co-workers reported an amorphous CeF_3 coated layered lithium-rich oxide cathode *via* a facile chemical deposition method.¹²² A 10 nm thick CeF_3 layer (2 wt.%) was evenly deposited on the surface of $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ cathode particles (**Figure 6b**). This CeF_3 -coated cathode demonstrated a higher capacity retention (97.1%) than that of the pristine sample (82.1%) after 50 cycles. Additionally, the rate performance of CeF_3 -coated cathode also surpassed that of the pristine sample at 1250 mA g^{-1} (103.1 mAh g^{-1} vs. 82.2 mAh g^{-1}). The author attributed the outstanding enhancement to this amorphous CeF_3 coating layer, which effectively hindered the continuous decomposition of the electrolyte on the cathode surface, thus controlling the growth of the insulated passivated interlayer and maintaining the structural stability of the cathode.

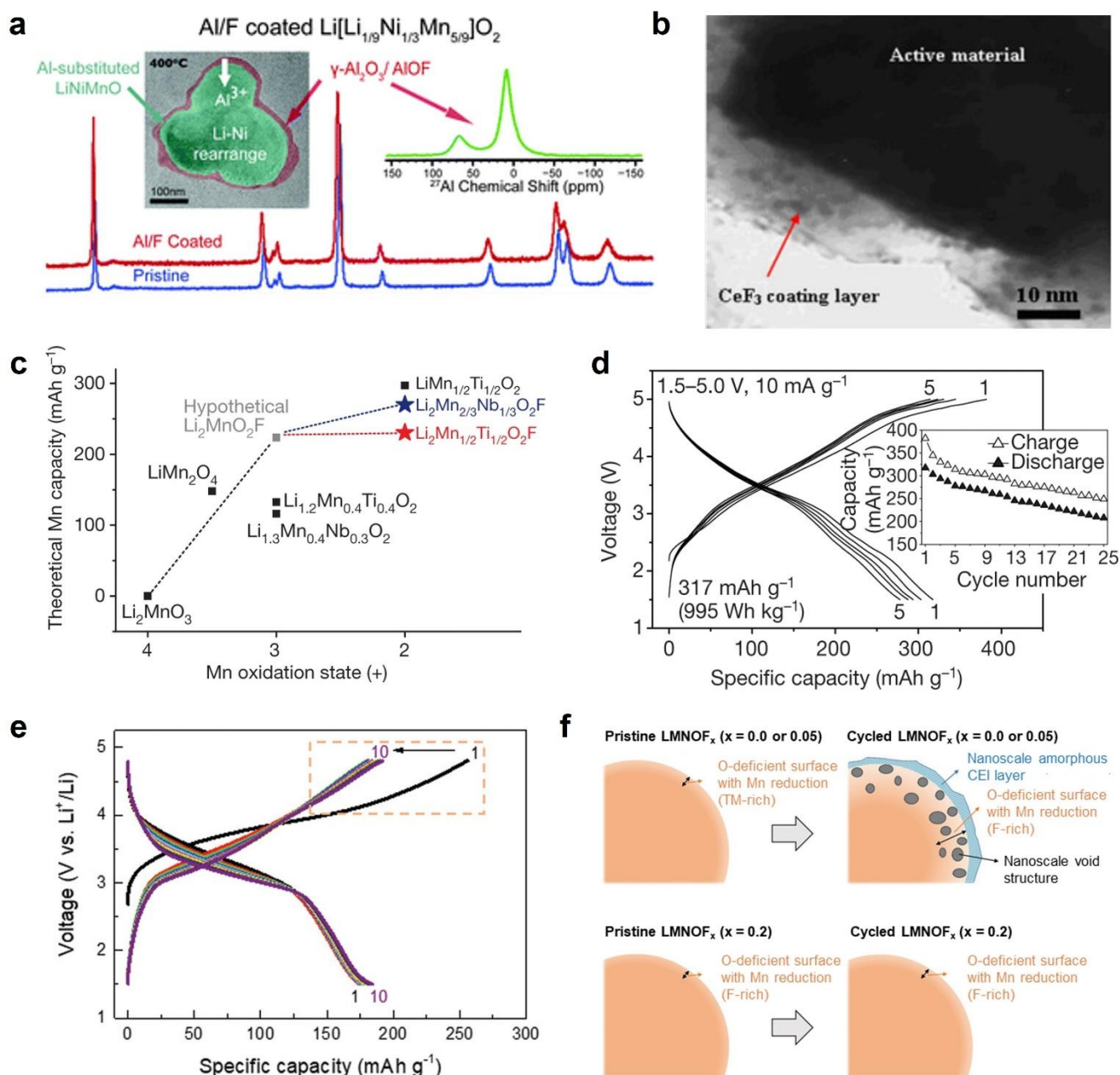


Figure 6. F-modified electrode materials. (a) Powder XRD pattern, TEM images and ^{27}Al NMR spectra of pristine and Al/F-coated $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$. Reproduced with permission from ref ¹²¹. Copyright 2012 Royal Society of Chemistry. (b) TEM image of 2 wt.% CeF_3 -coated $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$. Reproduced with permission from ref ¹²². Copyright 2014 Elsevier. (c) Theoretical Mn-redox capacity of various Mn-based cathode materials. (d) Voltage profiles and capacity retention of $\text{Li}_2\text{Mn}_{2/3}\text{Nb}_{1/3}\text{O}_2\text{F}$ under 1.5-5.0 V, 10 mA g^{-1} . Reproduced with permission from ref ¹²³. Copyright 2022 Springer Nature. (e) Voltage profiles at a higher voltage region during the first ten cycles for $\text{LMNOF}_{0.2}$. (f) Schematics summarizing the observation of the structural and chemical evolutions in the LMNOF_x cathode particles. Upper panel: for the LMNOF_x cathodes with zero or low F concentration ($x = 0, 0.05$), the cycling process leads to the formation of nanoscale amorphous CEI layers on the surface and void-like nanoregions featuring severe loss of O, Mn, and Li at the subsurface, all of which can be detrimental to the Li transport. Lower panel: for the LMNOF_x cathodes with high F concentration ($x = 0.2$), the crystalline structure at the cathode surface and the stoichiometric elemental distribution at the subsurface is mostly well preserved after cycling, which ensures facile Li transport at the surface. Reproduced with permission from ref ¹²⁴. Copyright 2021 Wiley-VCH.

The fluorine substitution strategy is also utilized to improve the performance of electrode materials for LIBs. In 2018, Ceder and colleagues reported Co/Ni-free disordered-rocksalt Li-rich intercalation cathodes $\text{Li}_2\text{Mn}_{2/3}\text{Nb}_{1/3}\text{O}_2\text{F}$ realized by the partial substitution of fluoride anion and high-valent cation,¹²³ which process a Mn^{2+} -involved theoretical specific capacity of 270 mAh g^{-1} , much higher than that of a typical Mn-based Li-rich cathode (**Figure 6c**). As shown in **Figure 6d**, this cathode delivered a high discharge specific capacity of 317 mAh g^{-1} and reached a state-of-the-art high energy content of 995 Wh kg^{-1} (3761 Wh l^{-1}) due to the high amount of $\text{Mn}^{2+}/\text{Mn}^{4+}$ redox couples combined with a small amount of O redox reactions. Giving rise to this strategy, the structural stability of the Mn-based Li-rich cathode was not affected by the extensive O redox, thus leading to high cathode performance.

The surface stability of disordered rocksalt cathodes can also be enhanced by fluorine substitution. Wang and co-authors unveiled the relationship between high-level fluorine substitution and good surface stability.¹²⁴ The Mn-based disordered rocksalt cathodes with various fluorine substitutions ($\text{Li}_{1.2}\text{Mn}_{0.6+x/2}\text{Nb}_{0.2-x/2}\text{O}_{2.0-x}\text{F}_x$, LMNOF_x , $x = 0-0.2$) were synthesized and compared in terms of electrochemistry and characterization. The cycling stability of LMNOF_x cathode was significantly improved by increasing F content from 0 to 0.2, while O redox peaks nearly disappeared (**Figure 6e**). The results demonstrated that increased fluorine substitution level in disordered rocksalt cathode reduced amorphous CEI layers at the top of the cathode surface, prevented the damage to the internal crystal structure of the cathode and maintained the uniform chemical distribution at the subsurface of the cathode particles (**Figure 6f**).

Fluorine chemistry is crucial in the development of Li-based batteries with high energy density and reversibility. High-voltage metal fluoride and oxyfluoride electrodes show great promise to improve the energy densities of Li-based batteries. In particular, metal fluorides based on multiple electron transfer reactions are expected to address the limitations of conventional cathode materials in LIBs.

2.2. Fluorinated Electrolytes

Electrolytes play a particularly essential and complex role in LIBs and Li metal batteries (LMBs). As the battery component is in contact with other active and passive parts of the battery, the electrolyte must fulfill requirements as follows: high degree of Li ion conductivity, good thermal and chemical stability, electronic insulation to avoid self-discharge, relative non-toxicity to avoid environmental hazards, and low cost. Commonly used commercial electrolytes consist of a conductive Li salt (usually LiPF_6) and an organic solvent mixture of cyclic and linear organic carbonates. The salt-solvent-additive combination determines the overall performance of rechargeable Li batteries, such as conductivity, thermal stability and electrochemical stability. However, demand for higher voltage Li batteries has forced researchers to look for new electrolyte formulations, including solid electrolytes, as current liquid electrolytes are unstable at potentials higher than 4.5 V and exhibit safety concerns. Power batteries typically contain high-energy active electrode materials, which tend to easily react with other elements, rendering the combination unusable. The fluorination of electrolyte components is a key strategy for advanced electrolyte engineering, which can enhance the electrode reaction reversibility, extend the battery life, and reduce the electrolyte flammability.

2.2.1. Fluorinated Salts. Li salts act as the conductor of Li ions in the electrolyte, and the nature of the Li salts is often determined by the structure of the anions. As shown in **Figure 7a**, F-substitution is widely applied in Li salts for LIBs and LMBs. The presence of fluorine atoms and the delocalized charge of the anions make such F-containing Li salts highly soluble in dipolar aprotic solvents.¹²⁵ For battery applications, Li salts need to possess characteristics such as low molecular weight, low toxicity, stability over a wide electrochemical stability window (ESW), as well as electrolyte|electrode interphase formation ability. Among the F-substituted Li salts, LiPF_6 and Li sulfonate salts are the most widely used. LiPF_6 salt exhibits the advantages of high ionic conductivity, good passivation ability for Al collectors, and high oxidation stability, *etc.* However, LiPF_6 salt processes a serious disadvantage of high sensitivity to water, which is easily decomposed to produce HF and cause serious corrosion to electrodes and the whole battery.¹²⁶ For comparison, benefiting from the presence of strong perfluoroalkyl electron-absorbing groups and conjugated structures leading to the delocalization of negative charges, the anion of Li sulfonate salts is relatively stable. Thus, Li sulfonate salts show the advantages of good thermal stability, high solubility, insensitivity to moisture, high dissociation constants, *etc.* However, severe Al foil dissolution occurs when charged to high voltage.¹²⁷ Furthermore, it is crucial to note that Li sulfonate salts, which contain $-\text{CF}_2-$ and/or $-\text{CF}_3$ function groups, potentially pose environmental risks during production and utilization. Thus, strategies to mitigate these impacts should be developed before the evolution to more eco-friendly alternatives.¹²⁸ In addition to the commonly used F-substituted Li salts mentioned above, researchers synthesized new Li salts through asymmetric molecular structure design. For

example, Liu *et al.* reported a new salt under the premise of retaining the strong electron-withdrawing group.¹²⁹ Ether skeleton was introduced to enable F- substituted salt electron-donating ability to capture the migrated Li⁺. The design molecule showed a large molecular dipole moment, which led to a high donor number (DN) and high Li⁺ transference number. Meanwhile, the quality of interphase film formation largely affects the compatibility with cathode and anodes, thus determining the cycling stability of the entire battery. Betar M. Gallant *et al.* discussed the interplays between CE and generic fluorine content across a wide range of electrolytes.²⁴ **Figure 7b** shows a positive correlation between CE and fluoride levels. Increasing the F concentration through ‘beneficial’ fluorination appears to be a reliable strategy to achieve high CE of Li plating/stripping, while further understanding of the chemistry and decomposition kinetics of the F source remains needed. Moreover, apart from the type of Li salts, their purity also has a significant impact on CE.¹³⁰ Enhancing the purity of LiBF₄ from 99.9% to 99.99% would result in a flatter morphology of the SEI, as depicted in **Figure 7c**. The purity of the conducting salt directly influences the morphology, composition, and possibly the quality of the formed protective layer. The formation of a more robust interphase that inhibits the growth of high surface area Li directly improves the cycling stability of cells containing fluorine-based conducting salts. To conclude, although LiPF₆ is not prominent in ionic conductivity, chemical stability and thermal stability, it is still dominant in the commercial market of LIBs due to the ability to provide the well-balanced properties. Selective fluorination of the anions of Li salts will decrease their interactions with Li⁺ cations, thereby increasing the dissociation of the salts in the electrolyte solution and lifting the ionic conductivity. To achieve better performance, two or more F-containing salts are synergistically used to supplement their native deficiencies.

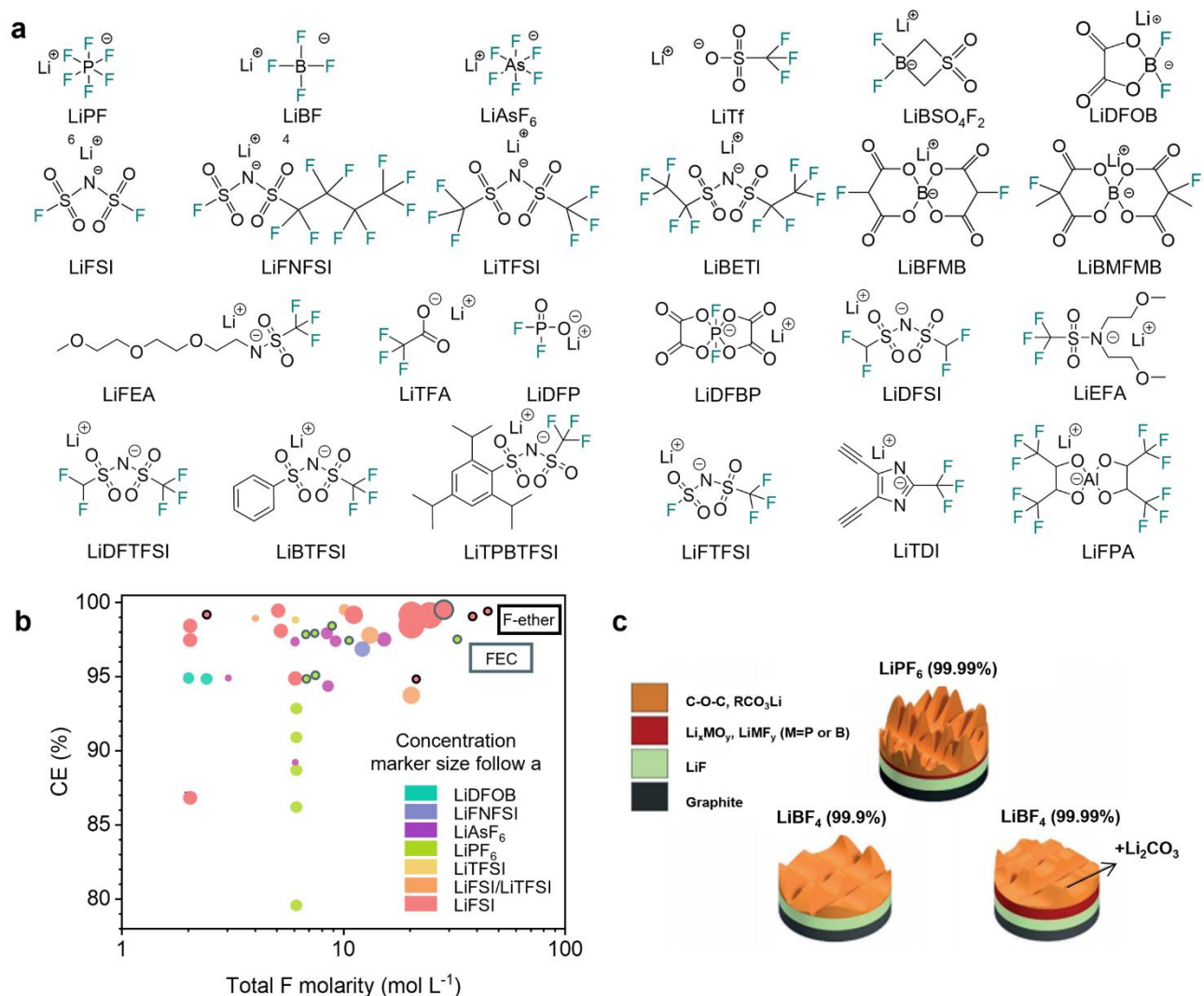


Figure 7. Fluorinated salts for Li-based batteries. (a) Structural formulas of the different Li salts. (b) CEs of Li||Cu cells with Li salts of different F molarity. Reproduced with permission from ref ²⁴. Copyright 2021 Springer Nature. (c) Schematic illustration of the SEI film obtained from electrolyte formulations based on LiPF₆ (battery grade purity: 99.99%), LiBF₄ (99.9% purity), and LiBF₄ (99.99% battery grade purity). Reproduced with permission from ref ¹³¹. Copyright 2013 Elsevier.

The properties of the electrolyte can be altered by adjusting the concentration of the Li salt. Conventional dilute electrolytes typically operate within a salt concentration range of 1–2 M, which strikes a balance between ionic conductivity, viscosity, and salt solubility. Thus, most of the studies use electrolytes in region C in **Figure 8a**. However, by carefully selecting appropriate salts and solvents, electrolytes can be relocated in regions A, B, and D, as depicted in **Figure 8a**, leading to some unexpected properties.¹³² Aqueous electrolytes possess a narrow ESW of 1.23 V, which is insufficient to support most electrochemical couples in LIBs. Besides, hydrogen evolution at the anode side is another serious challenge, as it occurs at a potential (2.21–3.04 V *v.s.* Li/Li⁺, depending on pH value) far higher than the operating voltage of most LIBs. Consequently, the maximum voltage achieved in aqueous LIBs was limited to 1.5 V.^{133, 134} Xu *et al.* developed a “water-in-salt” electrolyte by dissolving lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) at extremely high

concentrations (molality > 20 m) in water, leading to an anion-rich Li^+ solvation sheath and an expanded the ESW (~ 3.0 V),¹³⁵ as exhibited in **Figure 8b**. This remarkable shift resulted from the formation of a dense interphase on the anode surface, primarily caused by the reduction of salt anions. The $\text{LiMn}_2\text{O}_4||\text{Mo}_6\text{S}_8$ cells using “water-in-salt” electrolyte demonstrated an open circuit voltage (OCV) of 2.3 V, and the CE was nearly 100% for up to 1000 cycles.

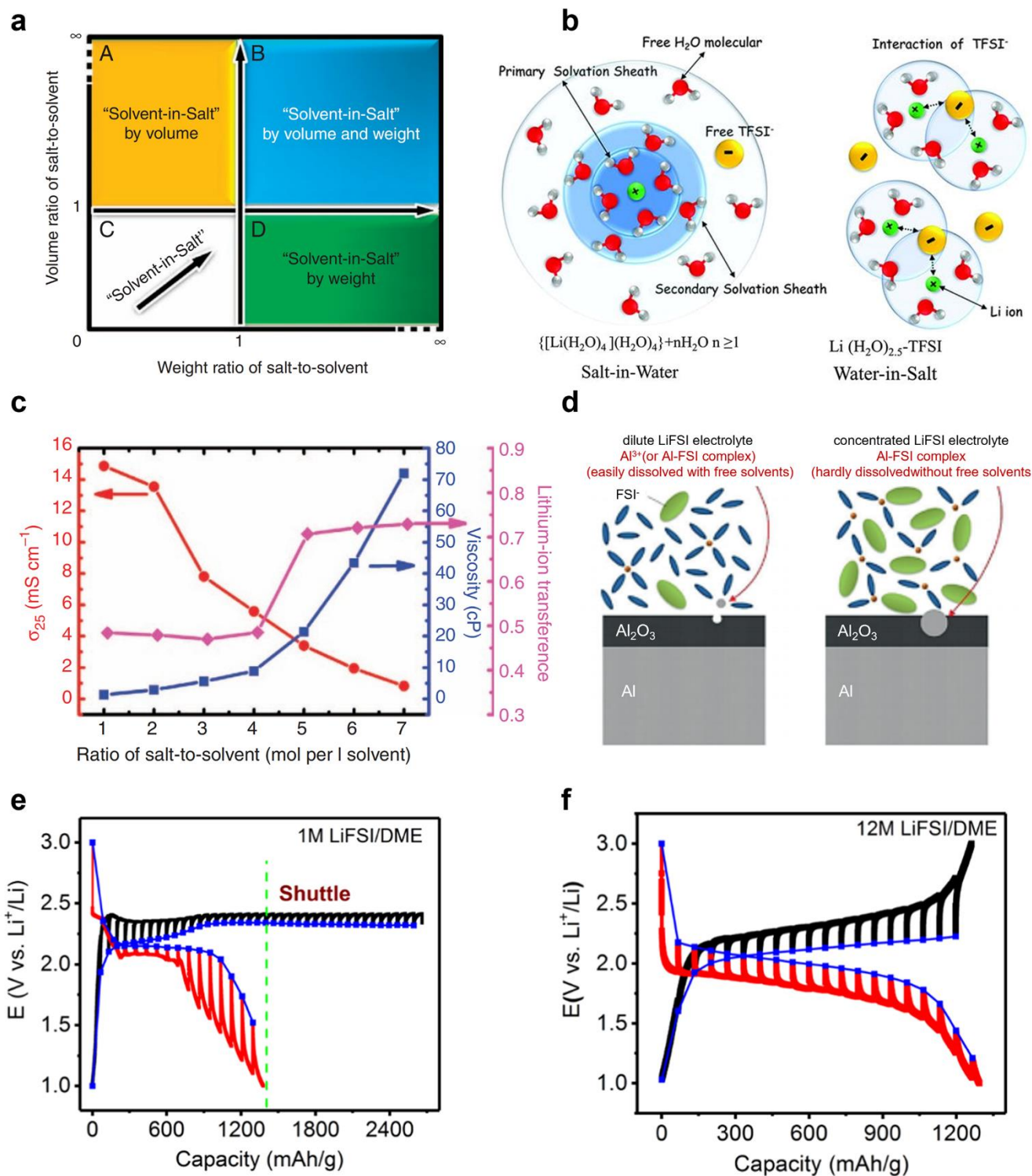


Figure 8. Electrolytes for Li-based batteries with highly concentrated fluorinated salts. (a) Classification of electrolytes according to volume ratio & weight ratio. Reproduced with permission from ref ¹³². Copyright 2013 Springer Nature. (b) schematic diagram of water-in-salt electrolyte. Reproduced with permission from ref ¹³⁵. Copyright 2015 American Association for the Advancement of Science. (c) Viscosity, ionic conductivity and Li ion transference number at room temperature for the various electrolytes. Reproduced with permission from ref ¹³². Copyright 2013 Springer Nature. (d) Schematic illustrations of the behavior of Al current collectors in a dilute LiFSI/ acetonitrile (AN) electrolyte (left) and a highly concentrated LiFSI/AN electrolyte (right) with little free solvent molecules and free FSI⁻ anions. Reproduced with permission from ref ¹³⁶. Copyright 2015Wiley-VCH (e) GITT curves in 1 M-LiFSI/DME electrolyte and (f) in 12 M-LiFSI/DME electrolyte. Reproduced with permission from ref ¹³⁷. Copyright 2018 Elsevier.

Research on non-aqueous electrolytes offers countless variations in aprotic solvents, Li salts, and their mixing ratios. For a given electrolyte with fixed salt and solvent, ionic conductivity depends on both viscosity and Li ion mobility.¹³² For 1 M LiTFSI-1,2-dimethoxyethane (DME)/1,3-Dioxolane (DOL) (1: 1 by vol.), as is concluded in **Figure 8c**, when the salt concentration is increased, more and more Li-solvent pairs form due to incomplete Li⁺ solvation shell, and the viscosity at room temperature increases obviously. At the same time, the Li ion transference number rises to a much higher value ($t_{\text{Li}^+} = 0.73$) than that of dilute salt-in-solvent electrolytes (0.2–0.4).¹³⁸ For such electrolytes, Li ions are mostly coordinated with solvent in the first solvation shell, leading to a large number of free anions and lower mobility of solvated Li cations. In the highly concentrated electrolyte system, more anions come into the first solvation shell and form more contact ion pairs (CIPs) and aggregates (AGGs), thus leading to a higher Li ion transference number and lower ion conductivity.¹³⁹ Apart from these changes in physical properties, the concentrated electrolyte demonstrates unusual electrochemical properties that are remarkably distinct from a conventional dilute electrolyte. In 2003, Ogumi *et al.* reported that highly concentrated propylene carbonate (PC) electrolytes have shown dramatic changes in the behavior of graphite electrodes.^{140, 141} Further in 2008, the reversibility of Li metal deposition/stripping was notably improved in highly concentrated PC electrolytes.¹⁴² From 2010 onward, Yamada *et al.* extended this method to a wide range of non-aqueous solvents of reversible graphite electrodes with EC-free solvent.¹⁴³⁻¹⁴⁵ After this path-breaking work, the highly reversible Li metal electrodes with excellent cycling stability was reported by Xu *et al.*¹³² in 2013 and Qian *et al.*¹⁴⁶ in 2015. These changes can be attributed to the reduction of free solvent in the solution, altering the solvation structure and shifting the energy level of the LUMO towards the salts, resulting in the reduction of the salts at a lower voltage.¹⁴⁴ For LiTFSI/ lithium bis(fluoro sulfonyl) imide (LiFSI)-containing electrolyte, Al dissolution is suppressed at high voltage.¹⁴⁷ The presence of fewer free solvents and anions in the electrolyte leads to less dissolution of the Al current collectors, as shown in **Figure 8d**. For Li-S batteries, the high-concentration electrolytes can inhibit self-discharge caused by polysulfide shuttle (**Figure 8e**), which significantly improves the reversibility of the batteries (**Figure 8f**).¹³⁷ However, the application of such highly concentrated electrolytes is limited by the high cost and high viscosity due to the extensive use of Li salts.

2.2.2. Fluorinated Solvents and Co-solvents. Introducing fluorine into the molecular structures of electrolyte solvents and co-solvents imparts unique physicochemical properties, such as non-flammability, robust LiF-enriched SEI, high resistance against electrochemical oxidation, and an expanded operating temperature window, *etc.* These advantages make fluorinated electrolytes highly attractive for advanced battery applications. Representative fluorinated solvents and co-solvents are shown in **Figure 9a**, showing the dielectric constant increasing from left to right. These fluorinated solvents and co-solvents exhibit unique physicochemical properties because of the very high electronegativity and high ionic potential of the fluorine atom.¹⁴⁸ Partially fluorinated organic solvents possess relatively high polarity compared to perfluorinated organic solvents. This property allows partially fluorinated solvents to be used as functionalized solvents, while perfluorinated solvents are primarily employed as anti-solvents due to their poor dissolving ability with Li salts. As shown in **Figure 9b**, Xie et al. proposed the dipole-dipole interactions model to enhance the compatibility of various electrolytes with graphite anode, thereby suppressing Li⁺-solvent co-intercalation, preserving the graphite lattice and improving electrochemical reversibility.¹⁴⁹ After introducing fluorobenzene (FB) into LiFSI-3DME system (LiFSI-3DME/7FB), the co-intercalation of the solvent was suppressed, leading to a high initial CE of 86% and stable cycling performance over 200 cycles with a capacity retention of up to 94%. The non-solvents kept out of the Li⁺ solvation shell while exerting considerable dipole-dipole interactions towards polar solvents, thus weakening the Coulombic attractions between Li⁺ and solvents. Rational design by partial fluorination on ethers, *e.g.*, locally polar -CHF₂, is identified as the optimal group compared with fully fluorinated -CF₃ in popular designs. Such weak solvents could achieve a balance between fast ion conduction and electrode stability through the fine-tuning solvation ability (**Figure 9c**).¹⁵⁰ These developed electrolytes simultaneously endowed high conductivity, low and stable overpotential, high CE (> 99.5%) and fast activation (CE > 99.3% within two cycles). Furthermore, some Li-unfriendly solvents can be optimized by fluorination. For instance, by introducing a fluorinated moiety into the non-flammable phosphate, the five-membered fluorinated cyclic phosphate solvent 2-(2,2,2-trifluoroethoxy)-1,3,2-dioxaphospholane 2-oxide (TFEP) was designed and synthesized, as shown in **Figure 9d**.¹⁵¹ Such fluorinated phosphate solvent not only performed effective non-flammability, but also exhibited excellent electrode compatibility. Besides, fluorine substitution can broaden the range of liquid electrolytes. In 2019, Meng *et al.* proposed liquified gas electrolytes, which showed high CE with Li metal anode (**Figure 9e**).¹⁵² The 0.5 M LiTFSI and 0.5 M tetrahydrofuran (THF) in fluoromethane (FM) electrolyte exhibited a maximum conductivity of 3.9 mS·cm⁻¹ at 20 °C. And the impressive low-temperature conductivity at -60 °C was 2.8 mS·cm⁻¹, which was competitive among state-of-the-art low-temperature electrolytes.^{153, 154} Such enhanced liquefied gas electrolytes demonstrated average CEs of 99.6%, 99.4%, and 98.1% (± 0.3%) at capacities of 0.5, 1, and 3 mAh cm⁻², respectively, during long-term cycling performance.

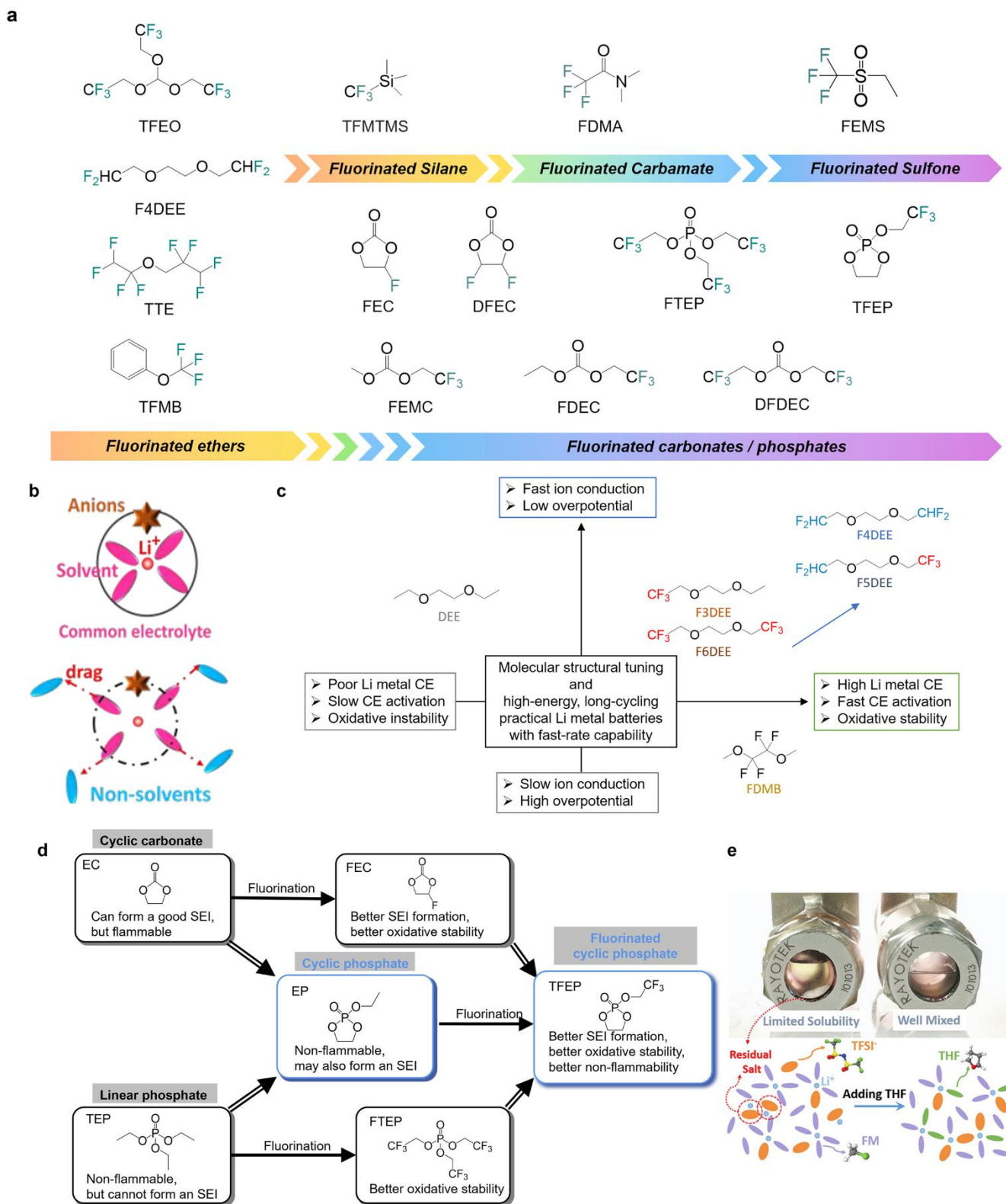


Figure 9. Fluorinated solvents and co-solvents. (a) Molecular structures of representative fluorinated solvents. (b) Established solvation structures of common diluent electrolyte, localized high-concentration electrolyte (LHCE), and non-solvent-added electrolyte and their desolvation processes. Reproduced with permission from ref ¹⁴⁹. Copyright 2023 Royal Society of Chemistry. (c) Optimization of ether electrolytes toward fast ion conduction, low overpotential, high Li metal efficiency, fast CE activation and high oxidative stability. Reproduced with permission from ref ¹⁵⁰. Copyright 2022 Springer Nature. (d) Design of the fluorinated cyclic phosphate solvent to achieve better SEI formation, better oxidation stability, and better non-flammability. Reproduced with permission from ref ¹⁵¹. Copyright 2020 Wiley-VCH. (e)

Photographs of solubility tests in window cells of 0.1 M LiTFSI in FM (left) and 0.3 M LiTFSI and 0.3 M THF in FM (right). Reproduced with permission from ref ¹⁵². Copyright 2019 Elsevier.

As mentioned above, per-fluorinated solvents are usually applied as anti-solvent or “dilute” in many works to make localized high-concentration electrolytes (LHCEs). Such LHCEs are widely investigated and always show enhanced interphasial stability.^{139, 155} Compared with HCEs, LHCEs exhibit lower viscosity and wider ESWs. Watanabe *et al.* used hydrofluoroether (HFE) and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (TTE) to dilute highly concentrated ionic liquid electrolytes.¹⁵⁶ The work indicated that the addition of HFE maintained the solvation structure of the original salt-solvent complexes and effectively reduced the dissolution of Li_2S_n , which greatly enhanced the power density of the Li-S batteries. By performing molecular dynamics (MD) simulation, the solvation structure can be shown pictorially. Zhang *et al.* introduced the concept of LHCEs, which consisted of 1.2 M LiFSI in a dimethyl carbonate (DMC)/bis(2,2,2-trifluoroethyl) ether (BTFE) (1:2 by mol) mixture, exhibiting low concentration, low viscosity, and good wettability that facilitated practical applications of LMBs. The dilution with BTFE slightly weakened the association between Li^+ cations and FSI^- anions, promoting FSI^- anions decomposition as the dominant reduction reaction, which formed a robust FSI^- -derived SEI layer. The average CE of the electrolyte was greatly increased to $\sim 99.7\%$. After that, LHCEs have been extensively applied in LIBs, LMBs, and other electrochemical systems.¹⁵⁷ The dilution with BTFE slightly weakened the association between Li^+ cations and FSI^- anions, which led to more FSI^- anions decomposition as the dominant reduction reaction, forming a robust FSI^- -derived SEI layer. The average CE of electrolyte were largely increased to $\sim 99.7\%$. After that, LHCEs were widely applied in LIBs, LMBs, and other electrochemical systems. As shown in **Figure 10a, b**, Zhao *et al.*¹⁵⁸ introduced HFE into initial HCE and simulated the solvation structure. The bulk phase structure of local HCE electrolyte did not greatly change with the addition of HFE diluent. Thus the salt usage was reduced, and the viscosity of the electrolyte became lower. As a result, the electrolyte has a better wettability with electrodes. Although the ionic conductivity usually increases with the decrease of the viscosity, the addition of diluent has a negative effect on the conductivity of LHCE.¹³⁵ The reason is probably the discontinuous Li-conducting network separated by the diluent medium. To achieve a balance, the content of diluent should be restricted during the preparation of LHCE. Fluorinated ether diluents typically exhibit lower LUMO and HOMO energy levels. As a result, they may participate in the formation of electrolyte|electrolyte interphase. Wu *et al.* reported the HFE co-solvent decomposition and metal anode dissolution phenomenon in ether-based LHCE systems.¹⁵⁹ Such light decomposition behavior comes from diluents synergistically decomposed with anions on the Li metal anode. **Figure 10c** shows the density of states (DOS) of LHCE-trifluoromethoxybenzene (TFMB). In LHCE-TFMB, the LUMO is located at either TFMB or FSI^- , with nearly equal probability, indicating that both the FSI^- anions and the TFMB molecules contribute to the SEI formation.¹⁶⁰ Besides, the existence of fluorinated ether anti-solvent also attributes to the anion decomposition. The solvation structures in LHCE-TFMB were validated by Raman spectroscopy

(**Figure 10d**). Upon coordination of DME with Li^+ , the corresponding peaks of both DME and FSI^- shifted to longer wavenumbers. For the 5.0 M-LiFSI/DME electrolyte, only the peak of Li^+ -coordinated DME was observed, indicating that few free DME molecules were present in HCE. In LHCE-TFMB, the peak positions were nearly the same as those in HCE, plus the vibration bands of free TFMB. Unlike TTE, which decomposed little at the anode side, the TFMB/benzotrifluoride (BZTF) diluents were partially decomposed along with the FSI^- anions and participated in forming the SEI on the Li metal anode (**Figure 10e**). This synergistic effect through anion-diluent pairing was expected to be of significant importance to the optimized electrochemical performance. Linear sweep voltammetry (LSV) was conducted on an Al electrode to unveil the electrochemical oxidation stability of these electrolytes (**Figure 10f**). The oxidation stability of LHCE-TFMB/BZTF was significantly improved, and no exponential increase in oxidation current was observed until 5.0 V. He *et al.* reported that the surface area in different electrostatic potential (ESP) ranges (**Figure 10g**) helped quantitatively analyze the characteristics of the molecular surface charge.¹⁶¹ The reduced relative abundance of ESP distribution on anions suggested that the reduction stability of FSI^- was reduced in the presence of anti-solvents. In previous reports, the LHCE-TTE electrolytes demonstrated better cycling performance of Li||Cu cells (98.9% and 99.6%) than LHCE-TFETFE (98.2 and 99.4%).¹⁶² However, the intensified inductive effect caused by anti-solvents reduced the binding energy of the Li-solvent interactions and changed with different anti-solvents. The binding energies of the Li-solvent and Li-anion interactions were decreased with the addition of anti-solvent compared with the HCEs, indicating the capability of anti-solvents to help lower the de-solvation energy and facilitate interphase kinetics in the electrochemical reaction.^{163, 164} The addition of fluorine also led to a decrease in the flammability of the electrolyte, as shown in **Figure 10h**.¹⁶⁵ Hereby, F^\cdot radicals were formed, which could scavenge the H^\cdot radicals. Owing to this approach, the free-radical reaction was quenched, and the flame propagation was suppressed. However, ether-based electrolytes are highly volatile and flammable, and flame retardancy cannot be achieved by adding fluorinated solvents/co-solvent alone. Aurbach *et al.* reported a synergy of fluorinated co-solvent and gelation treatment by a butenoxycyclotriphosphazene (BCPN) monomer, which facilitated the use of ether-based electrolyte for high-energy Li metal batteries.¹⁶⁶ The safety risks of fire and electrolyte leakage were eliminated by the fluorinated co-solvent and fireproof polymeric matrices.

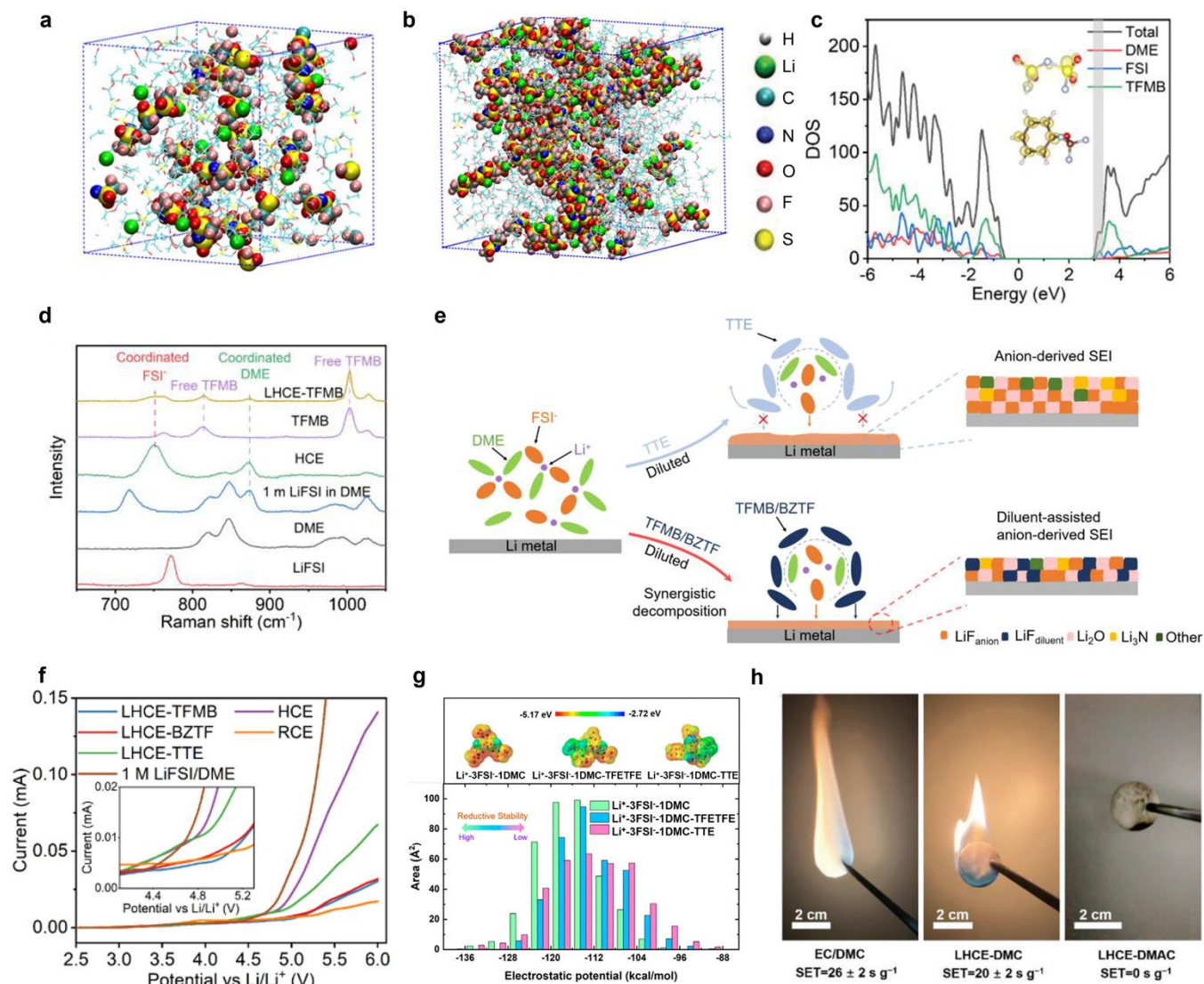
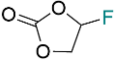

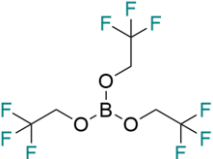
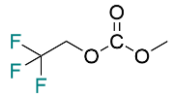
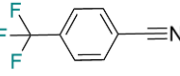
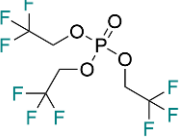
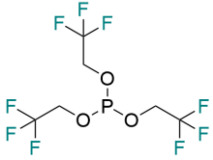


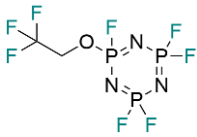
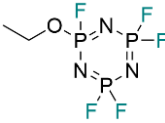
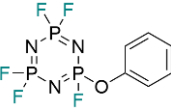
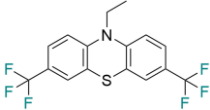
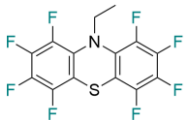
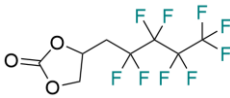
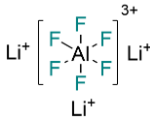

Figure 10. Functions fluorinated co-solvents of LHCEs. MD simulation results of (a) dilute electrolyte and (b) LHCE. Reproduced with permission from ref ¹⁵⁸. Copyright 2021 Wiley-VCH. (c) DOS obtained in quantum mechanical DFT-ab initio molecular dynamics (AIMD) simulations of LHCE with TFMB. Reproduced with permission from ref ¹⁶⁰. Copyright 2022 American Chemical Society. (d) Raman spectra of various solvents, diluents, and electrolytes. (e) Schematic diagram of the electrolyte structure and the correspondingly formed SEI in different LHCEs. (f) Oxidation stability of various electrolytes in Li||Al half-cells characterized by LSV at a scan rate of 0.5 mV s⁻¹ from 2.5 to 6.0 V. Reproduced with permission from ref ¹⁵⁸. Copyright 2022 American Chemical Society. (g) Electrostatic potential mapping of Li⁺ solvation structures and the surface area in each ESP range on the van der Waals (vdW) surface of the FSI⁻ anion part. Reproduced with permission from ref ¹⁶¹. Copyright 2022 American Chemical Society. (h) Flame-retarding testing of EC/DMC, LHCE-DMC, and LHCE-dimethylacetamide (DMAC). Reproduced with permission from ref ¹⁶⁵. Copyright 2022 Wiley-VCH.

2.2.3. Fluorinated Additives. Electrolyte additives are usually defined as the functional compounds added into the bulk electrolyte in a low amount (0.1–5%, either by weight or volume), by which electrolyte can be regulated economically and efficiently.¹³⁰ Compared to their non-fluorinated counterparts, fluorinated additives exhibit decreased cathodic stability, increased anodic stability, reduced flammability, *etc.*, which endow fluorinated additives with tremendous application potential in i) SEI/CEI formation, ii) flame-retardancy, iii) overcharge protection, iv) Li salt stability regulation, v) electrolyte wettability adjustment, and vi) electrolyte conductivity improvement.¹⁶⁷ **Table 2** summarizes the components and

functions of different fluorinated additives used in Li-based batteries. As the most widely reported organic additive, FEC is believed to be capable of improving the interphasial stability of anode by the formation of LiF-rich SEI layers. The substitution of a hydrogen atom in EC by a fluorine atom sharply reduces the LUMO energy level from -0.38 eV to -0.87 eV, which makes it easier to be reduced on the anode side and form SEI.¹⁶⁸ The C-F bond in FEC breaks first during the reduction process, eventually leading to the formation of a stable, compact SEI rich in LiF and poly(vinyl carbonate) (poly(VC)).¹⁶⁸ The combination of LiF and poly(VC) remarkably inhibits continuous electrolyte decomposition and facilitates uniform Li deposition, which even exhibits better passivation effect than the VC-containing electrolyte.¹⁶⁹ Apart from FEC, Archer and coworkers demonstrated that the direct use of 0.5 wt.% LiF to a conventional electrolyte could enable high surface stability and fast surface diffusion of Li ions over the layer rich in LiF crystals,¹⁷⁰ further confirming the vital role of LiF in stabilizing the SEI. Yin and coworkers adopted a fluoride boron-based anion receptor, tris (2,2,2-trifluoroethyl) borate (TTFEB), as a bifunctional electrolyte additive to improve the performance of LMBs.¹⁷¹ With 2 wt.% TTFEB, uniform Li deposition without uncontrollable Li dendrites can be realized due to the LiF-rich SEI layer. Moreover, the electron-deficient boron-center atoms acted as anion receptors to tether the PF_6^- anions in the electrolyte, causing the increased Li ion transference number.

Table 2 Fluorinated additives for Li-based batteries.

Additive	Structural formula	Original electrolyte component	Main function	Ref
5 wt.% FEC		1 M LiPF_6 -EC/ethyl methyl carbonate (EMC) (1:1 by vol.)	SEI formation	168
0.5 wt.% LiF		1 M LiPF_6 -EC/EMC	SEI formation	170
2 wt.% Tris (2,2,2-trifluoroethyl) borate		1 M LiPF_6 -EC/DMC (1:2 by vol.)	SEI formation	171
5 wt.% methyl (2,2,2-trifluoroethyl) carbonate		1 M LiPF_6 -EC/EMC (1:1 by vol.)	CEI formation	172
0.5 wt.% 4-(trifluoromethyl) benzonitrile		1 M LiPF_6 -EC/EMC/DMC (1:1:1 by vol.)	CEI formation	173
5 wt.% tris(trifluoroethyl)phosphate		1 M LiPF_6 -EC/EMC (3:7 by vol.)	Thermal stability; Stabilize LiPF_6	174
0.1-1.0 wt.% Tris(2,2,2-trifluoroethyl) phosphite		1.2 M LiPF_6 -C/EC/EMC (3:3:4 by wt.)	Thermal stability; Stabilize LiPF_6	175

5 wt.% (trifluoroethoxy)pentafluorocyclotriphosphazene-hazene		1 M LiPF ₆ -EC/DMC (3:7 by vol.)	Flame retardancy; CEI formation	176
5 wt.% (ethoxy)pentafluorocyclotriphosphazene		1 M LiPF ₆ -EC/EMC/DMC (1:1:1 by vol.)	Flame retardancy; CEI formation	177
2 vol.% phenoxy pentafluorocyclotriphosphazene		1 M LiPF ₆ -EC/DMC (1:1 by vol.)	Flame retardancy; CEI formation	178
3mM N-ethyl-3,7-bis(trifluoromethyl)phenothiazine		1.2 M LiPF ₆ -EC/EMC (3:7 by wt.)	Overcharge protection	179
0.08 M N-ethyl-1,2,3,4,6,7,8,9-octafluorophenothiazine		1.2 M LiPF ₆ -EC/EMC (3:7 by wt.)	Overcharge protection	180
2 wt.% (4-(2,2,3,3,4,4,5,5,5-nonafluoropentyl)-1,3-dioxolan-2-one		1 M LiPF ₆ -EC/EMC (3:7 by vol.)	Overcharge protection	181
0.1 M Li ₃ AlF ₆		1 M LiPF ₆ -EC/DMC (1:1 by vol.)	Suppress dendrite growth	182
0.01 M BF ₃		1 M LiPF ₆ -EC/DMC (1:1 by vol.)	Enhance the rate capability	183

In addition to the Li anode, the stability of the cathode is also crucial for the development of high-energy-density Li-based batteries. However, the CEI chemistry is even more complex, and the electrochemical performance of the cathode has been plagued by some challenges, including severe oxidative decomposition of electrolyte, gas evolution, transition metal dissolution, cracking of primary/secondary particles, *etc.*, especially for layered transition metal oxide cathode under high cut-off voltage.¹⁸⁴ The design of novel fluorinated additives such as fluorocarbonates, fluoronitriles and fluoroborates can improve the oxidation stability after fluorination due to the ability to *in situ* form F-containing CEI layer, which offers a promising solution for the aforementioned challenges.¹⁸⁵ Song and coworkers reported a fluorinated linear carbonate, methyl (2,2,2-trifluoroethyl) carbonate (FEMC), as a new electrolyte additive to achieve the performance improvement of commercial carbonate electrolyte at a 4.6 V cut-off voltage, far beyond the oxidation limit (4.3 V vs. Li/Li⁺) of conventional carbonate electrolyte.¹⁷² FEMC played a crucial role in generating a passivating layer rich in metal fluorides and C-F-containing species, which effectively delayed the cathode degradation and capacity fade.

The practical application of batteries may encounter different abuse conditions such as thermal abuse, electronic abuse, and mechanical abuse, which trigger a series of exothermic reactions and thermal runaway of batteries.¹⁸⁶ Generally, fluorinated phosphates and fluorinated phosphites such as tris(trifluoroethyl)phosphate (TFP),¹⁷⁴ and tris(2,2,2-trifluoroethyl) phosphite (TTFP),¹⁷⁵ exhibit superior flame retardance over non-fluorinated counterparts. When heated, F· radicals can scavenge the hydrogen radicals and quench the free-radical reaction and flame propagation.¹⁸⁷ The addition of fluorinated phosphates or fluorinated phosphites in the organic electrolyte can remarkably promote the thermal stability and suppress the thermal decomposition of LiPF₆.¹⁸⁸ However, to achieve nonflammable electrolyte formulation, the amount of fluorinated phosphates or fluorinated phosphites usually require to be greater than 5%.¹³⁰ Phosphazene derivatives rich in F, N, P elements are considered as more outstanding flame-retardant additives than phosphates and phosphites. Feng and coworkers synthesized a novel (trifluoroethoxy)pentafluorocyclotriphosphazene (TFPN) and deployed a flame test, which revealed that only 5 wt% TFPN addition can enable electrolyte nonflammability.¹⁷⁶ Moreover, the preferential oxidative decomposition of fluorinated phosphazene derivatives also produced a multiphase CEI layer consisting of linear/multi-ring polymers, Li₃N, LiF, *etc.*, which suppressed the decomposition of electrolyte and achieved high reversible capacity and better capacity retention.^{177, 178} As a typical electronic abuse, overcharge can cause premature electrode and electrolyte failure and catastrophic safety issues. Overcharge protection additives with an oxidation potential slightly higher than the de-lithiated potential (*v.s.* Li/Li⁺) can exert preferential redox reaction, resulting in circuit break or micro-short-circuit inside the batteries.^{189, 190} Electron-withdrawing substituent with F or CF₃ groups provides a promising method to increase the oxidation potential of overcharge protection additives for use as redox shuttles in high-voltage Li-based batteries. Odom and coworkers synthesized a series of F-substituted phenothiazine derivatives such as *N*-ethyl-3,7-bis(trifluoromethyl)phenothiazine (BCF3EPT) for LiFePO₄ cathode,¹⁷⁹ and *N*-ethyl-1,2,3,4,6,7,8,9-octafluorophenothiazine (OFEPT) for high-voltage LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ cathode,¹⁸⁰ which acted as reversible redox shuttles to protect batteries from overcharge. All in all, although numerous fluorinated additives have been explored, the physicochemical properties of fluorinated additives do not show a simple monotonous correlation with the content of fluorine substitution.¹⁹¹ Moreover, the decisive influence of fluoride substitution position on the performance of additives still needs further investigation.

2.2.4. Fluorinated Solid/Quasi-Solid-State Electrolytes. Exploration of highly affordable batteries with enhanced safety is crucial for achieving electric devices with energy densities of 400 Wh kg⁻¹. To address this need, the development of all-solid-state batteries has emerged as a promising pathway. Traditionally, liquid electrolytes select organic solvents with strong polarity, creating a high dielectric constant environment conducive to Li ion dissociation.¹⁹² This strategy also applies to the selection of all-solid polymer electrolytes. The electrostatic force between ions in SPEs is significantly influenced by the polarity of the polymer. Since

the report of ion conduction in poly(ethylene oxide) (PEO) in 1975, it has been considered as an intriguing polymeric matrix for electrolytes due to the excellent chemical and electrochemical stabilities.^{193, 194} However, the high crystallinity of PEO at room temperature results in low ionic conductivity (10^{-6} – 10^{-8} S cm⁻¹); meanwhile, the narrow ESW of PEO-based electrolytes also hinders their widespread application. Efforts to enhance PEO-based solid electrolytes are underway. As an example shown in **Figure 11a**, Hu *et al.* proposed a top-down design concept through atom transfer radical polymerization.¹⁹⁵ Through an orthogonal test method, the optimal composition of a F-rich macromolecule-containing all-solid-state polymer electrolyte (FMC-ASPE) was determined. This new PEO electrolyte exhibited significantly improved high-voltage stability and transference number ($t_{\text{Li}^+} = 0.88$) to suppress the side reaction at the cathode side and dendrite growth at the Li anode side, respectively. Additionally, the as-prepared FMC-ASPE showed improved physical and electrochemical properties, including higher ionic conductivity, higher toughness (2.7 times higher than PEO-ASPE), and higher thermal stability. Sun *et al.* synthesized a fluorine-containing ABA triblock copolymer electrolytes (FBCPEs) (perfluoroalkyl pendant in the A segment and PEO in the B segment) with a small number of -CF₂ repeating units (**Figure 11b**).¹⁹⁶ The addition of -CF₂ decreased the HOMO energy level of the whole electrolyte. Thus the antioxidant capacity of FBCPEs was improved, resulting in a wider ESW of 4.9 V. Jia *et al.* proposed a fluorinated bifunctional solid poly electrolyte, as shown in **Figure 11c**, in which fluorinated chains were covalently bonded to polyether-based fragments through the controlled radical polymerization.¹⁹⁷ Compared with conventional nonfluorinated polyether-derived solid poly electrolytes, FB-SPEs were able to provide an electrochemical window of 5 V. In addition to PEO, fluorination plays an essential role in other all-solid-state polymer electrolytes as well. Sun *et al.* selected poly-oxalic (POE) acid as the polymer matrix and found that the HOMO electrons of the POE were located at the terminal unit.¹⁹⁸ When trifluoroacetic acid was applied as the terminal unit (POE-F), the HOMO electrons were transferred to the middle oxalic acid unit, which improved the antioxidant capacity (**Figure 11d**). Furthermore, the interfacial compatibility between Li metal and POE-F was also improved by generating a LiF-based SEI, and the stability of Li||NMC811 full cells was significantly improved, which kept cycling stably over 200 cycles at 1 C.

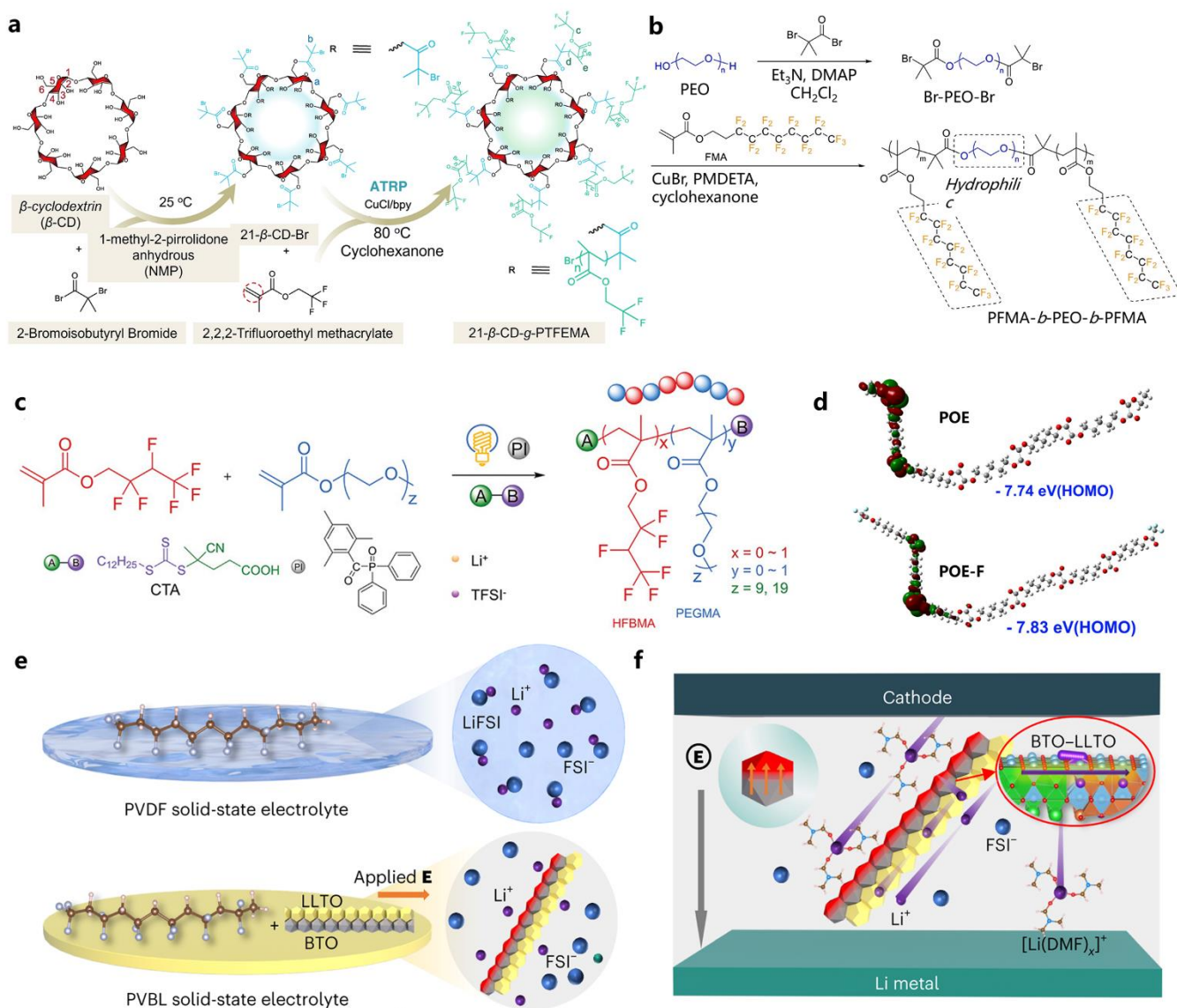


Figure 11. Fluorinated solid-state/quasi-solid-state polymer electrolytes. (a) Detailed synthetic scheme of 21-arm fluoropolymers. Reproduced with permission from ref ¹⁹⁵. Copyright 2022 Springer Nature. (b) Synthesis paths of FBCPs. Reproduced with permission from ref ¹⁹⁶. Copyright 2021, Elsevier. (c) Schematic of synthesizing FB-SPE by visible light driven photo-controlled radical polymerization (photo-CRP). Reproduced with permission from ref ¹⁹⁷. Copyright 2021 Wiley-VCH. (d) The simulated HOMO energy level of POE (upper panel) and POE-F (lower panel). Reproduced with permission from ref ¹⁹⁸. Copyright 2021 Wiley-VCH. Illustration of (e) the Li salt state in the PVDF and PVBL electrolytes and (f) the Li salt dissociation and Li $^+$ transport by the coupled BTO-LLTO in the PVBL electrolyte. Reproduced with permission from ref ¹⁹⁹. Copyright 2023 Springer Nature.

Apart from all-solid-state polymer electrolytes, quasi-solid-state gel polymer electrolytes (GPEs) can also be optimized by fluorination. One of the extensively studied materials for quasi-solid-state polymer electrolytes is PVDF, firstly investigated in the 1980s.²⁰⁰ In 1996, Warren *et al.* assembled the first LIB based on PVDF-HFP-based GPE. The copolymer exhibited advantages of low degree of crystallinity due to the addition of hexafluoropropylene (HFP), high mechanical flexibility and good compatibility with electrodes.^{49, 201} Afterwards, the number of studies on PVDF-based electrolytes gradually increased, with GPEs being the main focus. He *et al.* developed a highly conductive and dielectric GPE by compositing PVDF with coupled BaTiO $_3$

(BTO) and $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_{3-x}$ (LLTO) (named as PVBL) nanowires, as shown in **Figure 11e,f**.¹⁹⁹ The PVBL effectively restrained the formation of the space charge layer with PVDF, and the coupling effects contributed to an exceptionally high ionic conductivity ($8.2 \times 10^{-4} \text{ S cm}^{-1}$) and Li^+ transference number (0.57) of the PVBL at 25 °C. The PVBL also homogenized the interfacial electric field with electrodes. The $\text{Li|PVBL|}(\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2)$ NCM811 solid-state cells stably cycled 1500 times at the current density of 180 mA g^{-1} , and the pouch cells also exhibited excellent electrochemical performance and good safety. Nevertheless, various tough challenges need to be resolved before the practical application for PVDF-based electrolytes, including i) the in-depth understanding of interphase degradation mechanisms is still insufficient; ii) achieving considerable ionic conductivity in solvent-less conditions is of significant importance; iii) the rate performance should be promoted under high current density; iv) the solid interface still has natural deficiency compared with liquid electrolytes; v) to further improve the energy density, the thickness of the polymer electrolyte needs to be thinner up to 10–20 μm ; vi) the polymerized homogeneity of PVDF-based electrolytes in industrial conditions is insufficient, which will lead to uneven Li transportation. Understanding above specific challenges faced by PVDF-based electrolytes will contribute to the development of next-generation all-solid-state batteries.

For inorganic solid-state electrolytes, although fluorination strategies have been successfully applied on oxide, sulfide, and polyanion solid electrolyte systems, Li-fluoride solid electrolytes have yet to be reported.²⁰² To investigate the structure and corresponding synthesis strategy, Li *et al.* proposed a novel Li-rich fluoride electrolyte, Li_3GaF_6 , with a high ionic conductivity close to $10^{-4} \text{ S cm}^{-1}$ at room temperature (**Figure 12a**).²⁰³ The synergic effect of open bulk transport and compact interphase transport in Li_3GaF_6 endowed LiFePO_4 -based solid-state LMBs with an improved cycling performance for at least 150 cycles at 1 C. The crystal structure of Li_3GaF_6 derivative from cryolite phase is shown in **Figure 12b**. The characteristic building units are GaF_6 octahedra, and the Li atoms are octahedrally, pentahedrally or tetrahedrally coordinated by F. To understand the phase stability relative to their corresponding separated phases, including elemental, binary, and ternary ones, Lin *et al.* used the grand canonical linear programming method (GCLP) to explore the phase diagram of Li-M-F compounds (**Figure 12c**).²⁰⁴ The favorable combination was the decomposition of ternary Li_xMF_6 into binary LiF and MF_3 or MF_4 , with the order of decomposition energy ($\Delta E = [E(\text{phase equilibrium}) - E(\text{Li}_x\text{MF}_6)] N_{\text{atoms}}^{-1}$): Li_3GaF_6 (52 meV atom^{-1}) $>$ Li_3AlF_6 (38 meV atom^{-1}) $>$ Li_2ZrF_6 (13 meV atom^{-1}) $>$ Li_3ScF_6 (1 meV atom^{-1}). **Figure 12d** shows the sequence of fluoride materials determined by their ESW: Li_3ScF_6 (5.78 V) $>$ Li_3AlF_6 (5.49 V) $>$ Li_2ZrF_6 (5.34 V) $>$ Li_3GaF_6 (4.37 V). The fluoride materials exhibit a wider ESW compared to that of the sulfides. The Li_3AlF_6 exhibits a cathodic (anodic) limit of 0.56 V (6.0 V) versus bulk Li, while Li_3PS_4 operates within a narrow window of 1.6–3.0 V. The electronically insulating and ionically conducting phase LiF is formed at low voltage, which may potentially serve as a passivating interphase that can act as a barrier against further solid electrolyte decomposition.

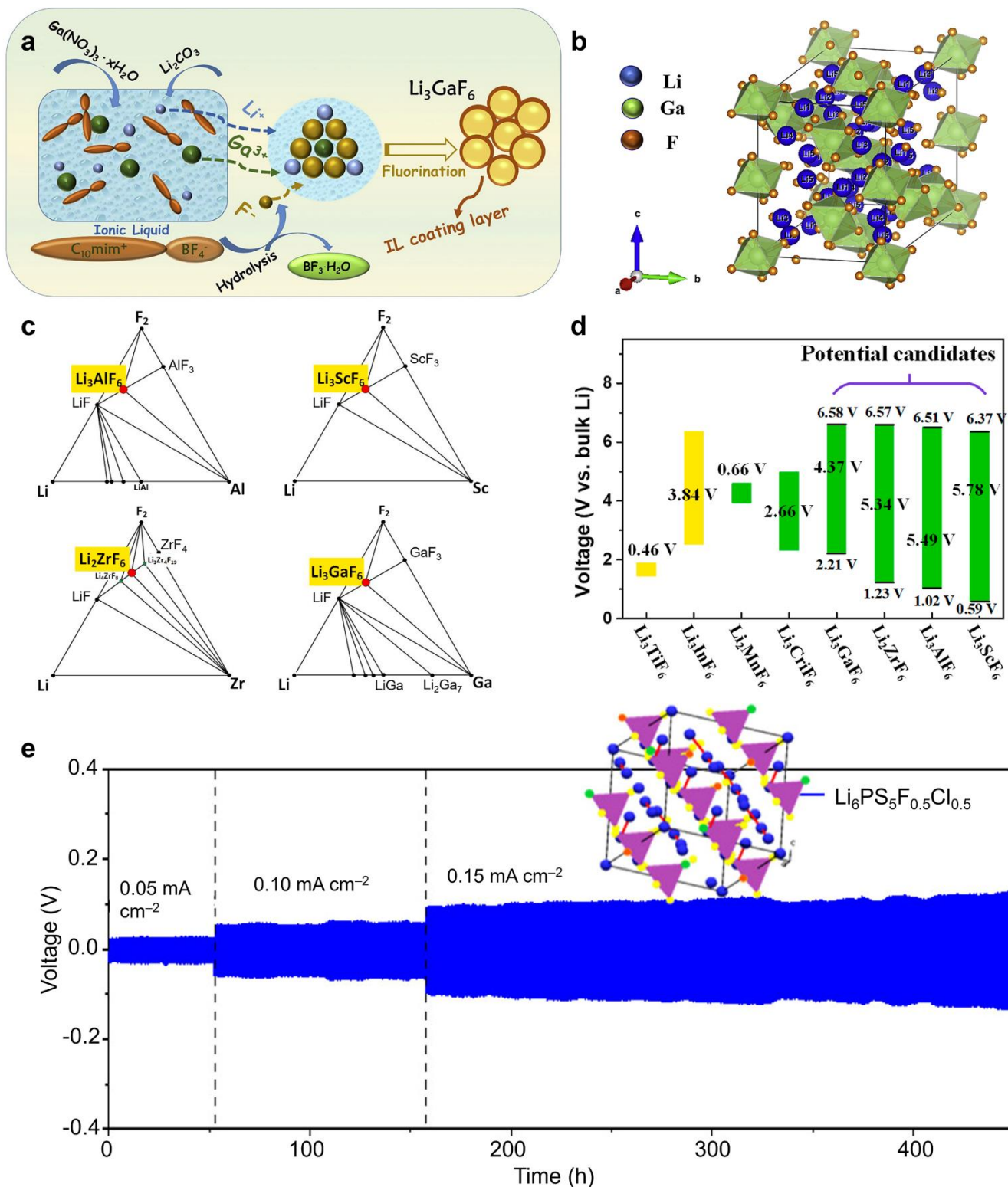


Figure 12. Fluorinated inorganic solid electrolyte. (a) Schematic synthesis of Li_3GaF_6 . (b) Crystal structures of $\beta\text{-Li}_3\text{GaF}_6$ viewed along [111]. Reproduced with permission from ref ²⁰³. Copyright 2022 Springer Nature. (c) Li-M-F ternary phase diagram assessing the computed stability of Li-M-F compounds. Black solid circles indicate stable phases, while red solid circles show the targeted fluoride materials. (d) Electrochemical stability ranges of Li_xMF_6 fluoride electrolytes. The yellow region reflects the possible extension of the voltage window over which decomposition occurs but without any metallic products. Reproduced with permission from ref ²⁰⁴. Copyright 2021 Elsevier. (e) The crystal structure of $\text{Li}_6\text{PS}_5\text{F}_{0.5}\text{Cl}_{0.5}$ and the voltage profile of $\text{Li}||\text{Li}$ symmetric cell cycling with $\text{Li}_6\text{PS}_5\text{F}_{0.5}\text{Cl}_{0.5}$ under the current density of 0.05 mA cm^{-2} , 0.10 mA cm^{-2} and 0.15 mA cm^{-2} . Reproduced with permission from ref ²⁰⁵. Copyright 2022 American Chemical Society.

The Li||NMC811 cells matched with Li₆PS₅Cl (LPSCl) electrolyte suffer from a fast capacity decay, because the sulfide solid electrolyte is not stable to both the Li anode and the NMC811 cathode.^{206, 207} To solve this problem, Wang *et al.* added a small amount (0.32 wt.%) of CuF₂-LiNO₃ (CL) into LPSCl electrolyte to *in situ* form a mixed-conductive-lithiophobic and self-healing LiF-Li₃N-Cu SEI. The compatibility of LPSCl-CL electrolyte to single-crystalline NMC811 was further enhanced by adding a small amount (0.02 wt.%) of AlF₃.²⁰⁸ Doping F into LPSCl electrolyte largely improved the oxidation stability; thus the Li||NCM811 full cell achieved a high capacity retention of 69.4% after 100 cycles at 2.55 mA cm⁻²/2.55 mAh cm⁻². In addition, Wang and co-workers reported F-doped Li_{5+y}PS₅F_y argyrodites with a tunable doping content and dual dopants (F⁻/Cl⁻ and F⁻/Br⁻) that were synthesized through a solvent-based approach, as shown in **Figure 12e**.²⁰⁵ Among all compositions, Li₆PS₅F_{0.5}Cl_{0.5} exhibited the best cycling performance in Li symmetric cells, owing to the enhanced interfacial stability against Li metal, which can be attributed to the formation of a stable SEI containing Li₃P, LiCl and LiF. Furthermore, Li||LiFePO₄ (LFP) cells using Li₆PS₅F_{0.5}Cl_{0.5} showed enhanced cycling performance with a specific discharge specific capacity above 105 mAh g⁻¹ after 50 cycles. However, F doping also significantly reduced the ionic conductivity of LPSCl due to the high bonding between F and Li.²⁰⁹ The excessive LiF precursor filled in the boundary/pore of the solid-state electrolytes after fluorine was incorporated into the LPSCl structure. This reduced the electronic conductivity while enhancing the rigidity to suppress the penetration of Li dendrites.

In conclusion, the electrolytes for high-performance Li-based batteries can be tailored by combining the benefits of different partially fluorinated/per-fluorinated electrolytes. Selective fluorination of the anions of Li salts will decrease their interactions with Li⁺ cations, thereby increasing the dissociation of the salts in the electrolyte solution and lifting the ionic conductivity. Fluorinated solvents can also inhibit the progress of combustion, thus improving the safety of the electrolytes. It is important to achieve a balance between Li salt solubility and interfacial compatibility. Fluorinated additives containing well-tailored functional groups can transform into uniform and thickness-controllable SEI/CEI films, which remains a hot field for the future research. For the polymer all-solid-state electrolytes, the graft of F-containing groups/chains on the polymer matrix can widen the electrochemical window and/or facilitate ion conduction; furthermore, F-containing polymers, such as PVDF and PVDF-HFP, have played a significant role in the quasi-solid-state gel polymer electrolytes. The exploration of fluorine chemistry in advanced solid-state battery systems aiming for enhanced performance is also in progress.

2.3. Other Fluorinated Battery Components

2.3.1. Fluorinated Separators. As an essential component in batteries, the separator not only offers transport paths for Li^+ migration between two electrodes, but also serves as a barrier isolating the cathode from the anode.²¹⁰ Despite their critical function, current commercial separators (*e.g.*, polypropylene (PP), polyethylene (PE) and their multilayer composites) suffer from insufficient mechanical strength, inferior liquid electrolyte affinity, low thermal stability, and high flammability. The separator failure/collapse can lead to internal short circuits, potentially triggering thermal runaway, energy release, explosion and other serious security risks in batteries.²¹¹ Over the past few decades, intensive efforts have been dedicated to overcoming these limitations, among which polymeric separators,²¹²⁻²²³ blends and composites,²²⁴⁻²²⁶ surface coating,²²⁷⁻²²⁹ surface grafting²³⁰⁻²³³ were mostly focused. In particular, PVDF and its copolymers (*e.g.*, PVDF-HFP, polyvinylidene-co-chlorotrifluoroethylene (PVDF-CTFE), polyvinylidene fluoride-trifluoroethylene (PVDF-TrFE)) have garnered great interest due to their high dielectric constant, strong polarity, excellent anodic stability, which contribute to their good affinity toward polar electrolytes and their ability to assist in the dissociation of Li salts. For a detailed and specific summary of separators based on PVDF and copolymers, readers are encouraged to consult the excellent review articles.^{234, 235} It should be noted that the practical applications of PVDF separators are hindered by the low mechanical strength (< 10 MPa) caused by their solubility in electrolytes, combined with inferior thermal stability due to their low melting point (172 °C).²²⁵ In addition, the formation of LiF and C=CF bond in the crystallized PVDF, through interactions between F and Li or lithiated graphite, can resist Li^+ transport and further deteriorate the rate capability of LIBs.^{236, 237} Blending two or more polymer solutions has been considered as an effective strategy to achieve complementary properties of each component. In 2014, Liu and coworkers blended the PVDF-HFP with polyimide (PI) by cross-electrospinning, arranging the two polymer solutions alternately to construct a PVDF-HFP/PI composite membrane. This composite separator, combining advantages of both polymers, demonstrated increased porosity, higher thermal dimensional stability, improved electrochemical stability and higher ionic conductivity compared to the commercial Celgard 2400 separator.²³⁸ Similarly, the poly(*m*-phenylene isophthalamide) (PMIA), known for its high mechanical strength and high temperature tolerance, was blended with PVDF to construct a sandwich-structured PVdF/PMIA/PVdF composite membrane. This membrane displayed high ionic conductivity, reinforced tensile strength (13.96 MPa), and excellent thermal stability as well as desirable electrochemical stability/rate performance for the assembled $\text{Li}||\text{LiCoO}_2$ battery.²²⁵ The enhancement of mechanical property and thermal stability of the PVDF-based separator was also achieved by blending with polyacrylonitrile (PAN).²³⁷ Nevertheless, blending polymer solutions can increase the fiber diameter size and influences the fiber morphology, generally leading to ununiform fiber structure. Besides, the obtained ionic conductivity of the resulting blends needs to be further improved. To address these issues and enhance

separator properties such as electrolyte uptake, thermal stability, ionic conductivity, nanoscale particles including Al_2O_3 , SiO_2 , TiO_2 , Sb_2O_3 have been successfully incorporated into the polymer matrix.^{239, 240}

A variety of modification strategies have also been employed to enhance the physiochemical and electrochemical performance of the separators, among which the surface coating/grafting method has been considered as a promising candidate to address the abovementioned drawbacks facing the common commercial separator.^{226, 234} By coating the composite material of graphite fluoride nanosheets (GFNs) and PVDF, the pristine PP separator was modified by Zhang *et al.* on a large scale. Attributed to the reaction between GFNs and Li, a concrete-like protective layer with improved mechanical properties was constructed on the Li metal anode, enabling fast Li^+ transport, resisting the Li dendrite growth and maintaining good integrity as well. In addition, owing to the lithiophilic feature of GFNs, sufficient physical contact between the Li anode and the protective layer was achieved, realizing low interphasial resistance and homogeneous Li deposition layer by layer.²⁴¹ As the most electronegative elements that have been known, F is capable of forming the strongest single covalent bond of C-F with a bond energy of 488 kJ mol^{-1} .²⁴² A F-modified (Poly-p-phenylene terephthamide) PPTA protective layer on the PP separator (F-PPTA@PP) was developed, via coating PPTA nanofibers on a commercial PP membrane and subsequent grafting F-containing groups on the separator. As shown in **Figure 13a**, an F atom was grafted on the PPTA (F-doped PPTA) via C-F bond, where the generated electronegativity around the C-F bond endowed a stronger organic affinity to promote the electrolyte wettability. This F-PPTA@PP separator exhibited high thermal stability to suppress thermal shrinkage, excellent physical strength to prevent the potential mechanical abuse, and good capability to simultaneously *in situ* constructed a LiF-rich SEI layer to promote the uniform electrodeposition of Li and eliminate Li dendrite risks (**Figure 13b**). With this separator, the assembled Li||NCM811 battery featured an initial capacity of 194.1 mAh g^{-1} at 0.5 C and a stable cycling performance for over 1000 cycles. Under various extreme conditions, such as wide temperature range within -10 to 100 °C, ultrafast charging/discharging rate of 30 C, and lean electrolyte/high mass loading, the battery exhibited promising electrochemical performance.²⁴³ Very recently, a novel fluorine-functionalized PVDF/fluorinated-PI (FPI) composite nanofibrous separator was developed for wide-temperature LMBs.²⁴⁴ On one side, the abundant polar $-\text{CF}_3$ groups in the F-PI composite provided an electronegative environment for the fast Li^+ transfer. Besides, the $-\text{CF}_3$ group contributed to enhanced thermal stability and fire retardancy for enabling the operation of LMBs in a wide temperature range. On the other side, the incorporation of PVDF enhanced the mechanical properties by increasing physical contacts among the F-PI nanofibers, and facilitated the uniform Li deposition via homogenizing the pore size as well. This F-functionalization treatment endowed the separator not only with increased affinity toward organic electrolytes and high value of ionic conductivity, but also a wider ESW (**Figure 13c-e**). Based on this separator, the Li||Li cell sustained a steady cycling of 2400 h at 1 mA cm^{-2} with the areal

capacity of 1 mAh cm^{-2} , which survived for 1000 h with a low overpotential of 15 mV under 60°C . Briefly, the fluorination method offers a promising and facial strategy for enhancing overall properties of the separator, including the electrolyte wettability, ionic conductivity, thermal stability, and electrochemical stability, thus effectively resisting safety risks and improving electrochemical performance of LMBs.

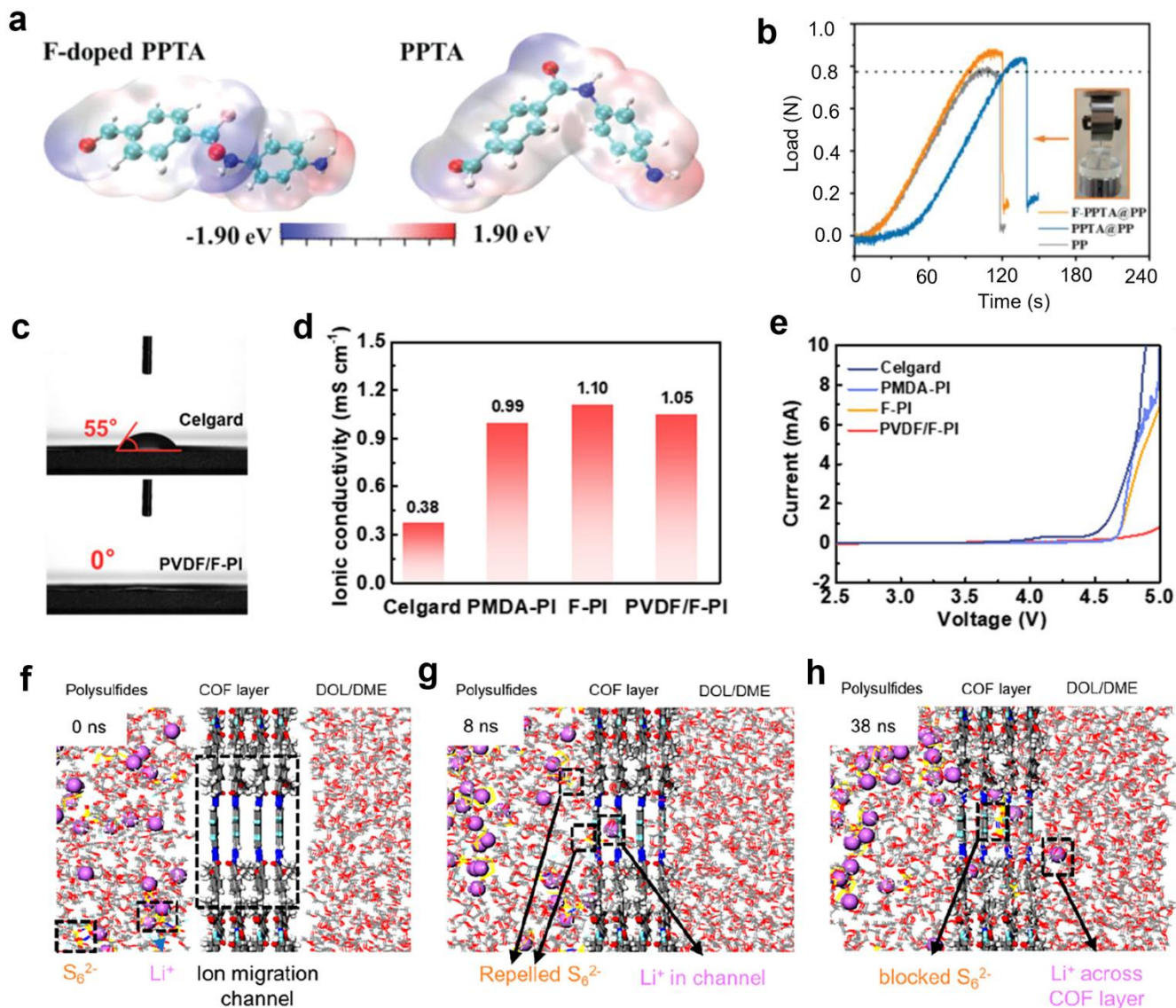


Figure 13. The functions of fluorinated separators in Li-based batteries. (a) The electrostatic potential surface for pristine PPTA and F-PPTA molecules, respectively. (b) The puncture strength curves of the PP, PPTA@PP and F-PPTA@PP separators. Reproduced with permission from ref ²⁴³. Copyright 2022 Wiley-VCH. Evaluations of (c) electrolyte contact angles, (d) the ionic conductivity and (e) LSV for the PVDF/F-PI separator and other separators. Reproduced with permission from ref ²⁴⁴. Copyright 2023 Wiley-VCH. Schematic illustration of ion transport behavior through the fluorinated COF nanofluidic nanochannels at (f) 0 ns, (g) 8 ns (f), and (h) 38 ns. MD simulation results elucidates that the fluorinated separator exhibits a higher Li^+ migration activity than anion (TFSI^- and S_6^{2-}). Reproduced with permission from ref ²⁴⁵. Copyright 2023 American Chemical Society.

As one of the most promising high-energy Li-based rechargeable battery systems, the practical Li-S battery has been restricted by the irreversible cathode consumption due to the polysulfide shuttling, as well

as notorious Li dendrite growth, inducing severe capacity fading during cycling. Introducing modification layers or interlayers on separators has been adopted as a feasible strategy for entrapping negatively charged sulfur species.^{246, 247} Particularly, to utilize the polar active site of F atoms for immobilizing polysulfides, Dominko *et al.* synthesized fluorinated reduced graphene oxide (F-rGO) for acting as a separator interlayer, which prevented the polysulfide shuttling and achieved improved cycling performance.²⁴⁸ Unfortunately, the usage of fluorine gas or XeF₂ brings safety concerns for practical applications. Via a facile, cost-effective, safe and scalable approach, fluorinated carbon was successfully constructed on a PP separator. Thanks to the strong chemical bonding ability of F groups and physical adsorption of mesoporous structure, the polysulfide shuttling was suppressed significantly. In addition, the F doping induced a pseudocapacitive effect for fast Li⁺ diffusion, affording a dense and homogeneous Li deposition during repeated cycling.²⁴⁹ However, most separator coating layers are unfavorable for the transfer/migration process of Li⁺.^{250, 251} Very recently, a fluorinated covalent organic framework (4F-COF)-based nanofluidic membrane was constructed for regulating Li-S battery performance. The fluorine functionalities endowed the 4F-COF permselective nanofluidic channels contain negatively charged sites, allowing Li⁺ cations to enter the 4F-COF layers while repelling the anion (S₆²⁻) transport (**Figure 13f-h**). With the fluorinated COF/PP separator, a highly stable Li metal was achieved with plating/stripping for 2000 h at 1 mA cm⁻². Besides, the assembled Li-S batteries demonstrated a stable cycling performance for over 1000 times with 82.3% capacity retention at 2 C, high-rate capability with 568.0 mA h g⁻¹ at 10 C, as well as areal capacity of 7.60 mA h cm⁻² at a high sulfur cathode loading (~ 9 mg cm⁻²).²⁴⁵

2.3.2. Fluorinated Binders and Current Collectors. It is commonly known that during battery cycling, the electrodes are vulnerable to mechanical stress (*i.e.*, severe volume changes for conversion-and alloy-type electrodes). Therefore, insufficient binding strength leads to severe pulverization and further capacity degradation. Thus, serving to provide the cathode and anode electrodes with both interconnected structures and mechanical strength for sufficient electron transport and ion migration upon charging/discharging, the polymeric binder is of vital significance to the battery performance.²⁵² Recently, owing to the high thermal stability, strong adhesive strength, and electrochemical/chemical inertness with a symmetrical linear F-bonded carbon skeleton, PVDF has been recognized as the earliest and most popular binder materials for commercial LIBs. However, with the increasing versatile requirements of practical battery technologies, the current polymer binders should not only act as a binding reagent but also provide different functionalities, including high ionic/electric conductivity, stable electrode|electrolyte interphase, excellent polysulfide anchoring capability, improved mechanical strength to buffer the volume change. These features cannot be achieved by the current PVDF binder. Especially at large volume expansion, conventional PVDF binder will lose the adhesion as a result of the slippage of the linear chain in the

electrode.²⁵³ More specific reviews focusing on different binders and their corresponding developments have been conducted earlier.²⁵⁴⁻²⁵⁶ In this section, we will mainly introduce the mechanisms and properties effects of fluorinated binders on electrodes and further on the battery performance. The design and application of fluorinated binders in Li-based batteries will provide opportunities to develop advanced binders.

When it comes to layered oxide cathode materials represented by LiCoO_2 , PVDF has been the most widely used binder in industry. It was found that the crystallinity of PVDF was reduced via embedding maleic anhydride-grated-PVDF (MA-g-PVDF) into PVDF, which is favorable for improving electrolyte uptake. As a result, the rate capability and cycle performance of the LiCoO_2 cathode were enhanced.²⁵⁷ However, it was pointed out that the reduced crystallinity of PVDF with lower molecular weight led to the decreased adhesion strength.²⁵⁸ Therefore, the crystallinity degree should be carefully optimized and balanced to fulfill the cathode performance. Unfortunately, it was demonstrated that the PVDF binder can be changed when charging the cathodes to a high voltage above 4.3 V. Due to the weak cohesive force, PVDF is unable to generate a robust layer on the cathode surface and easily causes de-attachment between cathodes and current collectors, which finally leads to continuous electrolyte decomposition and rapid capacity decay for high-voltage cathodes.²⁵⁹⁻²⁶¹ Therefore, it is necessary to explore electrochemically inactive binders beyond PVDF. With the obvious advantage of strong adhesion to the electrodes and good thermal stability, PI has been proved to improve battery performance. By introducing six $-\text{CF}_3$ functionalities per unit in the PI backbone (**Figure 14a**), the fluorinated PI (FPI) showed faster ion transfer, greater resistance to electrochemical oxidation as well as higher thermal stability. The FPI fulfilled excellent binding ability to mitigate the degradation issue of the Li-rich cathode at 4.7 V, and meanwhile, functioning as a surface protective layer on the cathode via constructing robust thin film. The resulting cathode presented improved cycle stability in both half cells and full cells when paired with graphite anodes.²⁶² Moreover, employing ionic conductive polymers such as poly(ionic liquid)s (PILs) or single-ion conducting polymers (*e.g.*, PEO) as binders has been considered as an effective strategy to improve the ionic conductivity and Li^+ diffusion rate for high-performance LIBs.²⁶³⁻²⁶⁷ Typically, cationic or anionic species are bonded to polymer backbones in the PILs, contributing to the high Li^+ ionic conductivity as well as wide ESW.²⁶⁸ By incorporating the ionic conducting lithiated poly(perfluoroalkylsulfonfyl)imide (PFSILi) ionene with PVDF to serve as the binder, the LiFePO_4 cathode exhibited increased working voltage, lower electrochemical polarization and higher reversibility than that with PVDF binder, especially operated at elevated temperatures or high current rates. Besides, higher reversible capacity and energy density (1.50 and 1.66 times) of the LiFePO_4 cathode was enabled compared to the cathode with PVDF binder.²⁶⁶ Lithiated perfluorosulfonate ionomer (Li-Nafion) was reported to demonstrate similar effects as the binder for LiMn_2O_4 cathodes. The resultant Li-Nafion binder displayed an ionic conductivity of $1.4 \times 10^{-4} \text{ S cm}^{-1}$

¹, generating an ion-conducting layer on the LiMn_2O_4 cathodes, which reduced the interphase resistance for high rate cycling (5 C-20 C) and stabilized the cathode even at high temperature (60 °C).²⁶⁷ Zhao *et al.* prepared an ionic conducting binder by pairing sulfonated polyether ether ketone with pendant lithiated fluorinated sulfonic groups (SPEEK-FSA-Li), in which sulfonated aromatic poly(ether ketone) fulfilled good thermal/mechanical stability; meanwhile, the charge delocalization over the lithiated fluorinated sulfonic side chains exhibited low lithium dissociation energy for improving Li^+ conductivity. The SPEEK-FSA-Li binder contributed to a much smaller interphasial and charge transfer resistance, an enhanced discharge plateau voltage and a higher reversible capacity for the LiFePO_4 cathode, in contrast with that using PVDF binder.²⁶⁵ Recently, the pyrrolidinium type poly(diallyldimethylammonium) (PDADMA) with fluorinated anions was used as cathode binder, wherein the fluorine content (*e.g.*, FSI, TFSI, bis(perfluoroethylsulfonyl) imide (BETI) and nonafluoro-1-butanesulfonate (CFSO)) led to highly delocalized charge density for facilitating Li^+ transport. The consequent high voltage $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM 523) electrode achieved improved rate capability and stable cycling performance.²⁶⁸ Introducing ion-conducting materials into polymer binders is considered as another effective strategy to improve the overall electrochemical performance of LIBs. Copolymerizing the hydrophilic 2-(perfluorohexyl) ethyl methacrylate (PFHEMA) and hydrophobic poly(ethylene glycol) methacrylate (PEGMA), Kuo and coworkers designed Li^+ conducting water-borne fluorinated binder (**Figure 14b**). The fluorinated moiety was expected to improve the electrochemical stability and adhesive properties, while PEO segments in PEGMA achieved higher ionic conducting ability. The copolymer can self-assemble into a series of spherical nanoparticles (150–220 nm) dispersed in aqueous solution. Results showed that with an optimal ratio of 3:1 (PFHEMA:PEGMA), the LiFePO_4 cathode delivered great cyclability over 150 cycles without obvious capacity decay and nearly 100% CE.²⁶⁹

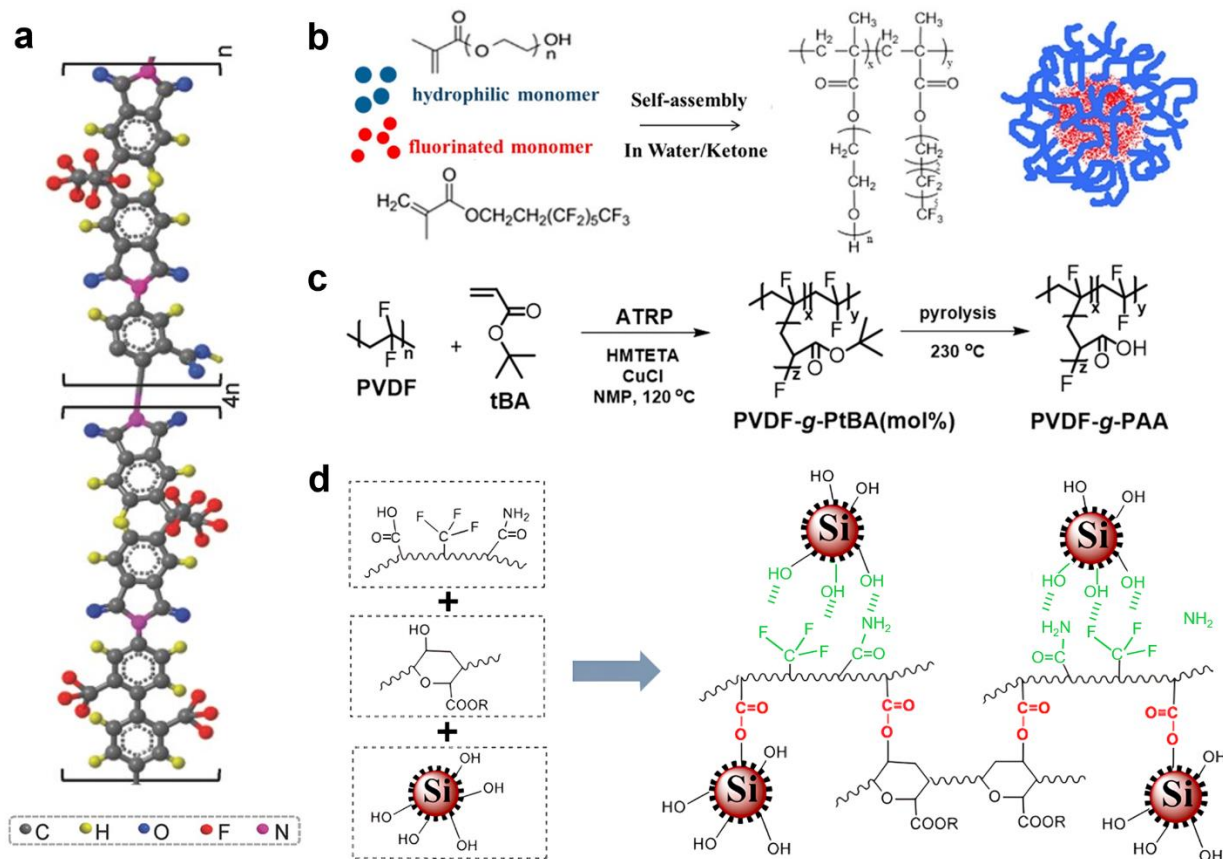


Figure 14. Developments of fluorinated binders for enhancing electrode performance. (a) The molecular structures of synthesized FPI. Reproduced with permission from ref ²⁶². Copyright 2018 Wiley-VCH. (b) The scheme of the preparation for self-assembled fluorinated copolymer. Reproduced with permission from ref ²⁶⁹. Copyright 2018 American Chemical Society. (c) The preparation routes for amphiphilic graft copolymer precursors (PVDF-g-PtBA) and pyrolytic transformation to PVDF-g-PAA. Reproduced with permission from ref ²⁷⁰. Copyright 2016 Wiley-VCH. (d) Illustration of the dual cross-linked network combining covalent bonds and hydrogen bonds among the designed fluorinated copolymer, sodium alginate, and Si surface. Reproduced with permission from ref ²⁷¹. Copyright 2019 American Chemical Society.

Relying on the weak van der Waals force to connect active materials and other components within the electrodes, conventional PVDF binder is unsuitable for alloy-type anode materials (*e.g.*, Si) with drastic volume changes during battery cycling. In general, the ideal binders for alloy-type anodes should be chemically stable at elevated temperatures, electrochemically inert to sustain a wide ESW, and mechanically tolerate to withstand extensive stresses while maintaining ionic or electronic conducting ability.^{272, 273} It has been elucidated that heating Si electrode containing 8 wt.% PVDF at 300 °C contributed to a more uniform distribution of PVDF on the surface of active materials, which largely enhanced the adhesive strength and viscoelasticity for improved cycle performance with 600 mAh g⁻¹ available capacity after 50 cycles.²⁷⁴ Nevertheless, less than 20% of the theoretical specific capacity of the Si anode was left, which is still far from the requirement of practical application. Thus, combining PVDF with other polymers can be developed to satisfy the needs of high-performance Si-based anode materials. Based on a tether model, in which the binder was filled with carbon black, Dahn and coworkers designed an elastomeric

binder of terpolymer PVDF fluoride-tetrafluoroethylene ethylene copolymer (PVDF-TFE-P) for the $\text{Si}_{0.64}\text{Sn}_{0.36}$ alloy anode.²⁷⁵ It was noted that 3-aminopropyltriethoxysilane was added as an adhesion promoter in the electrode, providing $-\text{NH}_2$ to bond with the carbon-carbon double bond in the backbone of PVDF-TFE-P. The resulting $\text{Si}_{0.64}\text{Sn}_{0.36}$ anode exhibited a stable reversible capacity of $\sim 800 \text{ mAh g}^{-1}$ with a volume change of 125%. To further improve the PVDF performance in Si-based anode materials, amphiphilic graft copolymer precursors PVDF-graft-poly(tert-butylacrylate) (PVDF-g-PtBA) have been synthesized, wherein poly(acrylic acid) (PAA) with abundant carboxylic acid ($-\text{COOH}$) groups was generated through *in situ* pyrolytic transformation of PtBA (**Figure 14c**). Taking the advantage of synergistic effects from polymeric backbones (PVDF and PAA segments), excellent mechanical properties against volumetric expansion were achieved, enabling high charge and discharge capacities of 2672 and 2958 mAh g^{-1} , respectively, along with a stable cycling performance over 50 cycles with 84% retention at 0.2 C. Moreover, this graft copolymer binder was proved to be effective in fulfilling the capability of both the $\text{LiN}_{0.5}\text{M}_{1.5}\text{O}_4$ cathode and natural graphite (NG) anode, contributing to a high energy density of 546 Wh kg^{-1} along with $\sim 70\%$ capacity retention after 50 cycles at both 0.5 C and 1 C (1 C = 145 mA h g^{-1}) for the $\text{Si/NG} \parallel \text{LiN}_{0.5}\text{M}_{1.5}\text{O}_4$ full battery.²⁷⁰ As an alternative choice, owing to the apolar structures and enriched hydrogen bonding sites, polytetrafluoroethylene (PTFE) possessing high mechanical strain and tenacity was introduced, forming a PVDF-b-PTFE copolymer binder combining the high viscosity of PVDF with high elasticity of PTFE. Besides, this binder achieved high ionic conductivity and thermal stability. As a consequence, the binder forms cobweb structures to coalesce Si particles, maintaining good electrical contact of the electrode materials during repeated cycles for superior cycle stability ($\sim 1000 \text{ mA h g}^{-1}$ capacity retained over 250 cycles).²⁷⁶

To strengthen the mechanical properties and further enhance the cycle stability of the Si-based electrodes, three-dimensional (3D) cross-linked binders with strengthened mechanical properties exhibited strong resistance to irreversible deformation of the Si-based electrodes, but they increase the stiffness of the electrode and finally deteriorated the electrochemical performance of the batteries.²⁷⁶⁻²⁸⁰ From this point, Zhang *et al.* designed a fluorinated copolymer with massive polar groups (carboxylic acid, amide, and fluorinated groups), followed by thermal polymerized with sodium alginate (SA) to construct a dual cross-linked network binder (FP2SA). It was found that esterification reactions among these functional groups formed chemical cross-linked network, and meanwhile, fluorine and nitrogen enhanced the reversible mechanical features during volume changes (**Figure 14d**). The uniqueness of this FP2SA, relying on both chemical and physical cross-linking, was able to maintain the structure integrity of Si electrodes, contributing to a high specific capacity of 1557 mAh g^{-1} after 200 cycles at 4 A g^{-1} . More importantly, FP2SA binder also significantly improved the cycling performance of the Si-C electrode and the SiO-C electrodes with specific capacities of 600 mAh g^{-1} after 200 cycles at 0.5 A g^{-1} and 310 mAh g^{-1} after 700

cycles at 1 A g^{-1} , respectively.²⁷¹ However, it was revealed that an excessive cross-linked degree and fluorine content of the fluorinated binder could reduce the capacity and cycle stability of the Si-based electrodes, indicating a moderate cross-linking degree should be considered in designing such binders. In addition, lithiated fluorine-containing ionomers have been demonstrated as effective binders to improve the Li^+ ion diffusion as well as ionic conductivity, especially cycling at high rates. Wen and coworkers developed a novel fluorine containing ionic binders (lithiated sulfonated poly(ether-ether-ketone)) with sulfonimide groups and structural flexibility, *i.e.*, SPEEK-PSA-Li. Compared with other binders, the ionic conducting SPEEK-PSI-Li binder exhibited high adhesion properties and significantly decreased over-potential during high-rate cycling. Owing to the combined features of high cohesion capability, low solubility in electrolytes, high adaptability to volume change, and high ionic conductivity, the Si anodes displayed superior electrochemical performance under high rate cycling, *i.e.*, maintained reversible capacities of 2000 mAh g^{-1} and 500 mAh g^{-1} at current densities of 400 mA g^{-1} and 2000 mA g^{-1} , respectively, after 50 cycles.²⁸¹

Serving as an indispensable component to support both electrodes and to transport electrons between electrodes and the external circuit, the current collector plays a critical role in guaranteeing the highly efficient operation of LIBs. Since the commercialization of LIBs, Al and Cu foils have been the most widely used current collectors in the cathodes and anodes, respectively.²⁸² Nevertheless, electrochemical dissolution of Al and Cu current collectors still occurs during cycling, which is induced by the electrolyte decomposition or side reactions between electrolyte components and these current collectors. As mentioned above, although the LiTFSI salt possesses advantageous properties such as high ionic conductivity, good thermal stability and chemical inertness towards active material, water contaminant, as well as other battery components, it fails to re-passivate the Al foil by forming fluorinated interphase. More specifically, the TFSI^- readily reacts with Al^{3+} , which is released from the Al_2O_3 passivation film, forming the soluble aluminum bis(trifluoromethanesulfonyl)imide ($\text{Al}(\text{TFSI})_3$) product. The $\text{Al}(\text{TFSI})_3$ then dissolves well in organic carbonate electrolytes and diffuses to the bulk electrolyte, causing severe capacity decay of Li-based batteries.²⁸³ Despite huge attentions have been paid on the electrode materials engineering to enhance battery performance, insufficient attention has been focused on this aspect, especially regarding the effects of fluorine chemistry on the current collectors. Since the review conducted by Lota *et al.* have discussed the positive influence of fluorinated species on the Al current collector on cathode performance, this section will mainly focus on the anode current collectors.²⁸³

Over the past few decades, intensive efforts have been devoted to achieving the dendrite-free plating/stripping of Li anode, including SEI re-construction,^{146, 168, 276, 284-292} uniformization of the Li-ion flux,^{293, 294} and 3D nanostructured scaffolds.²⁹⁵⁻³⁰⁰ Among the existing approaches, interphase design and construction have been considered as an effective way to overcome problems towards the anode. Especially,

the construction of halogenated interphases (*e.g.*, LiF) is expected to effectively passivate the active Li surfaces, regulate the Li⁺ migration, suppress Li dendrite nucleation/growth, and enhance the interphase mechanical stability.³⁰¹⁻³⁰³ A columnar and uniform Li anode was designed by Zhang and coworkers through a LiF-enriched Cu current collector. When directly immersing a Cu foil into an aqueous LiPF₆ solution, the *in situ* hydrolysis of LiPF₆ occurred and coated LiF particles on the Cu surface. The LiF (100) was calculated to give weaker binding energy and higher diffusion energy barrier to Li than that of Cu surface (**Figure 15a**), rendering uniform spatial distribution of Li⁺, and further contributing to the Li deposition with column structures. As a consequence, these ultrathin and columnar Li anodes exhibited highly improved cycle stability in both carbonate- and ether-based electrolytes.³⁰⁴ As discussed earlier, PVDF has been extensively used as binders, separators, or polymeric electrolytes in Li-based batteries. It is known that contrary to the nonpolar α phase PVDF with a trans-gauche-trans-gauche conformation, the β phase PVDF presents all trans conformation with F and H atoms distributed on the opposite sides of the PVDF backbone, which contributes to a high dielectric constant within 8-13. A thin ($\sim 4\ \mu\text{m}$) β -PVDF was coated on the Cu current collector, achieving a uniform plating/stripping of Li at high current densities of $5\ \text{mA cm}^{-2}$, a high plating capacity of up to $4\ \text{mAh cm}^{-2}$, along with excellent cyclability. It was inferred that the strong interactions between Li⁺ and polar C-F groups of β -PVDF could redistribute the Li⁺ flux, while the reaction of the PVDF surface and the fresh Li metal might form a stable and protective SEI layer. Besides, as illustrated in **Figure 15b**, the F alignment could not only promote the interaction between C-F and Li for layer-by-layer Li deposition, but also offered preferential diffusion paths for Li⁺ hopping across the coating layer. This work highlights that constructing electronegative F-rich interphase is favorable for the layer-by-layer Li deposition.³⁰⁵ Another effective approach to enriching LiF on Cu substrate is employing fluorinated carbon materials such as fluorinated porous carbon materials and fluorinated carbon nanotubes.^{306, 307} For instance, Zhi *et al.* designed a 3D-fluorinated porous carbon as the multifunctional host, which mitigated dendrite growth and retained for over 300 cycles with an average CE of 99% at $0.5\ \text{mA cm}^{-2}$ (cycling capacity of $1\ \text{mAh cm}^{-2}$). Nevertheless, this host matrix sustained only 70 cycles with fluctuated CE when increasing the current density and cycling capacity to $2\ \text{mA cm}^{-2}$ and $2\ \text{mAh cm}^{-2}$, respectively.³⁰⁸ Based on this work, a novel LiF-rich dual-functional coating layer was designed on Cu surface by Su and coworkers, using fluorinated electrochemically exfoliated graphene (F-ECG) as a modifier. Thanks to the strong interlayer adhesion, the F-ECG layer could prevent volume expansion during plating/stripping cycles. In addition, LiF-enriched SEI film was successfully generated due to the reaction between Li and CF. This suppressed side reactions and facilitated Li⁺ transport across the coating layer for a dendrite-free Li anode with long-term stability (**Figure 15c**).³⁰⁹ In another report, a self-assembled monolayer (EAM) of 1,3-benzenedisulfonyl fluoride was introduced on the Cu substrate, where the benzenesulfinate created lithiophilic sites, and meanwhile, fluoride generated a LiF nuclei *in situ* via self-

Apart from introducing F-rich coating/modification layer on the Cu current collector, the Li halides (*e.g.*, LiF) can also be formed via the reaction between metal halides and highly active Li, achieving highly enhanced interphasial stability.³¹² Through a one-step fluorination treatment, a hybrid NiF_x@NF current collector consisting of vertical lithiophilic NiF_x nanosheets and Ni foam was developed by Huang *et al.* The NiF_x decreased the Li nucleation barrier and served as even nucleation sites for Li deposition. Besides, a LiF-enriched SEI derived from the reaction between NiF_x and Li during the initial Li plating was constructed, ensuring smooth Li deposition (**Figure 15d**). Benefiting from this 3D NiF_x@NF current collector, outstanding Li stripping/plating with a CE of ~ 98% over 450 cycles was obtained (at 1 mA cm⁻² and 1 mAh cm⁻²). The Li@NiF_x@NF symmetric cell demonstrated a long cycle life over 1300 h with a low overpotential of ~ 20 mV (1 mA cm⁻², 1 mAh cm⁻²). Remarkably, the as-prepared Li@NiF_x@NF||LFP full cell exhibited reasonable cycle performance and rate capability.³¹¹ Recently, using a facile and safe NF₃ plasma fluoridized strategy, the NiF₂ layer was successfully coated on Ni foams (NFF). Following the same way, the Li⁺ flux preferentially deposited on the NiF₂ sites, which was evenly distributed around the Ni surface. Also, the LiF-rich SEI layer from the NiF₂ reaction toward Li greatly enhanced the interphasial stability. As a result, the NFF@Li anode sustained a long durability over 1600 cycles at 1 mA cm⁻² and over 2000 cycles at 2 mA cm⁻². Moreover, the NFF@Li||LFP full battery delivered a high-capacity retention of 93% over 250 cycles at 1 C. These works demonstrated that constructing a lithiophilic metal fluoride coating is effective in regulating the Li deposition for high-performance Li metal anode.³¹³

Besides current collector modifications, interphase engineering has been recognized as a crucial strategy to stabilize the Li anodes, since most of the knotty issues restricting the performance of Li metal anodes can be attributed to the instability of the Li anode/electrolyte interphase. Among them, constructing fluorinated interphases demonstrates prominent advantages in passivating active Li surfaces, regulating the diffusion and migration of Li⁺, as well as enhancing the interphase mechanical stability. In particular, the LiF has been determined to possess many extreme properties relative to other solids. The large bandgap (14.6 eV) and a wide electrochemical stability window (0 to 6.4 V vs. Li) of LiF contribute to high electrochemical stability for inhibiting the continuous corrosion of active metallic Li;³¹⁴ the high Young's modulus (65 GPa) along with a high shear modulus (49 GPa) effectively enhance the mechanical stability of the SEI to enable long-term cycling;³¹⁵ the high interphase energy (γ) can promote uniform Li distribution and smooth Li deposition behaviors,³¹⁶ meanwhile the negligible solubility of LiF in most electrolytes,³⁰³ *etc.* A variety of strategies, including physical methods and chemical strategies, have been developed to construct a LiF-rich artificial SEI.^{289, 317-329} Compared with physical methods, chemical approaches (*e.g.*, gas-, liquid- and solid-phase reaction methods) via regulating chemical reactions between Li and F-containing precursors was used to resolve the interphase issues between the artificial layer and the Li metal

matrix. As a representative F-containing gas reaction strategy, a LiF coating was developed via treating Li metal in fluorine gas flow. The LiF layer was chemically stable and mechanically strong, significantly suppressing the corrosion reaction between Li and carbonate electrolytes, and thus realizing steady cycling for over 300 times with a high current density of 5.0 mA cm^{-2} .²⁸⁹ The gas reaction method will not introduce other impurities; however, great attention should be paid to fluorine gas during operation to prevent leakage. In contrast, the LiF-rich interphases constructed via liquid-phase deposition/reaction strategies have been recognized as simpler and more effective strategies. By interposing an oil drop enriched in C-F (perfluoropolyether, PFPE) with low surface energy, a flowable fluorinated interphase was constructed for stabilizing the Li metal and regulating the Li plating. The electron-withdrawing feature of F endows the PFPE with high thermal and oxidative stability, along with good chemical inertness and non-flammability. In addition, the PFPE moieties close to the Li triggered C-F and Li-F species to reinforce the robustness of the SEI and the compactness of the Li plating.³²² Polymeric coating layers generally display superior mechanical deformability and low density, which are promising for constructing LiF-rich interphases. As reported by Goodenough *et al.*, after incorporating graphite fluoride (GF) in molten Li at 250°C , a LiF layer was produced by the strong reaction between Li metal and the GF, eventually obtaining a GF-LiF protective layer. This as-prepared composite Li metal anodes demonstrated high stability in ambient environment, as well as comparable electrochemical performance.³³⁰

To conclude, fluorine plays critical roles in modifying other components for enhancing the battery performance. Regarding separators, structural modifications and blending with other polymers or inorganic nanoparticles can address limitations such as low mechanical strength, thermal instability, and Li^+ transport restrictions of PVDF. Besides, fluorine modification (*e.g.*, surface coating and grafting method) can improve fire retardancy, mechanical abuse resistance, and LiF-rich SEI formation in Li metal batteries. Meanwhile, the abundant polar $-\text{CF}_3$ groups would offer an electronegative environment to promote Li^+ transfer. For binders, the fluorine group can be incorporated into polymer binders, enhancing ion transfer, oxidation resistance, and thermal stability, while fluorinated anions combined with ionic conductive polymers improve the binder performance for cathode. However, excessive fluorine content in binders may compromise the specific capacity and cycle stability of these electrodes. When utilizing to modify current collectors with Li metal anodes, construction of LiF interfaces on Cu current collectors is expected to passivate the active Li surface and regulate the Li^+ migration, further suppressing Li dendrite growth.

3. Understanding Fluorinated Interphases in Li-Based Batteries

3.1. Fluorinated Solid Electrolyte Interphases on Anodes

It is now broadly accepted that the SEI is significant for Li-based battery systems. In 1979, Peled *et al.* reported a SEI model that was applicable to all alkali metals in non-aqueous battery systems.³³¹ The SEI layer forms instantaneously upon contact between the anode and the electrolyte solution, and consists of insoluble and partially soluble products generated by the reduction of electrolyte components. It exhibits properties similar to a layer of solid electrolyte with high electronic resistivity. As reported in recent years, SEI played a significant role in determining the safety, power capability, reversibility and cycle life of Li-based batteries.³³² The SEI must be both mechanically stable and flexible and should adhere well to the anode, while it is crucial to prevent the dissolution or corrosion of the anode. Therefore, the electrolyte must be designed to contain at least one SEI precursor that reacts rapidly with anode to form an insoluble and stable SEI.

3.1.1. Components of SEI. The chemical composition of the SEI on the anode side is highly dependent on the type of conducting salts, solvents and additives. Although the role of these components in the formation of the SEI has not been fully understood, the presence of species such as LiF, fluoroborates, and fluorophosphates indicates the involvement of fluorinated components in the reduction mechanism of the electrolyte. LiF, in particular, has been identified as a major component of fluorinated SEI, playing a critical role in regulating the diffusion of Li ions and the strength of SEI.^{289, 333, 334} Archer and co-workers showed that the presence of halide anions, especially fluorides, significantly increases the surface diffusivity of Li ions at the interphase between the electrolyte and the Li metal anode.³³³ The role of LiF in fluorinated SEI in regulating the nucleation and growth of Li deposition in LMBs was further investigated by a designed model system.³⁰⁴ The fluorinated SEI facilitated uniform spatial diffusion of Li ions in carbonate and ether-based electrolytes, and guided the deposited Li into an ordered and aligned columnar structure.

Significant efforts have been made to develop artificial fluorinated coatings to enhance SEI performance, including inorganic LiF coatings and LiF-based composite coatings.^{320, 335, 336} While computational simulations have provided insights into the diffusion mechanism of Li ions through fluorinated SEI, the practical SEI in practical battery systems is more complex and needs to be fully understood.^{89, 337} Mashayek and co-workers elucidated that Li diffusion in the grain boundaries is generally faster than in bulk, and the heterogeneous LiF/Li₂O grain boundaries demonstrate the fastest Li ion diffusion rate compared to the homogeneous LiF/LiF and Li₂O/Li₂O.⁸⁹ Further research is needed to comprehend the diffusion mechanism of Li ions through SEI for practical applications.

3.1.2. Formation of Fluorinated SEI. The formation of SEI can be generally classified into three modes. The “native” SEI comprises multicomponent including inorganic and organic phases formed by parasitic reactions between the anode and the electrolyte,^{331, 338} “*in situ*” SEI formed over cycles of cells and “*ex situ*” SEI artificially applied on the anode surface.³³⁹ LiF is a recurring motif found in nearly all functional SEIs

(**Figure 16a**), given that fluorine is commonly present in prevailing electrolyte salts.³⁴⁰ Among SEI components, LiF is particularly spotlighted due to its high mechanical strength, low solubility, wide ESW (0–6.4 V vs. Li/Li⁺), and low calculated barriers to Li diffusion. Besides, Wang *et al.* calculated the interfacial energy of different SEI components, among which LiF exhibited the highest interfacial energy of 73.28 meV Å⁻², suggesting significant Li dendrite suppression ability.³²³ These properties suggest that LiF may contribute to a homogeneous Li flux and robust SEI, making it a beneficial phase for the SEI on anode side in recent years.³⁴¹

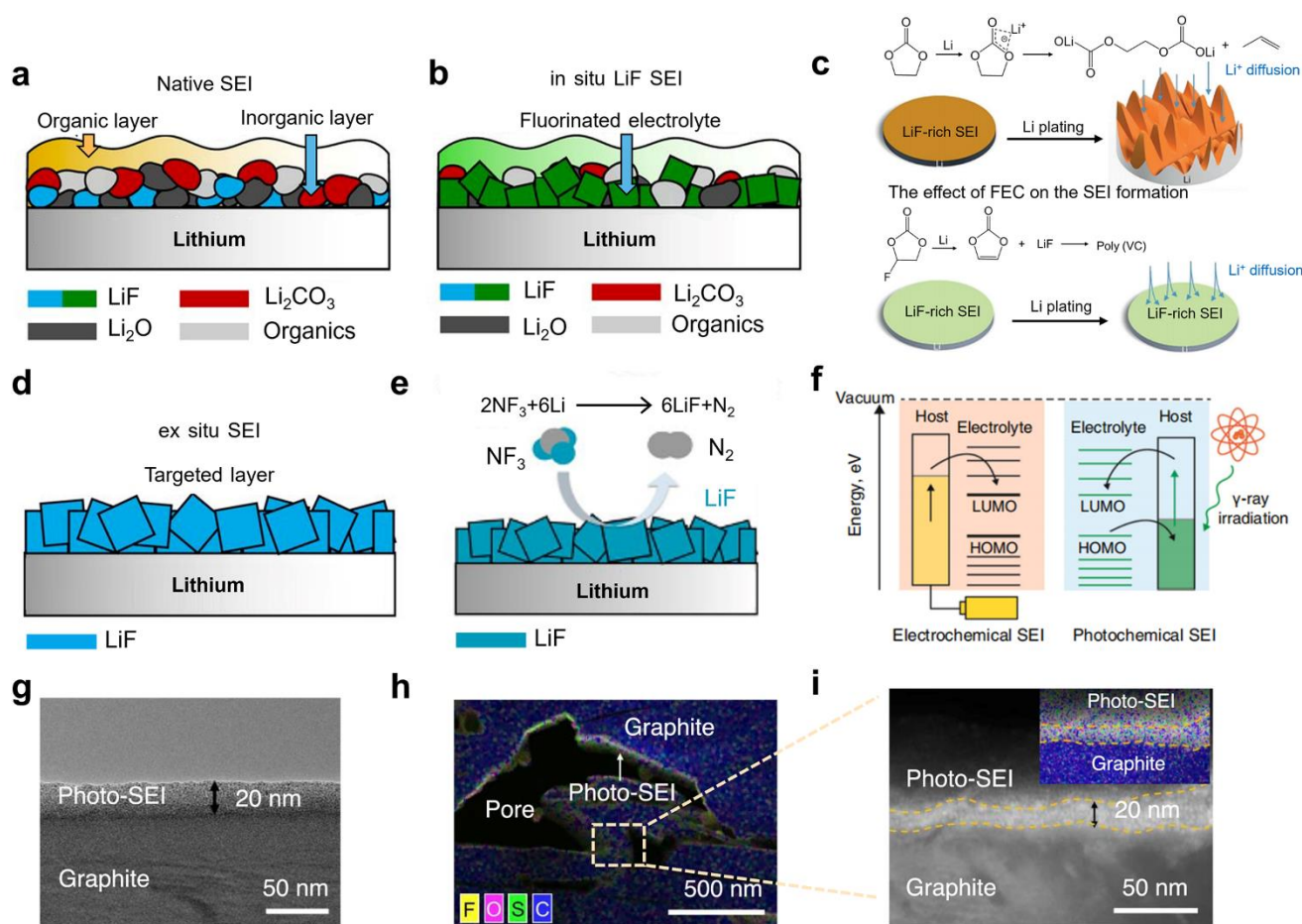


Figure 16. Different formation paths of the fluorinated SEI. (a) Native SEI from conventional carbonate electrolytes, without fluoride enrichment. (b) *In situ* LiF-enriched SEI from fluorine-rich electrolytes. Reproduced with permission from ref ³⁴². Copyright 2020 PNAS. (c) Decomposition mechanism of EC and FEC and the effect on SEI formation at the Li metal anode and Li diffusion near the anode surface. Reproduced with permission from ref ¹³⁰. Copyright 2019 Wiley-VCH. (d) *Ex situ* LiF-enriched SEI from nonelectrolyte fluorine sources. (e) Schematic of the Li-NF₃ reaction to form LiF layers on Li. Reproduced with permission from ref ³⁴². Copyright 2020 PNAS. (f) Distinct energy schemes in the formation of the SEI using electrochemical and photochemical approaches. (g) Cs-TEM image of the photo-graphite with the photochemically driven SEI layer. (h) Low-magnification Energy dispersive X-Ray Spectroscopy (EDS) elemental map of the photo-SEI inside the pores of the photo-graphite electrode. (i) High-magnification Cs-TEM image of the photo-SEI image and the corresponding EDS map (inset). Reproduced with permission from ref ³⁴³. Copyright 2021 Springer Nature.

Multiple studies have indicated that fluorine or fluoride enrichment in the electrolyte results in a LiF-enriched (*in situ*) SEI, as shown in **Figure 16b**. F-enriched electrolytes have included additives such as HF³⁴⁴ and high loadings of LiF salt,³³³ as well as solvents such as FEC,¹⁶⁸ thus making significant improvements in cycling stability and high CE (~ 89 to 99%). Postmortem analysis of cycled Li surfaces typically presents high levels of LiF. **Figure 16c** explains how the FEC molecule affects the mechanisms of SEI formation and the composition.³⁴⁵ The breaking of C-F bond leads to the formation of LiF and vinyl carbonate (VC),¹⁶⁸ which results in a thinner SEI that prevents further electrolyte decomposition.³⁴⁶ Such LiF-rich SEI prohibits high surface area lithium growth during Li stripping and plating.¹⁷⁰

Ex situ fabrication of LiF layers on Li or Cu current collectors has also been widely studied, leading to the formation of an artificial (*ex situ*) LiF-enriched SEI (**Figure 16d**). Synthetic methods include hydrolysis of LiPF₆ on Cu;^{304, 347} reactions between Li and fluorinated precursors;^{289, 319} physical vapor deposition,³⁴⁸ and atomic layer deposition (ALD).^{318, 349} To fabricate *ex situ* SEI layers, Gallant et al. used nitrogen trifluoride (NF₃) gas to directly grow LiF on the Li foil (**Figure 16e**).³⁴² The reduction of NF₃ as a fluorinated gas cathode in Li batteries led to copious amounts of LiF under electrochemical conditions.³⁵⁰ Additionally, γ -rays can induce an artificial SEI layer with a favorable composition, and the composition of the SEI layer has a substantial effect on the charging rate. Choi *et al.* reported a γ -ray-driven SEI layer that allowed the battery to be charged to 80% capacity in 10.8 min of 2.6 mAh cm⁻². This exceptional charging performance was attributed to the LiF-rich SEI induced by salt-dominant decomposition via γ -ray irradiation.³⁴³ **Figure 16f** illustrates the electron transfer in both electrochemical and photochemical processes. For the electrochemical process, electrons were transferred unidirectionally from graphite to the LUMO level of the electrolyte to form the SEI layer, regulating compositions with relatively fewer components of the SEI layer. Besides, γ -ray irradiation could drive radical intermediates, and irradiation with γ -rays could preferentially decompose compounds, which improved the tunability of the SEI composition. The Cs-TEM image of photo-graphite indicates that the photo-SEI layer was uniformly deposited on the graphite surface with a thickness of ~ 20 nm (**Figure 16g**). The photo-SEI layer was also observed to exist in the inner pores of the graphite particles (**Figure 16h, i**), implying that γ -ray irradiation was effective even in the interior of the graphite.

3.1.3. Distribution and Impacts of Fluorides on SEI. The structure and chemical components of the SEI layer at different depths can be investigated by X-ray photoelectron spectroscopy (XPS) depth profiles. Taking the electrolyte of 1 M LiTFSI in DME/DOL (1:1 by vol.) as an example,³⁵¹ the main elements of SEI are C, N, O, F, and S, which originated from the reduction reaction between the electrolyte and Li anode. The depth analysis curves of SEI are shown in **Figure 17a**. It can be observed that the signal of element F increased with the increase of sputtering time. The binding energies of 685.0 and 688.3 eV in the F 1s diagram represented Li-F and C-F. The intensity of C-F signal on the surface was higher than that of Li-F, which indicated that

residual LiTFSI salts existed on the surface. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) technique can be applied to further investigate the SEI (**Figure 17b**). The inorganic phases of LiF-based compounds in 1 M LiTFSI in DME/DOL (1:1 by vol.) with 2% LiNO₃,³⁵¹ such as LiF ($m/z = 26$), LiF₂ ($m/z = 45$), LiF₃ ($m/z = 64$), and Li₂F₃ ($m/z = 71$), were evenly distributed in the inner SEI layer. By overlaying the 3D distribution results of LiF ($m/z = 26$), C₂F₆S₂O₄N ($m/z = 280$), and C₆O₄H₁₁ ($m/z = 147$), it was found that the Li salt was evenly distributed at the outermost SEI layer, which completely covered the LiF product. The results indicate that SEI may not be a dense layer and the liquid electrolyte can be stored between the organic phase and inorganic phase.³⁵² As shown in **Figure 17c**, two circles with equal area were extracted from the mapping image to obtain their mass spectrum. Compared to the light region (**Figure 17d**), the intensities of the ion fragments with the mass charge ratios (m/z) of 14, 33, 59, 85, and 111 decreased in the dark region (**Figure 17e**). Such fragments may come from the inorganic phase products formed by the strongly electronegative atoms and Li metal after the decomposition of LiTFSI, such as N, Li₂F, Li₃F₂, Li₄F₃ and Li₅N₂O₃.³⁵¹ Among them, Li₂F ($m/z = 33$) and Li₃F₂ ($m/z = 59$) exhibited the highest density, which suggested a strong electronegativity of fluorine in LiTFSI. These products were the main component of the inorganic phase of the SEI layer.

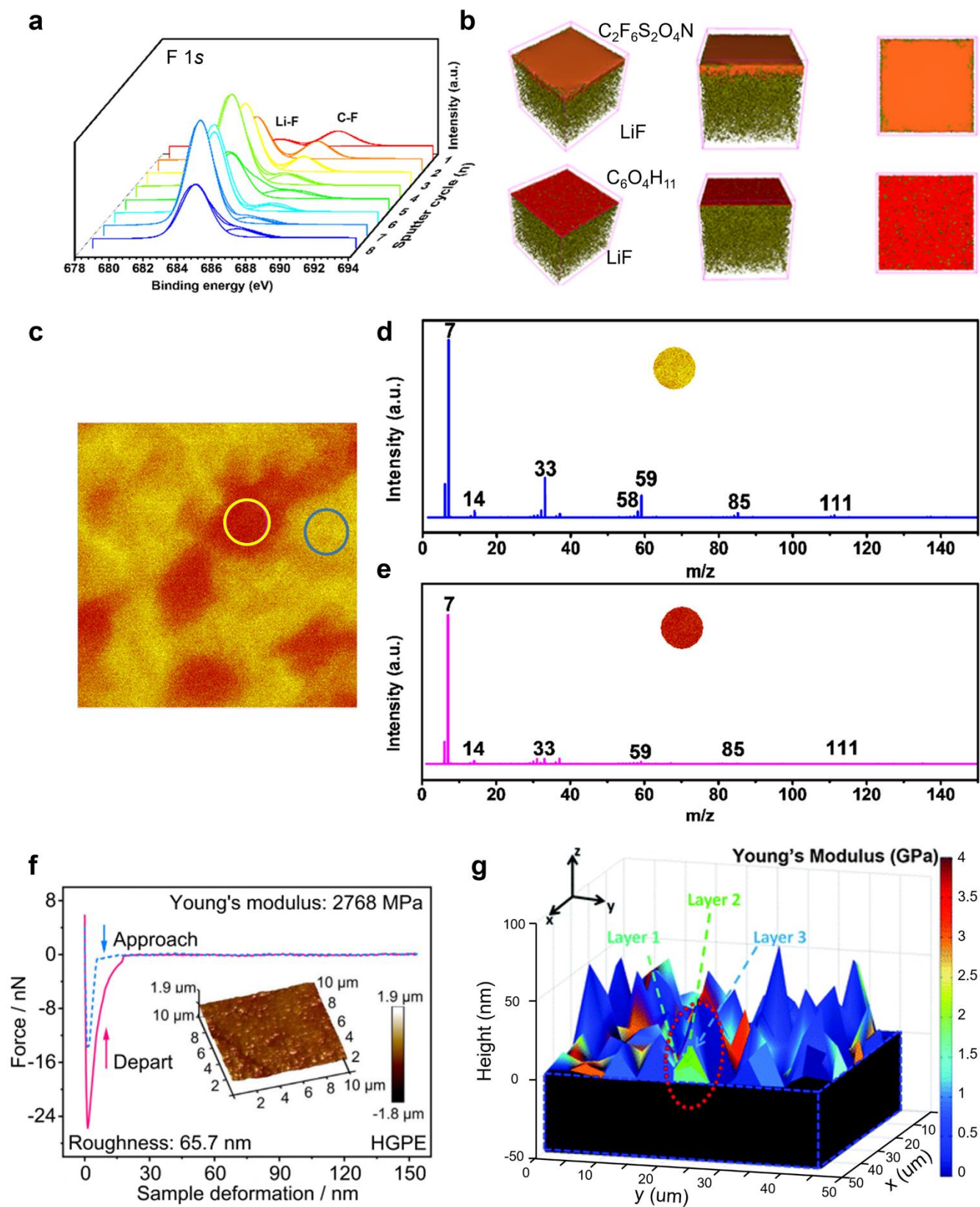


Figure 17. Characterization of fluorinated SEI in Li-based batteries. (a) F 1s XPS depth profile of the Li anode. (b) 3D distribution overlay between LiF and $C_2F_6S_2O_4N$ (upper panel) and between LiF and $C_6O_4H_{11}$ (lower panel). (c) Total mapping distribution and (d, e) related mass spectrum of the SEI on Li-metal anode (1 M LiTFSI-DME/DOL, 1:1 by vol. with 2% $LiNO_3$). Reproduced ref ³⁵¹. Copyright 2022 American Chemical Society. (f) Heteroatom-based gel polymer electrolyte (HGPE) derived SEI. Corresponding 3D-AFM scanning images of SEI layers are shown in insets. Reproduced

with permission from ref³⁵³. Copyright 2021 Springer Nature. (g) Cross section view of 3D plots. Black substrates indicate Li-Si alloys, and the z axis gives the thickness of SEI films. The color bar of 0–4 GPa shows Young's modulus for the SEI films. Reproduced with permission from ref³⁵⁴. Copyright 2014 Royal Society of Chemistry.

Young's modulus of the SEI layer serves as a crucial metric for assessing the strength of the SEI, since a robust SEI can suppress the repeated rupture-reconstruction of SEI due to the severe volume changes of the anodes during cycling. Such thin and stable SEI leads to low impedance of the interphase, thus enhancing cycling performance.¹⁶⁶ The Young's modulus of SEI can be evaluated by 3D atomic force microscope (3D-AFM) scanning. The proportion of LiF greatly increases the mechanical strength of SEI (*i.e.*, the LiF possesses a shear modulus of 55.1 GPa, almost 11 times higher than that of Li metal (4.9 GPa)), which can significantly enhance the strength and interphasial energy of SEI layers.³⁵⁵ As a result, SEI consisting of homogeneous LiF makes the anode more robust and uniform (**Figure 17f**). A 3D Young's modulus plot of discharged silicon electrodes with all force curves in a certain area can be drawn according to Young's moduli at each position at different indentation lengths on the surface of discharged anodes.³⁵⁴ Some area was not covered by SEI, and some area was covered by the thick SEI. The soft part of the SEI was always covering the outer layer. This can also be obtained from a cross-section view of the 3D plot, as shown in **Figure 17g**.³⁵⁴ The uncovered area and the area with different layered structures with different Young's moduli can be observed clearly. This indicated that the organic species usually situated on the outside with lower strength, and inorganic species like LiF support the internal SEI strength. It is, therefore, essential to explore the distribution and homogeneity of SEIs.

Despite the phenomenological improvements observed, it remains uncertain whether LiF has a directly beneficial function in the formation of SEI. Variations among LiF-forming approaches (*i.e.*, *in situ* vs. *ex situ*) and the electrolytes used would lead to confusion in the understanding. For example, conflicting results about *ex situ* LiF were found in different works. A standalone layer was found to decrease CE due to inhomogeneous Li deposition,³⁴⁹ whereas LiF layers on Li were elsewhere reported to improve cycle life in Li||Li symmetric cells.^{289, 318} Additionally, LiF is an ionic insulator ($\sim 10^{-13}$ to 10^{-14} S cm⁻¹), and it seems counterintuitive that LiF-enriched SEIs can impart benefits related to Li transport.³⁵⁶ It remains unclear how such physical properties of LiF can support performance improvements.

3.2. Fluorinated Cathode Electrolyte Interphases

The presence of CEI layer was first suggested by Goodenough *et al.* on the LiCoO₂ cathode.³⁵⁷ Considering the interphasial reactivity increases at high voltage cycling, the CEI layer behavior demonstrates an even more complicated response. When the cut-off voltage is increased to 4.5 V, the CEI layer becomes unstable and decomposes, as reported by Cherkashinin *et al.*³⁵⁸ Until now, the detailed constituents and electrochemical behavior of the CEI layer are still under debate. However, it is generally accepted that CEI is extremely sensitive to various factors, such as electrolyte composition, current densities, and cut-off voltage.

Previous studies usually treated the formation of CEI layer independently. However, recent research results discovered a close relationship between the formation of CEI on cathodes and the formation of SEI on anodes.³⁵⁹⁻³⁶¹ A well-known example is the transition metal ion dissolution from cathode materials, which affects the SEI formation on anodes.^{362, 363} Recently, Xiong *et al.* verified the interaction between the ternary cathode (*i.e.*, $\text{Li}(\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3})\text{O}_2$ and $\text{Li}(\text{Ni}_{0.42}\text{Mn}_{0.42}\text{Co}_{0.16})\text{O}_2$) and the graphite anodes in batteries operating at high temperature and high voltage.³⁶⁴ Jung *et al.* also demonstrated the enhanced cycling performance of the LiCoO_2 |graphite full cells by mitigating the coupled side reactions through Al_2O_3 coating on the cathodes.³⁶⁵ Noting that plenty of studies demonstrated if the cathode was cycled in the high voltage range, the effect of repeated formation-decomposition of SEI layers on Li anodes significantly influenced the formation of CEI layers on the cathodes. A deep investigation of the reactions on both the cathode and the Li anode is necessary to collect credible properties of the CEI layer on the cathode and achieve comprehensive understandings of the CEI formation mechanism.

3.2.1. Formation of Fluorinated CEI. It is widely accepted that the CEI layer contains both inorganic components (*e.g.* LiF) and organic species (*e.g.* carbonates and oligomers/polymers).³⁶⁶⁻³⁶⁸ *In situ* neutron scattering further proved that CEI layer presented dynamic evolution during battery cycling within low cut-off voltage (4.2 V vs. Li/Li^+). The thickness of the CEI layer gradually increases upon cycling.³⁶⁹ Li and co-workers reported the progress of CEI formation with and without electrolyte additives.³⁷⁰ As shown in **Figure 18a**, the CEI formed in the base electrolyte of 1 M LiDFOB -ethyl carbonate(EC)/DMC (1: 1 by vol.) was too loose to prevent direct contact between the electrolyte and the cathode; thereby, the carbonate solvents and salts underwent continuous decomposition reactions at high voltage, and the decomposition products were continuously deposited on the surface of the cathode, which caused the continuous growth of CEI layer. In contrast, for the CEI film formed in the electrolyte with the lithium difluorophosphate (LiDFP) additive, the preferred decomposition of LiDFP promoted the formation of a dense CEI film, effectively preventing the direct contact between the electrolyte and the cathode.

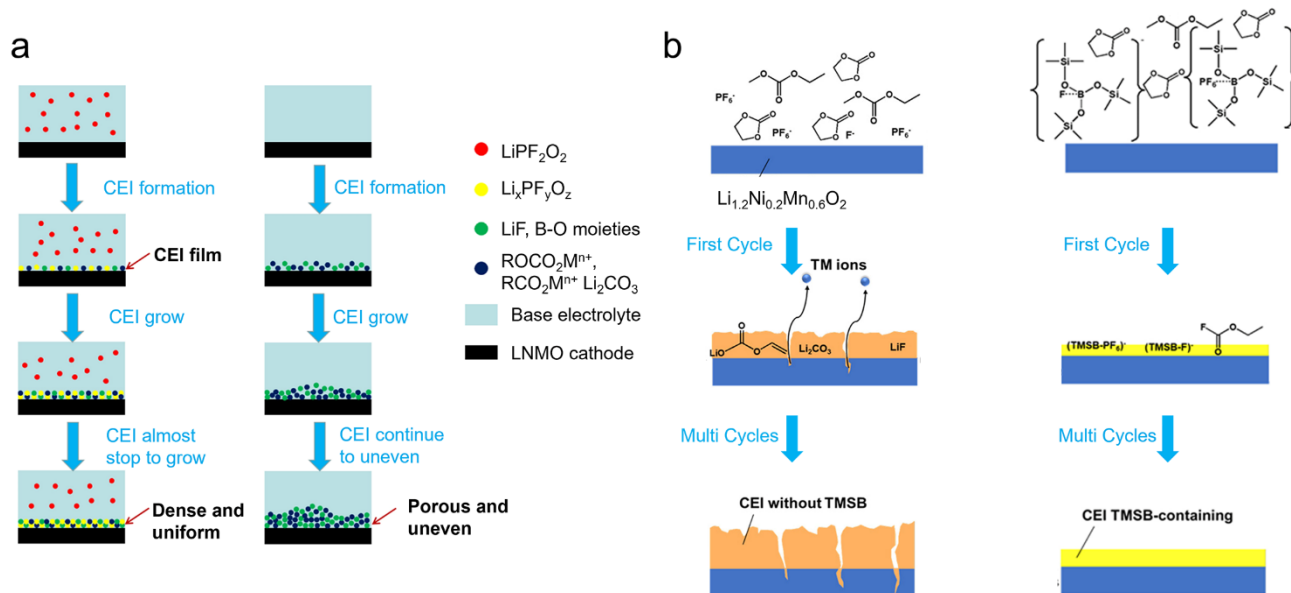


Figure 18. Formation of fluorinated CEI of Li-based batteries. (a) Proposed mechanism of the LiDFP participating in the formation of CEI film. Reproduced with permission from ref ³⁷⁰. Copyright 2019 Elsevier. (b) Schematic of CEI formation during cycling in conventional and TMSB-containing electrolytes. Reproduced ref ³⁷¹. Copyright 2019 American Chemical Society.

Figure 18b exhibits the mechanism of CEI formation with and without the fluorinated additive tris(trimethylsilyl)borate (TMSB).³⁷¹ Generally, the large polarity of EC molecules made them easily diffuse to the cathode surface with anions by a strong electrostatic force during the charge process. Hence, the cathode surface is EC/anion-rich before CEI formation, which makes EC easily decompose. However, this effect gets impaired after the addition of TMSB, because of the generation of the polyanion group (TMSB-PF₆)⁻ and (TMSB-F)⁻ with weaker electrostatic force and less electronegativity. As a result, EC decomposition is suppressed effectively. Moreover, TMSB can participate in CEI formation by electrochemical reactions or by directly entering the CEI layer in the form of a polyanion group to optimize the quality of the CEI. The HOMO level (-6.749 eV)³⁷² of TMSB is higher than that of the carbonate solvents (-11.905 eV for EC and -11.541 eV for EMC)³⁷³, which offers an opportunity to participate in the formation of a high-quality CEI film before the solvent decomposition to protect the active cathode material from the erosion of the electrolyte and alleviate the capacity and voltage fading of Li_{1.2}Ni_{0.2}Mn_{0.6}O₂.³⁷⁴

3.2.2. The Impact of Fluorinated CEI on Battery Performance. Unlike the SEI, CEI formation involves not only the electrolytes but also active components in the cathodes, including transition metal dissolution, H abstraction from the solvents, and the formation of super-oxides or peroxides. For unmodified NMC811 or LiCoPO₄ (LCP) cathodes (**Figures 19a**), electrolyte components experience continuous oxidation until a dense and uniform CEI layer forms and blocks the electron transfer from the electrolyte to the cathodes. Compared with EC/DMC and FEC/DMC-based electrolytes, the extremely high CEIs achieved by the all-

fluorinated electrolyte on aggressive cathodes should originate from the F-rich CEI that deactivated the catalytic activity of the NMC or LCP cathodes. Quantum chemistry calculations predict that direct oxidation of solvent molecules is energetically unfavorable around 5 V. Instead, solvent oxidation is accompanied by H transfer to another solvent and/or cathode surface. Intermolecular H transfer takes place around 5 V for EC and > 5.5 V for FEC, FEMC and HFE. When the oxidation potential is calculated assuming open-loop EC \cdot and FEC \cdot radicals as the products, the oxidation stability decreases to \sim 4.2 and 4.9 V, respectively. Thus, EC-containing electrolytes are expected to be oxidized from 4.2 V, even in the absence of the active materials. EC is a poor CEI former because the EC \cdot (-H) radical decomposes with a barrier of only 0.91 eV to evolve CO₂, leaving only a fraction of EC \cdot (-H) radicals to participate in the second H abstraction, eventually leading to polymerization. The resulting hydrogen-rich polymer is still susceptible for further degradation. Because of the higher barrier (1.28 eV) for the FEC \cdot (-H) ring opening reaction compared to that of EC \cdot (-H), the FEC \cdot (-H) is a longer-lived radical compared to EC \cdot (-H) and will probably react with the formed FEMC \cdot (-H) and 1,1,2,2-tetrafluoroethyl-2',2',2'-trifluoroethyl ether (HFE) \cdot (-H) radicals near the cathode surface, resulting in a fluorine-rich CEI as observed by Fourier-transform infrared spectroscopy. Alternatively, fluorinated radicals also bind to oxygen in CoPO₄, preventing the OH formation that facilitates transition metal dissolution. Thus, in all-fluorinated electrolytes, the composition of a protective CEI is inevitably highly fluorinated.³⁷⁵

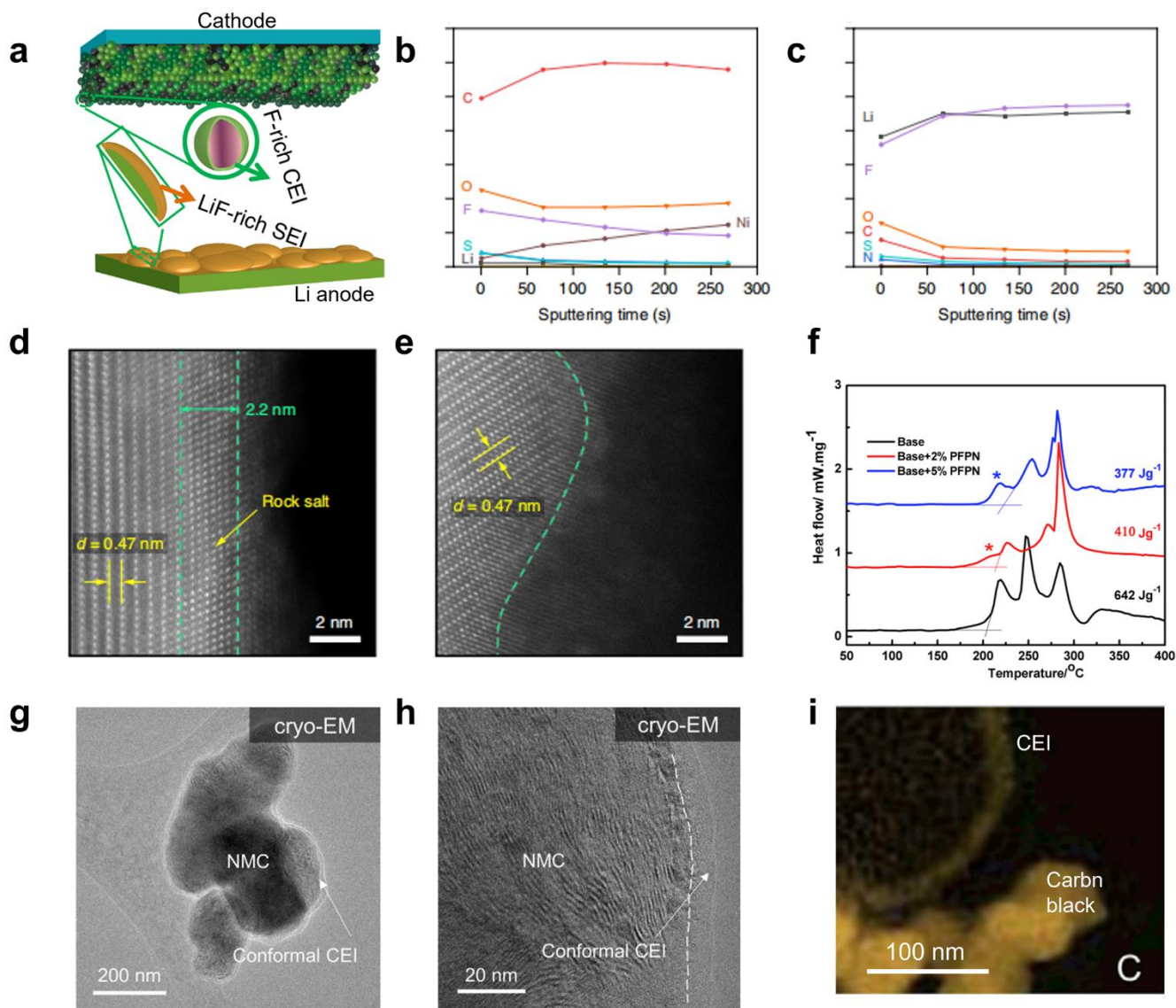


Figure 19. Characterizations of fluorinated CEI in Li-based batteries. (a) SEI and CEI chemistries formed in all-fluorinated electrolyte. Reproduced with permission from ref ³⁷⁵. Copyright 2018 Springer Nature. Quantified atomic composition ratios of the CEI obtained by XPS spectra for the NMC811 electrodes collected from cells with (b) 1 M LiFSI-DME and (c) 1 M LiFSI-DME/TFEO electrolyte after 100 cycles. HAADF-STEM of NMC811 electrodes collected from cells with (d) 1 M LiFSI-DME and (e) 1 M LiFSI-DME/TFEO electrolytes after 100 cycles. Reproduced with permission from ref ³⁷⁶. Copyright 2019 Springer Nature. (f) Heat flow profiles of the Li_xCoO_2 charged to 4.5 V after 2 cycles in the absence and presence of PFPN. Reproduced with permission from ref ¹⁷⁸. Copyright 2017 Elsevier. (g, h) Cryo-EM images of conformal CEI formed on NMC-cathodes. (i) Cryo-STEM EELS mapping of conformal CEI on NMC electrodes (yellow for carbon element). Reproduced with permission from ref ³⁷⁷. Copyright 2021 Elsevier.

Figure 19b and Figure 19c show the atomic ratios of the CEI layer formed on the surface of the NMC811 cathode in different electrolytes.³⁷⁶ An LiF-rich CEI was formed on the cathode surface in the tris(2,2,2-trifluoroethyl)orthoformate (TFEO)-based electrolyte, while in the controlled carbonate and 1 M LiFSI in DME electrolytes, organic-rich CEIs were obtained. **Figure 19d** and **Figure 19e** show the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging results of the cycled NMC811 electrodes.³⁷⁶ The structure reconstruction appeared in the NMC811 electrode cycled in 1 M LiFSI-DME, with a rock salt layer (~ 2.2 nm) (**Figure 19d**). The surface lattice layers of the NMC811 electrode

underwent some degree of mixing, with the Li sites partially occupied by antisite Ni ions.³⁷⁸ In contrast, the electrode surface maintained a layered structure under the same cycling condition in 1 M LiFSI-DME/TFEO (**Figure 19e**). Such a result indicated the effective suppression of detrimental phase transformation. These beneficial effects can be attributed to the formation of a uniform LiF-rich CEI layer,³⁷⁹ while the uneven and organic-rich CEI is less protective.

The thermal stability of both the electrolyte and the cathode material at the charged state is of vital importance to battery safety. Differential scanning calorimetry (DSC) was carried out to unravel the thermal stability of the electrolyte and electrode material, respectively. **Figure 19f** shows the DSC curves of the electrolyte with (phenoxy)pentafluorocyclotriphosphazene (PFPN) (red and blue) and without PFPN (black).³⁸⁰ It can be clearly seen that the main decomposition peak of the electrolyte shifted towards a higher temperature with the addition of more PFPN, indicating that the thermal stability of the electrolyte had been considerably improved. Several peaks can be identified in DSC curves, corresponding to the step-by-step decomposition of the charged Li_xCoO_2 material.³⁸⁰ The electrolyte decomposition/oxidation at the surface of Li_xCoO_2 electrode usually occurs at around 200 °C.³⁸¹ In the presence of 2% PFPN, a new peak (indicated by red asterisk) at 206 °C from the red DSC curve can be assigned to the thermal-polymerization reaction of PFPN. The calculation results (200–300 °C) demonstrate that the total exothermic heat generated from the Li_xCoO_2 electrode in the presence of PFPN (2% PFPN: 36.1% and 5% PFPN: 41.3%) was less than that from the Li_xCoO_2 electrode in the absence of PFPN (black), indicating that the thermal stability of the charged Li_xCoO_2 electrode was distinctively improved after the addition of electrolyte additive.¹⁷⁸ The layer of CEI after brief shorting on the positive electrode particle can be observed by cryogenic electron microscopy (cryo-EM) (**Figures 19g, h**). The electrode particle was uniformly coated with a thin layer of mostly amorphous materials, spanning from ~ 5 to 10 nm at the edge of the interphase. Furthermore, the conformal CEI and carbon black additives yielded an annular dark-field image along with a C K-edge map (**Figures 19i**), which indicated the organic polymeric composition of alkyl carbonates.³⁷⁷

Fluorinated electrolytes have shown significant potential in achieving improved performance and safety in high-voltage batteries. When hydrogen atoms in the electrolyte are replaced with fluorine atoms, the activation energy is reduced,¹⁶⁹ and the HOMO and LUMO energy levels decrease, leading to increased reduction and oxidation potentials.^{345, 382-384} The decrease in HOMO energy level enhances cycling performance by promoting the early formation of an effective CEI layer and reducing overall impedance.^{130, 384, 385} Numerous fluorinated CEI-forming additives have been reported in recent years.³⁸⁶⁻³⁸⁸ Future research should focus on understanding the impact of the fluorine atom on the overall performance of Li-based cell chemistry, involving i) correlating the molecular and ii) electronic structures of fluorinated electrolyte components, iii) identifying relevant physicochemical properties and iv) reactivity, which includes investigating synergistic effects between fluorinated and non-fluorinated electrolyte components, studying

main operation and failure processes in Li-based cells, exploring different plausible reaction pathways, and analyzing the limiting and determining steps that rationalize the results. Systematic research on CEI electrochemistry/chemistry will enable the development of high-performance Li-based batteries with high energy density, energy efficiency, and superior capacity retention.

3.3. Critical Role of Fluorinated Interphases for Extreme Li-Based Batteries

With the continuous upsurge in demand for energy storage, Li-based batteries are increasingly required to survive/operate under extreme conditions, such as wide temperature range (*e.g.*, ± 60 °C), extended charge/discharge cycling life, fast cycling rate (*e.g.*, ≤ 15 min), and high working voltage (*e.g.*, > 4.5 V).⁵⁵ For instance, electric vehicles call for battery systems to sustain a stable operation in both hot conditions and cold environments. Some specific applications, including subsurface exploration, defensive arsenals, space vehicles, *etc.*, require the operation of rechargeable batteries under even more extreme conditions. Apart from these external influences, internal factors also trigger thermal fluctuations in Li-based batteries,³⁰³ significantly raising safety concerns. As an essential region in which electrochemical reactions occur involving Li^+ ions and electrons, the interphase on the electrode plays an essential role in maximizing the electrochemical performance of Li-based batteries. Regarding an ideal interphase, several features should be possessed, including high Li^+ ion conductivity, compact structure with proper compositions, high chemical/electrochemical stability, and high elastic strength. However, the design of interphases under mild conditions makes it difficult to satisfy the requirements under extreme conditions. When a battery is operated under extreme conditions, the interphase formed on the electrode surface can grow much thicker and lose its protective ability, further causing battery performance decay through various aging mechanisms.³⁸⁹ Currently, the features and roles of interphases at certain extreme conditions remain significant challenges in the operation of Li-based batteries. Fluorinated interphases have emerged as effective strategies for enhancing battery performances under various operation conditions. In particular, the fluorinated interphase is featured with its main component LiF .^{316, 375, 390} However, the role of LiF for extreme Li-based batteries remains elusive. In the following section, recent in-depth understanding and key progress of fluorinated interphase at extreme operation conditions of Li-based batteries are summarized, where the SEI formed on the anode will be focused.

It is generally recognized that the bulk LiF is considered as a favorable SEI component formed both via *in situ* (derived from electrolyte components) or *ex situ* (artificial fabrication) approaches. It should be noted that despite the electric/ionic insulation nature of the bulk LiF ,^{356, 391} the LiF -enriched SEI at the nano-scale level can yield a high ionic conductivity, low diffusion energy, and high surface energy, contributing to a uniform and highly stable Li deposition.^{333, 392} The difference between the macroscopic and microscopic

properties of LiF remains to be elucidated in the future. Moreover, understanding the role of LiF in electrochemical performances of batteries is inevitably limited by several factors, including the distributions, particle sizes, and formation approaches, requiring great attention to identify the effects of fluorinated interphase in extreme batteries.

Commercial carbonate electrolytes have largely restricted the battery operation temperature range (-20 to $+50$ °C), leading to fast capacity degradation and even battery failure at low temperatures. The successful operation of typical Li-based batteries at low temperature depends on the melting points of the liquid electrolytes. For instance, the commercial electrolytes of Li-ion batteries contain a high proportion of EC solvent that freezes under -20 °C, which results in extremely low ionic conductivity.^{393, 394} Besides, the thick SEI usually continuously consumes Li, significantly increasing the diffusion energy of Li^+ ions.³⁹⁴ In addition to the ionic mobility, the low-temperature performance of batteries is dominated by the sluggish kinetics of Li^+ transport across the interphase, which is related to high charge transfer resistance and poor structure stability of SEIs.³⁹⁵ To construct an effective interphase on the surface of both cathodes (*e.g.*, LFP) and anodes (*e.g.*, graphite or Li metal), various additives, such as FEC, LiPO_2F_2 , fluorosulfonyl isocyanate (FI), have been introduced to optimize the electrolytes.^{394, 396-398} In addition, fluorinated anti-freezing agents have been introduced as electrolyte co-/solvent for low-temperature applications, such as 2,2,2-trifluoroethyl butyrate³⁹⁹, iso-butyl formate,⁴⁰⁰ and 2,2,2-trifluoroethyl n-caproate⁴⁰¹. Recently, He *et al.* developed a fluorine-sulfur-based electrolyte by applying iso-butyl formate (IF) as an anti-freezing agent with an ultralow melting point of -132 °C. This electrolyte demonstrated excellent physiochemical and electrochemical properties at ultra-low temperature, *e.g.*, forming stable LiF-rich SEI (10.48%) and CEI (17.91%) layers, achieving high Li^+ conductivities (1.00×10^{-5} mS cm^{-1} for SEI and 6.65×10^{-5} mS cm^{-1} for CEI), and high diffusion coefficients (1.10×10^{-21} m² s⁻¹ for SEI and 2.07×10^{-20} m² s⁻¹ for CEI). It also enabled a stable cycling performance of the Li|| LiCoO_2 (LCO) battery at -70 °C with a high retainable capacity of 110 mAh g⁻¹ over 170 cycles.⁴⁰⁰ Typically, it has been accepted that the LiF-rich SEI formed on anode materials exhibited low interphase impedance and charge transfer resistance, as well as high stability, thereby enhancing the Li^+ diffusion at low temperatures. These results are consistent with the DFT calculations by Arias *et al.* They pointed out that the surface diffusivity of Li^+ over a layer of LiF crystal was excellent, which also improved the stability of SEI.⁴⁰² However, the role of LiF in CEI on low temperature performance is still under debate. Contrary to the desirable effect of LiF-rich CEI on promoting the rapid Li^+ diffusion as a result of the lower energy barrier,⁴⁰³ Gao *et al.* observed less LiF content formed in SEI with the FEC-containing electrolyte than that with the FEC-free electrolyte. They ascribed the smaller interfacial impedances to the less LiF, which would promote the low-temperature performance of LFP electrode.⁴⁰⁴

Recently, by introducing low-polarity diluents, LHCEs have demonstrated great potential in achieving high Li^+ mobility as well as low electrolyte viscosity for low-temperature batteries.⁴⁰⁵⁻⁴⁰⁷ However, the SEI derived from LiPF_6 in LiPF_6 -based LHCEs generally exhibited high interphase resistance. After adding lithium difluorobis(oxalato) phosphate (LiDFBOP) as a sacrificial additive, the SEI was regulated to be much thinner, which delivered low interphase impedance due to the decreased Li^+ transport path. It was demonstrated that the addition of LiDFBOP changed the SEI composition, with inorganic LiF and porous organic $\text{Li}_n(\text{FOP})_n$ -based layers facilitating Li^+ diffusion, and LiF along with $\text{Li}_2\text{C}_2\text{O}_4$ increased the stability of SEI. Benefiting from this regulated interphase chemistry, the commercial graphite anodes exhibited outstanding low-temperature performance ($\sim 240 \text{ mAh g}^{-1}$ at -20°C with 0.1 C) and high-rate performance ($\sim 225 \text{ mAh g}^{-1}$ at 2 C).³⁹⁵

To satisfy the demand for high energy densities, Li-based batteries are developed to operate at extreme voltages, which are beyond the thermodynamic stability limits of traditional electrolytes. Meanwhile, these electrolytes, mainly consisting of carbonates or ethers, are extremely flammable, causing safety concerns for practical applications. LiF possesses the largest bandgap (13.6 eV) and the widest ESW, which is believed to protect the high voltage cathode.³¹⁴ To control the LiF formation, Li *et al.* designed an all-fluoride electrolyte with a large donatable fluorine concentration, *i.e.*, 7 M LiFSI in FEC , in which both the solvent and the salt donated F. It was revealed that LiF formation on the cathode with a large bandgap resulted in a fast-tunneling decay rate, protecting Al from dissolution and suppressing electrolyte oxidation beyond 5 V (**Figure 20a**). When pairing the $5 \text{ V LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode with the Li metal anode, the full cell ($1.4 \times$ excess Li) cycled stably for over 130 times at industrially loading level of 14.7 mg cm^{-2} , 1.83 mAh cm^{-2} at a current rate of 0.36 C . The promising performance was ascribed to the LiF nanolayer constructed on the surfaces of both the cathode and anode; therefore, its features, such as a wide bandgap, high surface energy, and small Burgers vector, favored the high voltage stability and also resisted rupture during Li deposition.³¹⁶ Unlike using the sole solvent, Wang *et al.* proposed another all-fluorinated electrolyte consisting of 1 M LiPF_6 in a mixture of FEC : FEMC : HFE with a weight ratio of $2:6:2$.³⁷⁵ The high degree of fluorine substitution in each co-solvent rendered a F-rich CEI, where these F-containing species (*e.g.* CF_x and PO_xF_y) deactivated the catalytic activity of the cathode surface and further resisted unwanted oxidation reactions even charging to 5 V . Besides, the fluorinated co-solvents yielded a robust SEI with an extremely high LiF content ($\sim 90\%$), promoting Li^+ migration along the interphase and tuning the growth of the deposited Li in parallel to reduce the specific surface area. The resulting batteries exhibited outstanding cyclability with high CEs of 99.2% for Li plating/stripping and $\sim 99.81\%$ for a 5 V LiCoPO_4 cathode. Interestingly, the designed electrolyte displayed non-flammability, with F-fluorination on the alkyl moiety of each co-solvent inhibiting the propagation of oxygen radicals during combustion.³⁷⁵ Besides, using the fluorine-containing additives (*e.g.*, FEC , LiPO_2F_2 , LiDFOB) can also construct more robust

SEIs/CEIs that consist of fluorinated species/polymers, which further blocks the continuous side reactions between the electrolyte solvents and the extremely oxidized cathode surface.⁴⁰⁸⁻⁴¹⁰ As reported by Ma et al., the perfluorophenylboronic acid (PFPBA) additive was preferentially oxidized on the $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622) cathode surface due to the strong coordination with PF_6^- , forming armor-like CEI with LiF-rich inner layer and LiB_xO_y -based outer part. The LiF inner layer in CEI with high mechanical strength effectively resists the breakdown of the NCM622 cathode during repeated cycling and enhances the Li^+ conductivity. Besides, the outer layer with LiB_xO_y exhibited extremely low solubility in carbonate solvents, maintaining the stability of internal CEI species such as LiF. Consequently, the armor-like CEI prevented unwanted electrolyte decomposition as well as detrimental cathode structural change at high voltage, contributing to an excellent cycle stability with 92.1% capacity retention over 400 cycles at 4.6 V, and it sustained the battery to cycle for 150 times (with 75.67% retention) even at ultra-high voltage of 4.8 V.⁴⁰⁸ As discussed above, the chemical sources of F were typically confined to negatively-charged salt anions or fluorinated solvents/additives in electrolytes, which could not populate the inner-Helmholtz layers of the electrode surface (*e.g.*, Li anode) with a high Fermi energy level, and thus hindering their participation in the interphasial chemistry. Zhang *et al.* synthesized a fluorinated cation, 1-methyl-1-propyl-3-fluoropyrrolidinium, and coupled it with an FSI^- anion to form an ionic liquid ($\text{PMpyr}^+\text{FSI}^-$).⁴¹⁰ This electrolyte exhibited complete non-flammability and strong anti-anodic ability up to 5.5 V. More importantly, the fluorine sources on the cation and the anion offered unprecedented interphasial chemistries on both NCM622 cathode and Li anode, contributing to excellent battery electrochemical performances. The SEI enriched in SO_2F , C-F, and LiF contributed from the decomposition/defluorination of FSI^- and PMpyr^+ cations. Stable cycling performance without obvious capacity deterioration after 100 cycles was achieved with high average CE of 99.9%. This work highlights the importance of exploring fluorinated cations in tailoring highly fluorinated interphases for batteries operated at extreme voltages.

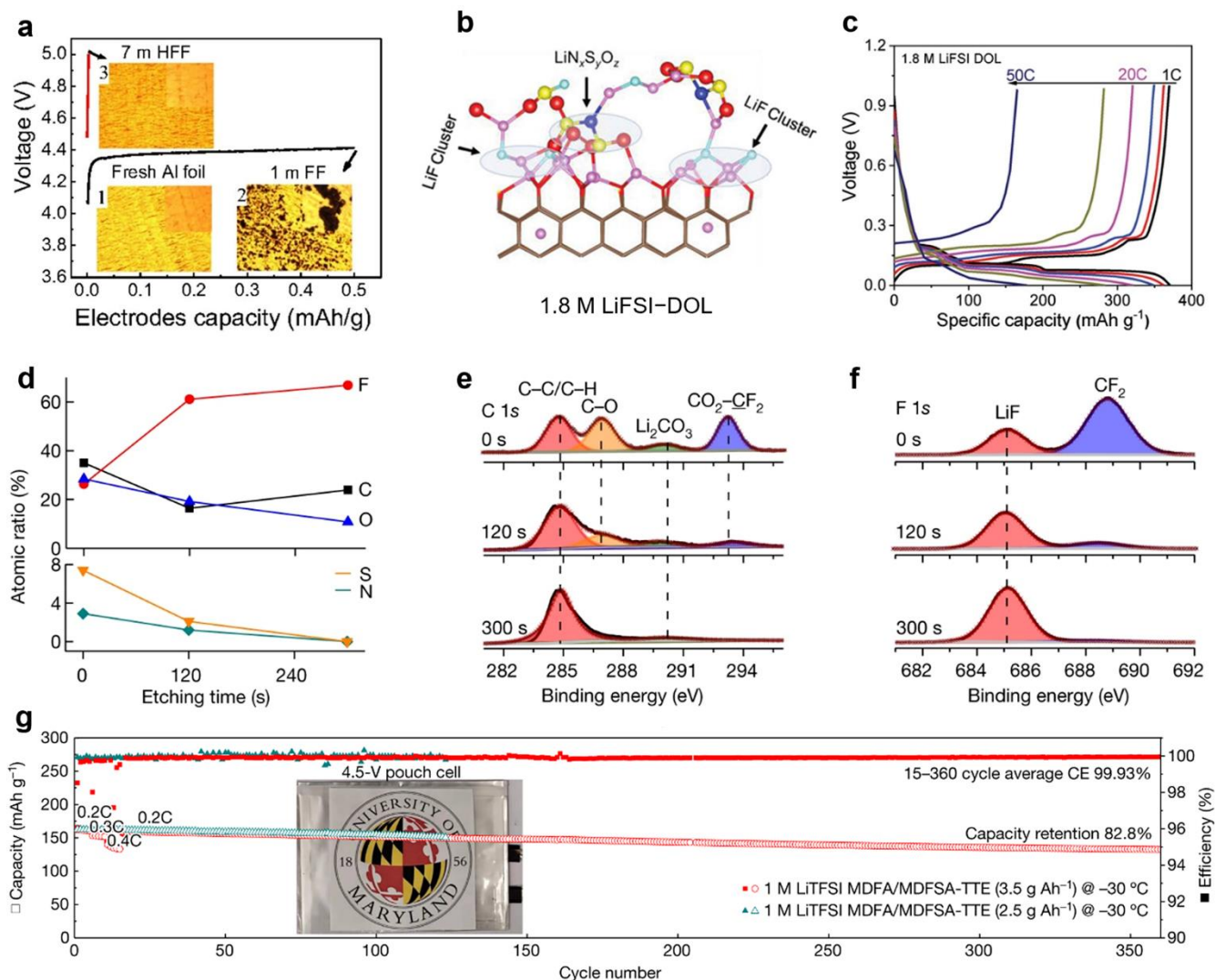


Figure 20. The role of fluorinated interphases for Li-based batteries operated at extreme conditions. (a) Al dissolution in 1 M LiFSI-FEC (1 M FF) and 7 M LiFSI-FEC (7 M HFF) electrolytes when charging to 5 V at 0.5 mA. Insets show optical microscopy images of (1) fresh Al foil, Al foil in (2) 1 M FF electrolyte after charging 1 h, and in (3) 7 M HFF after charging to 5 V. Reproduced with permission from ref ³¹⁶. Copyright 2018 PNAS. (b) AIMD simulated atomic SEI structure between the electrolyte and the graphite anode. Li: pink, P: purple, F: cany, C: brown, O: red, N: blue, S: yellow, graphite: brown wireframe. (c) The charge/discharge curves of graphite||Li cells with 1.8 M-LiFSI DOL at various current rates. Reproduced with permission from ref ⁴¹¹. Copyright 2022 Wiley-VCH. XPS results of the SEI on graphite anode in 1 M LiTFSI-MDFA/MDFSA/TTE electrolyte: (d) quantified atomic ratios of the elements, (e) C 1s and (f) F 1s spectra displayed in columns of the corresponding depth profiling results. (g) Graphite||NCM811 pouch cell performance at -30 °C and 0.2 C rate using 2.5 g Ah⁻¹ or 3.5 g Ah⁻¹ electrolytes. Rate performance was conducted at various C rates (0.2 C for 5 cycles, 0.3 C for 5 cycles, 0.4 C for 5 cycles and 0.2 C for 345 cycles) of 3.5 g Ah⁻¹ (red color). Inset shows the photo of a 4.5 V pouch cell. Reproduced with permission from ref ⁵⁵. Copyright 2023 Springer Nature.

Considerable efforts have been devoted to using FEC-based electrolytes for generating fluorinated SEIs in Li-based batteries, particularly with the graphite anodes or Li metal anodes.^{168, 412-417} The FEC-derived fluorinated SEI is characteristic of high LiF amount, which exhibits low electronic conductivity ($\sim 10^{-31}$ S cm⁻¹) and high Young's modulus (~ 64.9 GPa).⁴¹⁸ Unfortunately, the low Li⁺ conductivity of LiF ($\sim 10^{-12}$ S cm⁻¹) component largely restricts the fast charging capability especially for Li metal anodes, as a result

of the blocked transportation ability of Li^+ and further aggravated Li dendrite growth at high current rates (*e.g.*, above 2.0 mAh cm^{-2}).⁴¹⁹⁻⁴²³ Very recently, a dual-anion regulated electrolyte was designed by Xu's research group via using LiTFSI and LiDFBOP as anion regulators.⁴²⁴ The TFSI⁻ anion reduced the desolvation energy of Li^+ , while the DFBOP⁻ anion promoted the formation of highly ion-conductive and robust inorganic-rich interphases on both cathodes (less LiF and stronger $\text{Li}_x\text{PO}_y\text{F}_z$) and anodes (large amounts of $\text{Li}_x\text{PO}_y\text{F}_z$ and $\text{Li}_2\text{C}_2\text{O}_4$). These interphase features contributed to an outstanding cyclability (84.6% capacity retention over 150 cycles) in 6.0 Ah pouch cells ($\text{Li}||\text{LiNi}_{0.83}\text{Co}_{0.11}\text{Mn}_{0.06}\text{O}_2$, NCM83), along with an ultrahigh rate capability (5 C) in 2.0 Ah pouch cells. More interestingly, a practical $\text{Li}||\text{NCM83}$ pouch cell with an ultra-large capacity of 39.0 Ah realized an ultrahigh energy density of 521.3 Wh kg^{-1} , promoting the practical utilization of high-energy-density Li-based batteries via a facile electrolyte design. Apart from the beneficial effect of $\text{Li}_x\text{PO}_y\text{F}_z$, other interphase species have also been incorporated in enhancing the battery cycling stability, especially at fast charging rates. Interestingly, there exists another viewpoint believing LiF-rich SEI is promising for fast kinetics, since the wide band gap and high chemical/electrochemical stability of LiF could block the continuous side reactions.^{323, 425, 354} An extremely fast charging graphite anode as high as 50 C without Li plating was achieved by designing two electrolytes, *i.e.*, low-voltage 1.8 M LiFSI-DOL and high-voltage 1.0 M LiPF₆-FEC/AN (7:3 by vol.). It was revealed that the LiF formed on graphite anode (**Figure 20b**) with high interphase energy and low ionic electronic significantly suppressed side reactions of electrolytes, thus benefiting fast kinetics. The former electrolyte enabled the graphite anode to deliver a high reversible capacity of 180 mAh g^{-1} even at 50 C ($1\text{C} = 370 \text{ mAh g}^{-1}$) (**Figure 20c**) and endowed the graphite||LFP full battery to retain a capacity of 60 mAh g^{-1} at an extreme rate of 60 C (representing 1 min for fully charge and discharge). The second electrolyte aided the graphite||NCM811 full battery (cathode loading 2 mAh cm^{-2} , N/P ratio = 1) in providing a capacity of 170 mAh g^{-1} at 4 C charge and 0.3 C discharge rates.^{411, 426} Briefly, whether the LiF component in SEI is sufficiently effective for high stability and fast Li^+ transport of Li-based batteries remains unclear, especially under fast charging conditions.

As mentioned above, the most widely used electrolytes based on carbonates fail to simultaneously meet all requirements for supporting extreme Li-based batteries such as higher voltages ($\geq 4.5 \text{ V}$), fast charging (≤ 15 minutes), cycling over a wide temperature range ($\pm 60^\circ\text{C}$), and non-flammability.^{12, 58, 427, 428} To tame the high affinity between the solvents and the ions and the high flammability of carbonate-based electrolytes, Wang and coworkers dissolved fluorinated electrolytes into highly fluorinated non-polar solvents (*e.g.*, tetrafluoro-1-(2,2,2-trifluoroethoxy)ethane (D2)) to obtain an electrolyte formulated with 1.28 M LiFSI-FEC/FEMC/D2. This designed electrolyte yielded both LiF-rich SEI and CEI. The high thermal stability and the excellent Arrhenius behavior of Li^+ conductivity for the LiF-rich interphases enhanced the high-temperature performance of both the cathode and anode. The ionic conductivities of SEI and CEI at ultralow

temperatures were also significantly improved. Li metal anode achieved high cycling CE of 99.4%, and the graphite anode achieved a high charge/discharge CE of 99.9%. As for the high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (5.0 V) and LiCoMnO_4 (5.4 V) cathodes, high CE of 99.9% and 99% were obtained, respectively. Especially, the $\text{Li}||\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ battery maintained 56% of its capacity obtained at room temperature, even charging/discharging at $-85\text{ }^\circ\text{C}$, along with high cycling stability at $60\text{ }^\circ\text{C}$. In addition to significantly improved wide temperature performance, this electrolyte design displayed non-flammable characteristics.⁴²⁹ Furthermore, Wang's group have dedicated to exploring guiding principle to address the relationships between battery performance, electrolyte solvation structure and interphase chemistry, especially focusing on extreme operating conditions. Their recent report validated an electrolyte design strategy based on a group of soft solvents with a relatively low DN (less than 10) and high dielectric constant (larger than 5) that stroke a balance between Li^+ -solvent interactions, sufficient dissociation of Li salts and satisfactory electrochemistry. As a proof of concept, 1 M LiTFSI-methyl difluoroacetate (MDFA)/methyl 2,2-difluoro-2 (fluorosulfonyl)acetate MDFA (MDFSA)/TTE electrolyte was developed successfully, in which MDFSA with a high reduction voltage of 2.2 V was introduced as a co-solvent for further strengthening the LiF-rich SEI and CEI. It was demonstrated that the similar LiF-enriched interphases on the NMC811 cathode and the graphite anode balanced the thermodynamic (capacity) and kinetic (interphase resistance) matching between the two electrodes at extreme conditions, enabling the 4.5 V graphite||NMC811 full batteries to keep 75% of RT reversible capacity (0.1 C) at $-50\text{ }^\circ\text{C}$ ($-60\text{ }^\circ\text{C}$) with a practical areal capacity of 2.5 mAh cm^{-2} , and the pouch cells with lean electrolyte (2.5 g Ah^{-1}) to stably cycling at $-30\text{ }^\circ\text{C}$ for over 300 times with an average CE of 99.9% (**Figure 20d-g**). This work opened a new electrolyte design direction for tuning fluorinated interphases toward practical batteries with high-voltage, fast-charging and wide-temperature operating features.⁵⁵

For practical Li-based batteries, there is a growing need for their stable operation under all conditions, including high voltage (*e.g.*, $\geq 4.5\text{ V}$), fast cycling rate (*e.g.*, ≤ 15 minutes), wide temperature range (*e.g.*, $\pm 60\text{ }^\circ\text{C}$), and extended charge/discharge cycling, which are highly related to the interphases. In this case, fluorinated interphases featured with LiF component demonstrate attractive prospects. LiF exhibits low solubility, high mechanical property, wide bandgap, and excellent anti-oxidation ability, high interphasial energy against Li metal, contributing to a robust SEI. Moreover, the high shear modulus of LiF suppresses the anode pulverization. Unfortunately, the low Li^+ conductivity of LiF ($\sim 10^{-12}\text{ S cm}^{-1}$) in the interphase restricts the high-rate performance, particularly toward Li metal anodes. Incorporating fluorinated conducting components (*e.g.*, $\text{Li}_x\text{PO}_y\text{F}_z$) into the LiF-rich interphase can improve cycling stability and fast-charging capability. Fluorinated components can also be combined with organic SEI matrix to accommodate the large volume change of the Li anode. Although LiF-enriched SEI displays low impedance and high stability to improve Li^+ diffusion at low temperatures, it remains controversy over the impacts of

LiF in CEI components on low-temperature performance. Further investigation is needed to unlock the roles and influencing factors of macroscopic and microscopic properties for LiF, particularly under extreme conditions.

3.4. Techniques to Probe Fluorinated Interphases

As described above, the passivated interphase is electronically insulting but ionic conducting, arising from the decomposition of the electrolyte components on the surface of the electrode, which plays a vital role in determining the capacity, cyclability, rate performance, CE, and safety properties of Li-based batteries. Understanding the morphologies, chemical compositions, and mechanical properties of CEI/SEI is significant for further designing fluorinated interphases on the active materials especially on the anodes.⁴³⁰ Since its first demonstration by Dey *et al.* in the 1970s, the SEI has attracted significant interest regarding the formation mechanisms, structures, phase, and chemical compositions, however, due to its spatially and temporally dynamic nature, the in-depth comprehensive understanding of SEI, especially on the atomic scale remains a huge challenge.^{284, 389, 431-437} Generally, it is difficult to discern the SEI/CEI chemical components from solvent species, and the SEI/CEI thickness is also hard to quantify with ambiguous boundaries. Besides, the SEI/CEI properties are highly affected by test conditions (*e.g.*, electrolytes, operation temperature, current density, voltage range and electrode materials) and the sample preparation environments (*e.g.*, washing solvent, exposure to the air³⁸⁹ and moisture), which undergoes dynamic evolution process during the charging and discharging. To provide valuable information of the interphase characteristics, various advanced techniques, including microscopy and spectroscopy have been applied extensively. Scanning electron microscopy (SEM) and TEM are two powerful and most widely used tools for visualizing and monitoring the interphase directly,^{340, 438-442} particularly when conducting at cryogenic temperatures for preserving the pristine states of interphases.^{24, 352, 376, 420, 443-449} In addition, some properties of the growing interphase can be quantified to establish their correlation with the electrochemical performances of batteries, *e.g.*, developing electrochemical quartz crystal microbalance (EQCM) for quantifying the interphase dissolution phenomenon.⁴⁵⁰ Various interphase analysis techniques, such as SIMS,⁴⁵¹⁻⁴⁵⁷ XPS,⁴⁵⁸⁻⁴⁶¹ AFM,⁴⁶²⁻⁴⁶⁷ XAS,⁴⁶⁸⁻⁴⁷² Neutron reflectometry (NR),⁴⁷³⁻⁴⁷⁵ XRD,⁴⁷⁶⁻⁴⁷⁸ NMR⁴⁷⁹⁻⁴⁸² and scanning electrochemical microscopy (SECM)⁴⁸³⁻⁴⁸⁶, have also been widely employed to probe the elemental compositions, interphase morphology, and mechanical/electrical properties of interphase. Notably, due to the elusory and highly dynamic properties, different techniques need to be combined to comprehensively recognize the fluorinated interphases at the atomic level. However, most of these advanced techniques for investigating fluorinated interphases are under *ex situ* conditions, requiring the disassembling of the batteries after charging/discharging to various states, which may cause the exposure of the samples to ambient conditions during the transport process for characterization. These processes may

change the interphases by affecting the morphology, microstructure, chemical compositions, mechanical properties, *etc.*, which may cause misleading results.^{437, 473} Therefore, *in situ/operando* measurements conducted at the operating conditions without disassembling the batteries are more reliable and valuable technologies to provide real-time information about the characteristics and evolution process of fluorinated interphases during battery cycling.

Since several review articles have comprehensively summarized the technical details, research progress and applications on understanding the SEI using traditional techniques,^{430, 437, 473, 487, 488} in this section, the focus will be state-of-the-art developments of updated characterization techniques for fluorinated interphases, elucidating the chemical compositions, morphologies, micro-/nano-structures, and other properties. Important features of each technique, including the spatial resolution, the useful information, as well as corresponding strengths and limitations for probing the interphase, are compared in **Table 3**. To capture the moment of the reactions at the interphase, which occurs at the picosecond timescale,^{310, 489, 490} the DFT and MD simulations have been extensively utilized. Besides, theoretical calculations can also help to predict and quantify the correlation between the structure and the properties of the interphases. Therefore, theoretical calculations and simulations are associated with the micro-/nano-structure and properties of SEI, in turn offering guidance in rational designing and regulating SEI characteristics for high-performance Li-based batteries. Considerable technical details of theoretical calculations and simulations for understanding the interphases can be found in previous specialized reviews, which will not be discussed in this section.^{437, 491}

Table 3. Comparison of the spatial resolution, useful information (*e.g.*, composition, structure, morphology), as well as corresponding strengths and limitations of each technique for probing the interphase.

Characterization techniques	Spatial resolution	Composition	Structure	Morphology	Other information	Strengths	Limitations	Ref.
Cryo-(S)TEM	0.1 nm	✓	✓	✓	/	Preserving the electrochemical state, corresponding structure and chemical information of the interphase without destruction at cryogenic temperatures	Hard to probe organic-enriched SEI that derived from solvent decomposition, explaining chemical details in the disordered and amorphous phases remain challenging	444, 445, 447, 492, 493
Cryo-FIB/SEM	nm	✓	✓	✓	Obtain cross-sectional view of the interphase	Obtain spectroscopy imaging from the cross-sectional view at the nanoscale	The transfer time even within seconds may not be sufficient for some sensitive samples, requiring optimizing the procedures to	494, 495

								eliminate sample exposure	
EQCM	5×10^{-11} g	✓	/	✓	Gravimetric information	Quantify and monitor the real-time interphase evolution and component dissolution during electrochemical process	Lack of exact structural information		450, 496-503
TGC	10^{-7} g	✓	/	/	/	Quantify the contribution of the interphase Li^+ and unreacted metallic Li^0 to the capacity decay	Require non-destructive approach to quantify residual Li during electrochemical cycling		504
XPS	nm	✓	/	/	/	Precise in monitoring the electronic structures of interphase compositions	<i>In situ</i> XPS has yet to be fully designed due to ultrahigh vacuum, big challenges with the sample preparation, data collection protocols, and data processing that can lead to misleading conclusions		458, 459, 461, 505-507
SIMS	nm	✓	✓	/	/	Visualize the growth of the interphase microstructure	Creation of secondary products due to the high-energy beam		457, 508-510
NMR	-	✓	✓	/	The amount and timescale of Li^+ transport through the interphase	Noninvasively identify chemical compositions and structures of the interphases	Fail to probe the dynamic nature of the interphase		479, 480, 487
AFM	nm	/	/	✓	Mechanical and electrical features	Offer high resolution topographical images, evaluate mechanical evolution of the interphase	Fail to unveil chemical information, restricted magnification and vertical range		462, 511, 512
TERS	nm	✓	✓	✓	/	Provide both topographical and chemical mapping of the interphase with high sensitivity and selectivity	Need to increase the efficiency of motivation and collection to probe the interphase		466, 467, 513-515
NR	nm	✓	✓	✓	Interphase evolution	Quantitatively determine interphase properties, detect evolutions of the interphase structure	Require a flat specimen to generate a strong signal, very limited facilities to handle the produced neutrons outside		437, 473-475, 516

							the particle accelerator	
XAS	0.001 nm	✓	✓	✓	The local atomic arrangement and electronic structure	High sensitivity to local chemical bonds and solvent environments for interphase investigation	Require a separate kind of electrochemical cell design for <i>in situ</i> operation	471, 472, 517-520
SECM	10 nm- 1 um	✓	/	✓	/	Monitor the formation and evolution of the interphase, and determine electrically insulating feature	The probe positioning is complicated by the different faradaic current behavior for conductive and insulating surface	483, 484, 521

3.4.1. Cryo-EM. As discussed earlier, SEI layers are sensitive to oxygen and moisture during the transfer process to electron microscopes (e.g. TEM and SEM), causing insufficient resolution for characterizing the micro-/nano-structures of SEI. In addition, under the ultrahigh vacuum of the TEM chamber, Li metal anodes are extremely vulnerable to radiation damage, such as sample ionization and bond breakage, caused by high electron dose in the incident beam, and side chemical reactions induced by free radicals and secondary electrons. Inspired by biological imaging techniques, cryo-EM with low electron dose and frozen sample at low temperature has been used to resolve the crystalline atomic lattices of SEI/CEI, while preserving delicate chemical composition and spatial features, which has demonstrated its advantage in visualizing and elucidating nanostructures and compositions of the beam-sensitive SEI at atomic level.^{24, 443}

To preserve the pristine state of chemically reactive and beam-sensitive materials, especially the Li metal anode, Cui and coworkers pioneered cryo-TEM investigation by designing a cryo-transfer method.⁴⁹² As illustrated in **Figure 21a, b**, Li was electrochemically deposited onto a copper grid, followed by washing with 1,3-dioxolane to remove Li salts and flash-freezing the specimen in liquid nitrogen immediately. Therefore, the electrochemical state, as well as the corresponding structure and chemical information of Li dendrites, were retained at cryogenic temperatures. Through visualizing individual Li dendrites, they achieved a high atomic resolution (0.7 Å) image on the spherical aberration-corrected TEM. In contrast to the air-exposed Li dendrites with rough surfaces and darker contrast due to the formation of polycrystalline artifacts, the cryo-transferred Li dendrites preserved their states, which constructed a much smoother and thinner SEI layer on Li metal (**Figure 21c, d**). Notably, with a standard EC/DEC electrolyte, the formed SEI was composed of small crystalline domains (diameter ~ 3 nm) embedded randomly in the amorphous matrix. On the contrary, with 10 vol.% FEC as the additive, a more-ordered multilayer SEI was generated, which was consistent with the structure proposed by Aurbach *et al.*⁵²² However, LiF was not observed in the SEI layer, which may be because TEM is sensitive to crystalline phases when probing a

small selected surface area.^{444, 492} In another work, Meng *et al.* developed a new cell configuration to obtain electrochemically deposited Li (EDLi) for cryo-TEM imaging. A copper grid was placed on the Cu foil and used as a part of the counterpart substrate.⁴²⁰ After deposition, the cell was disassembled and rinsed with DMC before transferring. Then, the grid was loaded in a covered cryogenic dewar with continuous Ar flow, and the holder was pumped down to 10^{-5} bar and immediately loaded into a vacuum chamber (cooled to 100 K) for transfer. It was revealed that the EDLi is amorphous with uneven SEIs, containing amorphous organic species and crystalline LiF. Nevertheless, the crystalline LiF in the SEI layer possessed a low conductivity of $<10^{-12}$ S cm⁻¹, and the amorphous $\text{Li}_x\text{PO}_y\text{F}_z$ species could display a higher ionic conductivity,^{523, 524} which questioned the favorable effect and the working mechanism of LiF for high CEs. Sooner after, using cryo-TEM, Cui and coworkers discovered the fundamental effects of SEI nanostructures (*i.e.*, mosaic and multilayer) on the performance of Li metal anode, pointing out that fluctuations in crystalline grain distribution within the SEI played a vital role in differentiating the mosaic structure from the multilayer structure, thus dictating the battery performance.⁴⁴⁵ Specifically, multilayer nanostructure favored uniform Li stripping behavior, while mosaic nanostructure resulted in fast Li dissolution.

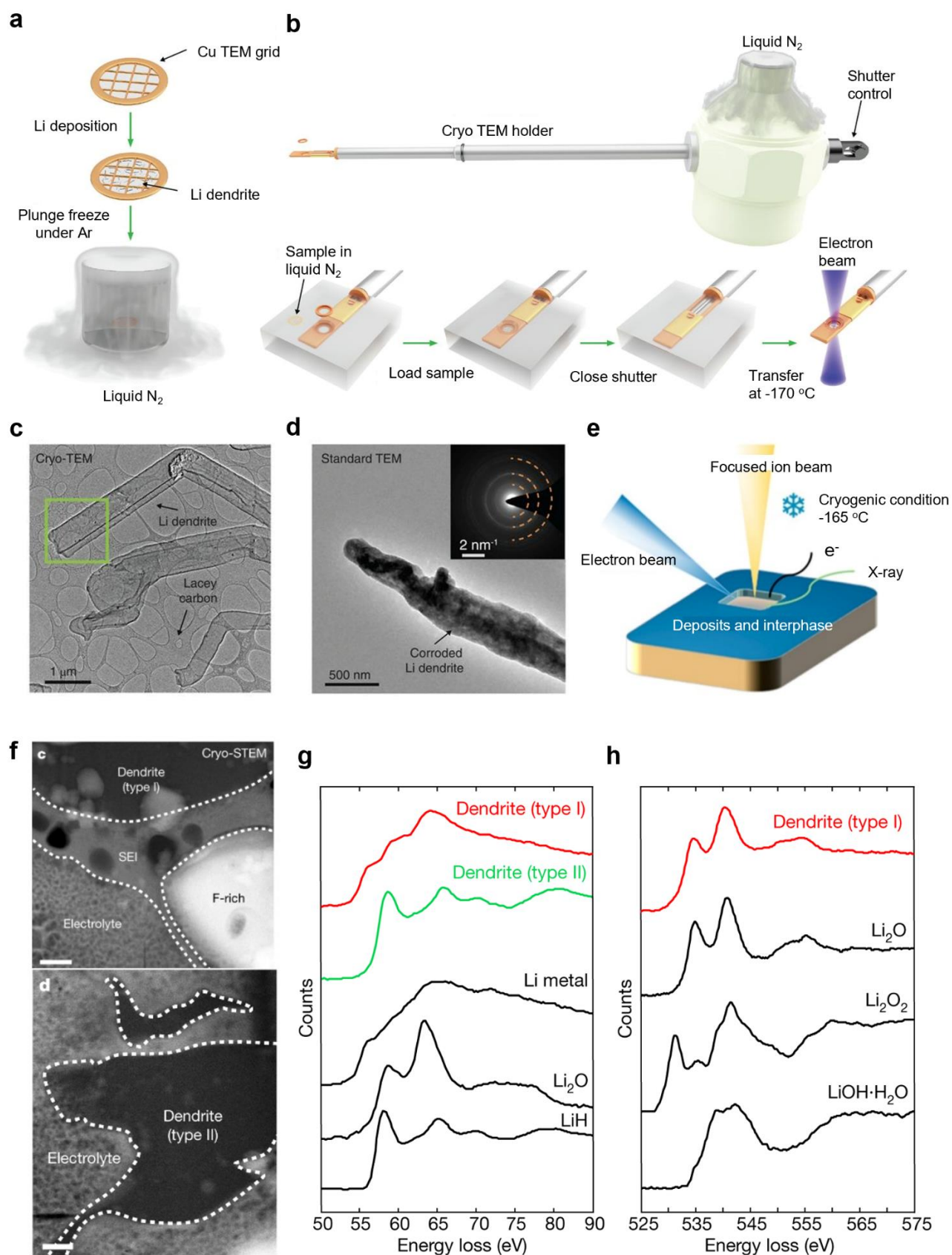


Figure 21. Probing critical characteristics of sensitive interphases by cryo-EM. (a) Electrochemically depositing Li metal dendrites onto a copper TEM grid followed by plunged into liquid nitrogen after battery disassembly. (b) The specimen is then placed onto the cryo-TEM holder while still maintained in liquid nitrogen and isolated from the environment by a closed shutter. (c) Cryo-TEM image of Li metal dendrites with the electron dose rate $<1 \text{ e}^- \text{ \AA}^{-2} \text{ s}^{-1}$. (d) Typical TEM image

of a Li metal dendrite after exposing it to air for ~ 1 s at room temperature. Inset shows the corresponding SAED pattern. Reproduced with permission from ref ⁴⁹². Copyright 2017 American Association for the Advancement of Science. (e) Illustration of the cryo-FIB/SEM setup at liquid nitrogen temperature. Reproduced with permission from ref ⁵²⁵. Copyright 2020 American Chemical Society. (f) HAADF cryo-STEM images displaying an extended SEI layer on (upper) type I dendrites, but not on (lower) type II dendrites. EELS elemental mapping of SEIs on (g) type I dendrite enriched in O and Li, and (h) type II dendrite without carbon. Reproduced with permission from ref ⁵²⁶. Copyright 2018 Springer Nature.

To identify the dominant components and nanostructure of the SEI layer, an effective strategy to minimize Li pulverization was demonstrated by Zhang *et al.* via using a fluorinated orthoformate solvent-based electrolyte. The *in situ* formed SEI on Li anode displayed a monolithic feature with the same composition from the surface to the bottom, along with horizontally homogeneous coverage of the SEI observed from cryo-TEM imaging. This unique SEI with enriched inorganics significantly suppressed electrolyte depletion and minimized pulverization for a stable Li anode.³⁷⁶ Moreover, the evolution of SEI layer during cycling can be tracked with the aid of cryo-TEM.⁴⁴⁶ Cui *et al.* revealed that the initial SEI generated during the first cycle was thin and amorphous, which evolved into two morphologies upon further cycling, *i.e.*, a compact SEI containing inorganic components that passivated the electrode surface, and a large extended SEI without inorganics due to incomplete passivation.⁴⁹³ The extended SEI growth inevitably consumed massive Li and led to porosity reduction, which could be prevented by inorganic species in the compact SEI layer. These results via cryo-TEM indicated the vastly heterogeneous process for SEI growth could be effectively regulated by sufficient passivation of the SEI. Very recently, the same research group further adapted a thin film vitrification approach to preserve the SEI film in its native liquid electrolyte environment, yielding uniform thin films inside the holes of the Cu grid. Afterwards, these samples were probed through cryo-(S)TEM to visualize the intact structure and chemistry of the SEI films. It was demonstrated that anion-derived SEI enriched with more inorganics contributed to a smaller swelling ratio, preserving its mechanical property and chemical stability for enhancing electrochemical cycling.³⁵² Encouraged by the successful interphase characterization in liquid electrolytes, the cryo-TEM was also utilized to visualize the interphase structure between the anode and solid polymer electrolytes atomically.⁵²⁷⁻⁵³³ In 2020, the cryo-TEM results revealed a mosaic interphase between Li anode and PEO electrolyte, where various inorganic nanocrystals (Li_2O , LiOH , and Li_2CO_3) were randomly distributed inside the amorphous phase. The Li_2S addition favored the decomposition of $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ and thus promoted the enrichment of LiF nanocrystals in the Li/PEO interphase, as verified by both cryo-TEM and simulations. The LiF nanocrystals not only enhanced the Li^+ diffusion kinetics and prevented the chain breaks of C-O, but also suppressed side reactions between the Li anode and the PEO electrolyte, thus enabling outstanding electrochemical performance for both half cells and full cells.⁴⁴⁷

Cryo-TEM has been regarded as a powerful tool for confirming and refining SEI models, which have long been hypothesized. Nevertheless, compared to the extensively investigated inorganic components (*e.g.*,

LiF) by cryo-TEM, properties of organic-enriched SEI that are derived from solvent decomposition remain an enormous challenge. Besides, more efforts need to be put in regarding cryo-EM techniques for guiding the optimization of high-performance Li-based batteries, including exploring and explaining the chemical details in the disordered and amorphous phases, revealing more in-depth information from lattice imaging, and *etc.*

Since cryo-TEM requires a thin specimen (<100 nm) on the TEM grids, it is hard to probe the bulk electrode materials. In contrast to previous TEM investigations focusing on the surface structure, the focused ion beam (FIB) technology with milling capability has been applied for preparing TEM samples by lifting out the bulk structure of the electrode materials. Unfortunately, the FIB conducted at room temperature leads to various artifact issues, including surface damage, re-deposition of beam-sensitive Li metals, and mechanical deformation related to “cutting” approaches. Therefore, cryo-FIB is necessary to process the electrode samples and interphases at cryogenic temperature (−170 °C).^{437, 534}

Combining milling characteristics of FIB at cryogenic temperatures to preserve solid-liquid interphases with the SEM technique to obtain spectroscopy imaging from the cross-sectional view at the nanoscale, the SEI film formed on anode materials can be precisely characterized (**Figure 21e**).⁵²⁵ Using the cryo-FIB/SEM characterization, Archer *et al.* reported a pinhole-free Al₂O₃ coating (with a thickness of 15 nm) served as an artificial solid-electrolyte interphase on the Cu foil, revealing that the deposited Li consisted of both dense and porous structure, highly improved the stability of Li deposition.⁴⁹⁴ Via conducting imaging and spectroscopic mapping on the cross-sections of Li deposits prepared by the cryo-FIB milling, Kourkoutis *et al.* revealed the intact surface layers and interphase compositions of the exposed reactive materials experienced negligible change, which could be characterized down to the nanoscale.⁴⁹⁵ Obviously, cryogenic sample temperature enabled energy dispersive EDX mapping of Li with increased signal over an extended period when coupling the new EDX detectors with the cryo-FIB/SEM technique. However, the rapid transfer time, even within seconds, may not be sufficient for some sensitive samples, requiring further improvements in these techniques to eliminate sample exposure.

It has been recognized that the element distribution and contents of electrode materials can be determined by EDS and the EELS, offering valuable information about the chemical compositions, especially for some amorphous species.⁴⁴³ Recent progress in cryo-TEM has been successfully used for beam-sensitive battery materials,^{420, 448, 492, 526, 535} achieving atomic-resolution imaging for SEI layers formed on the Si,⁴⁴⁹ carbon⁴⁹³ and Li metal anodes.^{445, 446, 536} To restrict the destructive change in structures and interphase chemistry during the cell disassemble and solvent-washing processes before the cryo-TEM characterization, cryo-Scanning transmission electron microscope (STEM) combined with the cryo-FIB lift-out procedure was applied for visualizing SEI layers. Significant work was conducted by Kourkoutis *et al.* using cryo-STEM, identifying two distinct types of dendrites on the Li anode.⁵²⁶ According to the

HAADF cryo-STEM imaging (**Figure 21f**), an extended SEI (300-500 nm thick) existed in the type I dendrite, suggesting a typical washing process had removed a large portion of the SEI layer. On the contrary, the type II dendrites with the thickness of hundreds of nanometers are more likely to disconnect with the electrodes due to much smaller contact areas, which could result in dead Li formation and capacity attenuation of batteries. In addition, abundant oxygen and Li in type I SEI layer without F were observed from EELS elemental maps, while notably, extended type II SEI was absent with a C-free, Li- and O-enriched type II dendrite (~ 20 nm). Based on the fine structures of the Li and O K-edge (**Figure 21g, h**), type I dendrite mainly contained Li metal and partial Li₂O, while type II dendrite was unexpectedly dominated by pure lithium hydride (LiH). More significantly, the fluorinated electrolyte was confirmed to be able to mitigate the LiH dendrite formation and largely altered the Li deposition. The discovery of extended SEI layers as well as LiH dendrites on Li metal was informative to further efforts on overcoming their detrimental effects. Based on these recent progresses, it was surprising that the recognized favorable LiF was not observed in the SEI, even using fluorinated electrolytes. Utilizing cryo-STEM and EELS techniques, Cui and his group elucidated that instead of participating in the compact SEI (15 nm) directly, LiF precipitated as large nanoparticles (100-400 nm) across the electrode surface, extending outside of the compact SEI for the indirect SEI regime. In other words, LiF cannot play a dominant role in passivating Li metal or promoting Li⁺ transport through the compact SEI. This report refined the traditional SEI structure across multiple length scales and nuanced the effects of SEI species on the anode stability.⁵³⁷ Besides SEI formed on Li metal, the structural and chemical evolution of SEI layers on Si anodes were unveiled in three dimensions via combining sensitive elemental tomography with cryo-STEM. Owing to the continuous void growth and the condensation during the delithiation process, the unstable SEI on the Si anode grew towards the interior, which formed the core-shell structure in the initial cycle and further evolved to a ‘plum-pudding’ structure comprising abundant voids and dead Si upon longer cycling. As a consequence, the engulfing of Si domains by the SEI was revealed, causing the disruption of electron transport pathways and generation of dead Si, which further depleted the electrolyte and deteriorated the battery performance.⁴³⁷

3.4.2. Quantifying Techniques. Based on the piezoelectric effect, where the mechanical shear stress is induced in the crystal as a function of the applied voltage, EQCM has been regarded as an extremely sensitive mass monitoring approach to studying electrochemical reactions.⁴⁹⁹⁻⁵⁰³ The electrode is generally deposited on an oscillating sensor (made of quartz crystal), which exhibits a linear relationship between resonance frequency and its mass, based on the Sauerbrey equation in the ideal case of a homogeneous and rigid layer adhered to the sensor surface. Then, through probing the shift in resonance frequency, the mass change of the electrode can be obtained quantitatively. Therefore, the EQCM technique allows monitoring the real-time SEI evolution and component dissolution phenomenon as a function of applied voltage.^{450, 498}

Through *in situ* EQCM measurement, Pan *et al.* revealed that LiF and Li alkylcarbonates comprised the main SEI components on graphite anodes (1 M LiPF₆-EC/DMC electrolyte) at various voltages. LiF was formed at 1.5 V, and EC was initially reduced at 0.74 V. Moreover, it was very interesting to observe that the nascent interphase could be partially re-oxidized during the very first delithiation cycle, which could be the reason for the reported meta-stability of the SEI ingredients in the nascent form.⁵³⁸ In recent years, EQCM has been well developed, in which the energy dissipation of the resonating sensor is additionally considered. Introducing the SEI shear viscosity coefficient, SEI shear storage modulus, and electrolyte properties in a multilayered viscoelastic Voigt model, the dissipative properties of a nonrigid SEI and change in electrolyte viscosity are considered.⁵³⁹ Combining the EQCM with dissipation monitoring (EQCM-D), gravimetric and viscoelastic changes in Li₄Ti₅O₁₂ anodes were assessed during the insertion/extraction of Li⁺ and formation/growth of SEI. These results indicated that intrinsic viscoelastic properties of the growing SEI layers could be quantified, and the SEI quality (recognized from the EQCM-D data) was improved by optimizing the electrolyte system (*e.g.*, adding vinylene carbonate additive or using LiTFSI salt).⁴⁹⁷ Typically, the EQCM-D technique can provide information of the structural change in more realistic non-rigid viscoelastic interphases.⁴⁹⁶

One should note that among all the SEI properties, the dissolution in the electrolyte can directly influence the formation and growth of SEI in the subsequent cycles. Generally, additional Li and electrolyte have to be consumed to repair the partially dissolved SEI, which will inevitably increase the SEI thickness,^{540, 541} resulting in severe capacity loss through the repeated SEI formation and growth process. The EQCM has been applied to quantify the mass loss of SEI layer (after formation) upon standing at an open circuit. The SEI was found to lose more than half of its mass, demonstrating the potential of EQCM to quantify the SEI dissolution and further reveal the mechanisms of SEI formation and growth.^{450, 542, 543} Very recently, utilizing *operando* EQCM, Cui *et al.* successfully quantified the SEI mass loss in ether-based electrolytes (**Figure 22a, b**).⁴⁵⁰ By establishing the correlation among solubility, passivity, and cyclability, it was concluded that SEI dissolution was a major factor influencing the subsequent SEI formation and growth. In addition, it was elucidated that the calendar life of Li-based batteries can be extended by reducing the SEI dissolution, highlighting the significance of regulating the dissolution phenomenon for mitigating the SEI degradation.

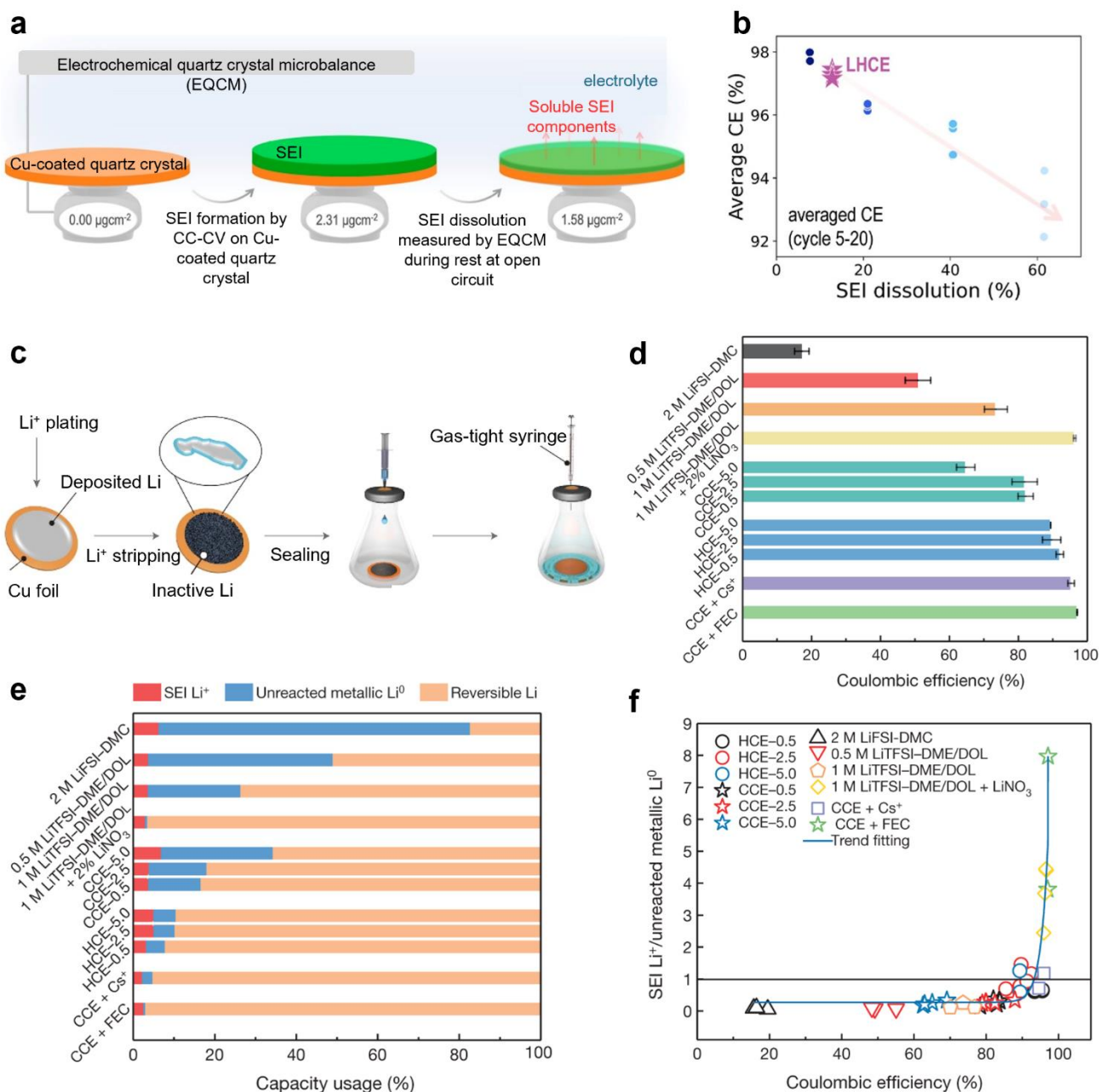


Figure 22. Quantifying the correlation between interfacial chemistry and electrochemical performances by EQCM and TGC methods. (a) The procedure for analyzing the SEI formation and dissolution with EQCM technique. (b) Relationship between the average CE of Li||Cu half-cell, and SEI dissolution results from EQCM. Reproduced with permission from ref ⁴⁵⁰. Copyright 2023 American Chemical Society. (c) Schematic illustration of the working principle of the TGC technique. (d) The average 1st CE of Li||Cu cells with various testing conditions. Eight electrolytes (HCE, CCE, 2 M LiFSI-DMC, 0.5 M LiTFSI-DME/DOL, 1 M LiTFSI-DME/DOL, 1 M LiTFSI-DME/DOL + 2% LiNO_3 , CCE + Cs^+ , and CCE + FEC) and three stripping rates (0.5, 2.5, and 5.0 mA cm^{-2} to 1 V) are used. (e) The TGC method for analyzing the capacity usage (SEI Li^+ , unreacted metallic Li^0 and reversible Li) with various testing conditions. (f) The ratio of SEI Li^+ to unreacted metallic Li^0 calculated by the TGC (The blue line refers to exponential fitting results). Reproduced with permission from ref ⁵⁰⁴. Copyright 2019 Springer Nature.

Utilizing advanced characterization techniques, it has been recognized that establishing the correlation between interfacial chemistry and electrochemical performances is significant for resolving issues related to Li metal anode. Recently, using an analytical technique of titration gas chromatography (TGC), Meng *et*

al. quantified the contribution of Li^+ in the SEI components (*e.g.*, LiF , Li_2CO_3 , Li_2O) and unreacted metallic Li^0 to the total amount of inactive Li, respectively, which was critical for understanding the real mechanisms causing rapid capacity deterioration.⁵⁰⁴ The critical difference exploited between the SEI Li^+ species and metallic Li^0 is their chemical reactivity, where only the metallic Li^0 reacted with protic solvents. For instance, Li^0 reacts with H_2O to create H_2 gas ($2\text{Li} + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH} + \text{H}_2\uparrow$). The H_2O titration (all metallic Li^0 is reacted) was paired with a gas chromatography facility (quantify generated H_2 in the reaction) to a single analytical tool (TGC), exactly quantifying the amount of unreacted metallic Li^0 (**Figure 22c**). Then, a high resolution of 10^{-7} g was obtained for analyzing metallic Li^0 , after combining with an advanced barrier ionization H_2 detector. Using this TGC methodology, the relationship between the amount of inactive Li with the CEs of $\text{Li}||\text{Cu}$ cells in different electrolytes was correlated (**Figure 22d**). By quantifying the amount of metallic Li^0 directly by the TGC, the content of SEI Li^+ was calculated accordingly. Interestingly, as shown in **Figure 22e**, the content of Li^+ components in SEI remained constant at a low level, whereas the amount of unreacted metallic Li^0 increased significantly as the CE decreased. In addition, the ratio of Li^+ components in SEI and unreacted metallic Li^0 elucidated the CE below 95%. It was the unreacted metallic Li^0 rather than SEI formation that dictated the amount of inactive Li, further causing the capacity loss (**Figure 22f**). The SEI formation only dominated at very high CEs. This work provided interesting insights for advancing LMBs. Nevertheless, a non-destructive approach to quantify residual Li upon cycling without disassembling the cell is still urgently required.

3.4.3. Composition Analysis Techniques. To examine the surface chemistry of the interphases, various analysis approaches such as XPS, SIMS, and NMR have been extensively employed in recent research.^{517, 544-550} By utilizing the photons in the X-ray range that lead to the emission of the core electrons from the specimen, XPS has been widely used for detecting all elements in the periodic table except H and He. Therefore, XPS is an ideal technology for monitoring the electronic structures of SEI compositions, such as LiF , Li_2CO_3 , organics, and other species.⁵⁰⁵⁻⁵⁰⁷ In 1985, based on a LiBF_4 -containing electrolyte, the existence of LiF in SEI components was proved for the first time by Takehara *et al.* using XPS.⁴³⁴ Nevertheless, the *ex situ* XPS fails to disclose the natural state and properties of the interphases, making it necessary to develop *in situ* XPS to capture the real-time state of interphases during the battery cycling. Unfortunately, as a surface-sensitive technique with microscale in-plane spatial resolution, *in situ* XPS has yet to be fully designed due to the ultrahigh vacuum condition.⁴⁵⁸

To solve this challenge, *in situ* spectroscopies, such as ambient pressure photoelectron spectroscopy (APPEs), were employed by Hahlin *et al.* (**Figure 23a**), providing insights for future *operando* measurements on the dynamic chemical evolution of SEI.⁴⁵⁹ Although liquid electrolytes could be used in this investigation, the electrochemical cycling tests were not applied, making this technique fail to reflect

the real-time state of SEI in batteries. Despite the extensive application in analyzing the SEI chemical compositions,^{460, 488, 551-555} XPS still exhibited some big challenges related to the sample preparation and data collection protocols, which can lead to misleading conclusions. Recently, an informative and significant work was conducted by Bent *et al.*, identifying some key factors to be carefully considered to avoid erroneous interpretations of XPS for SEI investigation, including the spatial location of the sample, periods of sample inactivity under the ultrahigh vacuum in XPS chamber, and Ar⁺ sputtering conditions.⁴⁶¹ Especially, the poorly rinsed sample introduced artifacts to the SEI components, with a 40% variation across the x-y plane for atomic percentage. It was also pointed out that SEI experienced obvious changes in chemical components with the ultrahigh vacuum condition or Ar⁺ sputtering. This report offered rigorous guidelines to circumvent issues existing in XPS analysis, which will provide valuable guidelines in SEI understanding with accurate chemical characterization.

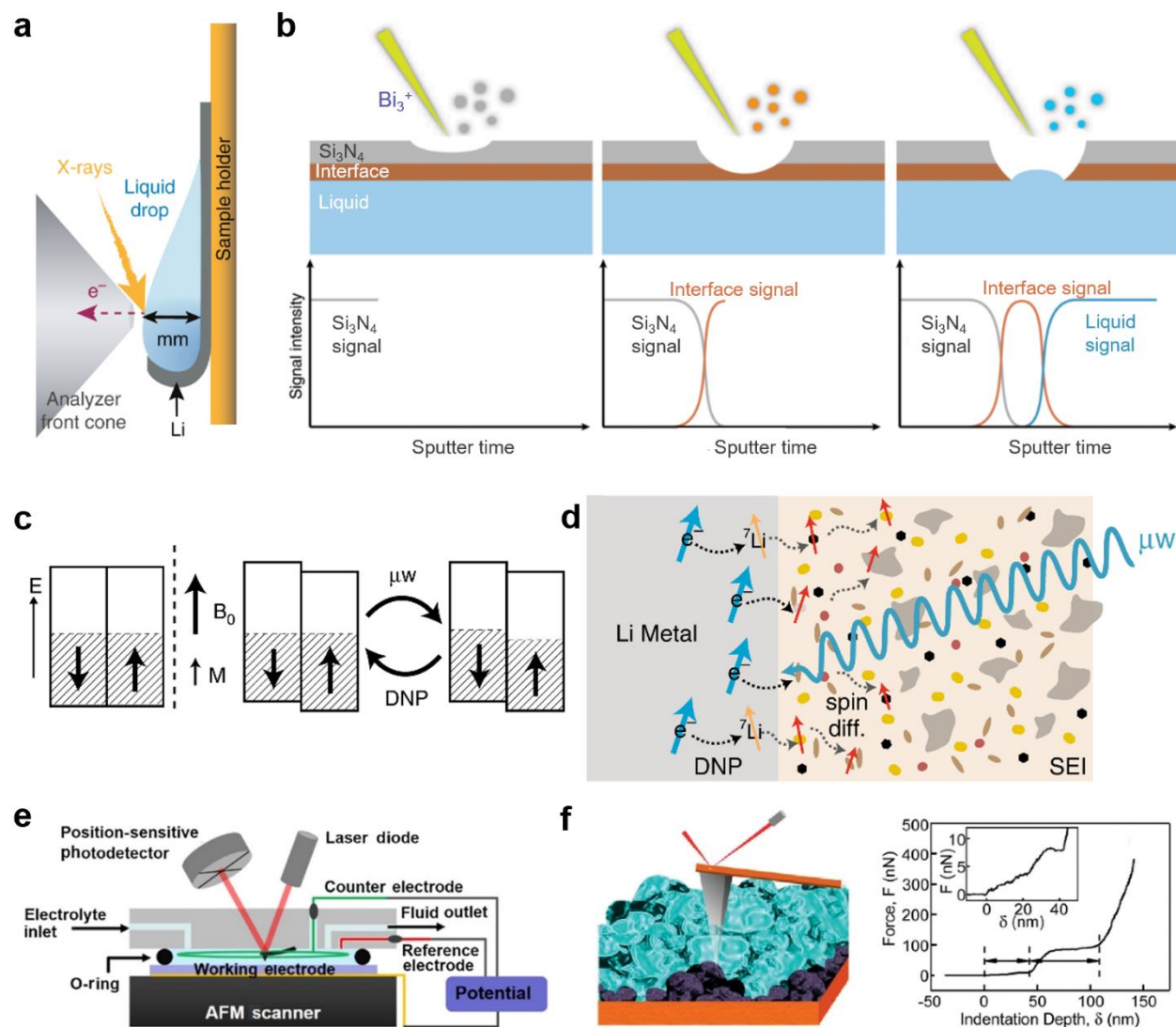


Figure 23. Advanced characterizations for analyzing chemical compositions, morphologies, structural information, mechanical properties, *etc.* for interphases. (a) Schematic illustration of liquid droplets on the Li substrate for APPES

measurements. Reproduced with permission from ref ⁴⁵⁹. Copyright 2019 Springer Nature. (b) Schematic illustration of the developed *in situ* liquid-SIMS technique for SEI characterization. Reproduced with permission from ref ⁵⁰⁹. Copyright 2020 Springer Nature. (c-d) The mechanism of Li metal DNP. (c) The conduction electron spin-bands of a metal, plotted against energy (E): in the absence of a magnetic field (left); (middle) in an applied magnetic field (B_0), leading to a Pauli paramagnetic moment (M); and after microwave (μw) irradiation at the CESR frequency (right). Note: the arrows for each spin-band denote the electron magnetic moment. (d) Schematic for hyperpolarisation of Li metal on application of microwaves (DNP, black dashed arrows) and subsequent spin diffusion in the heterogenous mixed organic/inorganic SEI (grey dashed arrows). Reproduced with permission from ref ⁵⁵⁶. Copyright 2020 Springer Nature. (e) Cross-sectional schematic diagram of an electrochemical AFM cell. Reproduced with permission from ref ⁵¹¹. Copyright 2015 Elsevier. (f) Schematic illustration of the AFM force spectroscopy measurements. Inset gives the indentation curve. Reproduced with permission from ref ⁴⁶². Copyright 2012 American Chemical Society.

Through analyzing the ratio of gravimetric mass to surface charge (m/z) for specific elements, TOF-SIMS has been applied to obtain the chemical compositions of SEIs quantitatively. Generally, when interacting with a surface, the energetic primary ion beam emits secondary ions. These secondary ions pass through a flight tube, and then they are continuously analyzed, with the corresponding intensities being recorded over time. The ion intensities are proportional to element contents, thus forming a semiquantitative concentration-depth image for probing the chemical composition of SEI layers.^{451, 557-559} Peled *et al.* pioneered in applying the SIMS for investigating the mechanism of SEI formation on the basal plane and cross-sectional edge of graphite. Since then, the depth profiling by SIMS has been utilized widely to probe the SEIs generated on Cu,^{452, 560} graphite,^{426, 453, 454, 518, 561-563} Si,^{452, 455, 564-567} Li metal,^{351, 452, 456, 568-571} *etc.*, demonstrating its ability to analyze the dynamic properties of SEI layers with high sensitivity. Especially, the speculating SEI chemical compositions can be confirmed via SIMS by profiling their distribution in depths in the SEI layer. For instance, Wang *et al.* developed a Li-11 wt.% Sr alloy anode to form a SrF_2 -rich interphase in fluorine-containing electrolyte.³²⁵ With the aid of TOF-SIMS, the thickness of the SrF_2 enriched SEI on the alloy anode was determined. After immersing in 2 M LiFSI for 12 h, the anode surface was investigated by beam over a $5\ \mu\text{m} \times \mu\text{m}$ area. Strong signals of both F and Sr were observed with the thickness of the interphase to be 250 nm, which were consistent with the XPS results. In another report, a crowding dilutant (1,2-difluorobenzene) modified ionic liquid electrolyte (M-ILE) with energetic kinetics and superhigh AGG portion was designed for a stable Li metal anode. TOF-SIMS was performed to reveal the distribution of the chemical components in the SEI layer with different sputter times. LiF_2^- intensity was much higher than that for the ILE-induced SEI, confirming the M-ILE electrolyte contributed to a LiF enriched SEI. Besides, the 3D reconstruction of the LiF_2^- distribution map demonstrated that LiF was uniformly dispersed in the M-ILE-induced SEI. However, LiF only existed in the superficial layer of the ILE-derived SEI.⁵⁷² The SEI formation mechanism and the in-depth understanding of the interphasial chemistry and structure are still restricted by the *ex situ* measurements. Inspired by increasing requirements, a real-time SEI formation was monitored by Zhu and co-workers, by developing an *in situ* liquid secondary ion mass spectrometry (liquid-SIMS),^{457, 508, 510} as illustrated in **Figure 23b**. To be specific, firstly, a thin Si_3N_4 membrane was used to separate the liquid from the high vacuum, ensuring only Si_3N_4 -related signals

were detected at the initial stage. Then, the interfacial signals could be detected until a Bi^{3+} primary ion beam drilled through the Si_3N_4 membrane. As soon as the interfacial layer was drilled through by the primary ion beam, the liquid signals were obtained. By bombarding the back of the Cu electrode and creating fragments, the liquid-SIMS induced the dynamic chemical mapping of interfacial components. The liquid-SIMS supported the establishment of an electric double layer before SEI formation. Furthermore, this technique displayed a structured SEI consisted of a dense and inorganic, but LiF-depleted inner layer (electronic insulator whereas Li^+ conductor), along with an organic-rich outer layer.⁵⁰⁹

As a non-destructive technique, NMR spectroscopy has been applied to investigate various SEI components (such as inorganics like LiF (^{19}F), Li_2CO_3 (^{13}C), and organic compounds) via collecting ^1H , ^7Li , ^{13}C , ^{19}F , as well as ^{31}P signals in a time scale. Combining solution with solid-state NMR (ssNMR), Grey *et al.* characterized the soluble and insoluble SEI components derived from FEC decomposition.⁵⁷³ To promote the characterization of organic SEI, ^{13}C -FEC was prepared to conduct ssNMR with enhanced dynamic nuclear polarization (DNP) measurements. Notably, the defluorination reaction of FEC molecule to soluble vinoxyl species (HCOCH_2OR) was detected from the ^1H and ^{13}C NMR. In the following step, they reacted to form both soluble and insoluble branched ethylene-oxide-based polymers, while neither vinoxyl species nor cross-linking units were investigated for the FEC-free electrolyte, suggesting that the generation of cross-linked polymers could be significant for improving the SEI stability on the Si anodes. Besides, Wagemaker *et al.* accessed the spontaneous Li^+ transport via 2D Li-ion exchange NMR, disclosing that Li^+ interfacial transport through the interphase was the major limitation for the Li^+ transport through the Li_2S - $\text{Li}_6\text{PS}_5\text{Br}$ solid-state batteries, which were largely affected by the electrode preparation and battery cycling conditions. For instance, ball milling treatment was required to enable faster Li-ion exchange through the interphase and enhance the kinetics with regard to the high utilization of Li_2S cathode. This report exhibited the ability of exchange NMR as a noninvasive measurement to investigate Li^+ interfacial transport behaviors, quantifying the amount and timescale of Li^+ transport through the interphase in the bulk solid-state batteries.⁴⁷⁹ NMR technique was also applied to determine the cathode-to-anode crossover species that caused the SEI disruption on the Li metal anode and further catalyzed side reactions. It was disclosed that the crossed-over transition metal ions from $\text{LiNi}_{0.9}\text{Mn}_{0.05}\text{Co}_{0.05}\text{O}_2$ cathode exerted minimal impact on the Li metal anode. In contrast, decomposition products such as POF_2OH (doublet of ^{19}F spectra and the triplet in the ^{31}P spectra) and polycarbonates from reactive Li metals crossed over to the cathode side, significantly altered the CEI. As a result, this crossover phenomenon accelerated impedance increase and capacity fading of the cathodes and caused instability of the anodes by dissolving these species into the electrolyte.⁴⁸⁰

Moreover, DNP-enhanced NMR has been recognized as a powerful tool for obtaining useful structural information under magic-angle spinning (MAS), which exploits the $\sim 10^3$ times greater gyromagnetic ratio

of paramagnetic electrons to hyperpolarize nuclear spins to increase the signal in NMR measurements.⁴⁸¹ The mechanism of Li metal DNP is illustrated in **Figure 23c**. Without applying magnetic field, the partially filled up and down electron spin-bands of a metal were degenerated, whereas the energies of these bands were shifted in opposite directions while maintaining a common Fermi level with an applied magnetic field. After Irradiating the conduction electron spin resonance (CESR) transition, the populations of the spin-bands were (partially) equalized. Based on this theory, Grey *et al.* reported the hyperpolarisation by investigating the interphase between Li metal and the SEI (**Figure 23d**).⁵⁵⁶ They selectively enhanced the ^7Li , ^1H and ^{19}F NMR spectra of the SEI species, which provided the chemical nature and spatial distribution of these species. To exploit the significant enhancement of the ^7Li , $^7\text{Li} \rightarrow ^1\text{H}$ cross polarisation (CP), and $^7\text{Li} \rightarrow ^{19}\text{F}$ CP, ^7Li rotational echo double resonance (REDOR) experiments were conducted, successfully identifying some SEI species, such as polymeric compounds, organic carbonates and LiF. *In situ* measurements based on this technique will be more informative in identifying chemical compositions and structures of the interphases in rechargeable batteries. Reduced collection time and enhanced signal-to-noise ratio of ^{13}C to confirm organic species in SEI are among the most prominent advantages of the DNP technique. Unfortunately, it fails to probe the dynamic nature of the interphase, which requires the combination of NMR and cryogenic techniques. Moreover, *in situ* NMR has been realized for probing the real-time SEI evolution in batteries. The differences in plating processes and transport properties of the interphase in commercial electrolytes (1 M $\text{LiPF}_6\text{-EC/DMC}$) without and with FEC additive were investigated via *in situ* NMR. The $^6,^7\text{Li}$ isotopic labelling was employed to monitor the exchange between the bulk Li metal and the electrolyte via NMR, and a numerical model was developed to describe the process. It was revealed that compared to those of the FEC-free electrolytes, the $^6\text{Li}/^7\text{Li}$ exchange was twice as fast in FEC-containing electrolyte with a much faster SEI formation rate, which could account for a more uniform Li deposition behavior. The authors also use this *in situ* NMR technology to quantify some critical SEI parameters for regulating the nature of Li deposition, such as the Li^+ transport and the healing rate of SEI. Other electrolyte additives or components should be explored via this methodology to optimize SEIs for uniform Li plating/stripping under practical conditions in the future.⁴⁸² It should be noted that a strict observation condition should be satisfied to avoid interfering signals when conducting the *in situ* NMR for real-time monitoring of SEI during cycling.⁴⁸⁷

3.4.4. Functional Features Analysis Techniques. Based on the scattering of X-rays, the interference of which produces diffraction patterns from crystalline or partial crystalline structured materials, XRD has been widely employed to investigate the changes in crystal structures as well as phase transformations of electrode materials or the ordering and structures of interphases. For instance, according to the analysis of XRD, Huang and coworkers exhibited that the byproducts LiOH derived from side reactions between Li

and oxygen-containing electrolyte was significantly suppressed via boric acid (BA) additive, suggesting the beneficial role of BA in inhibiting unwanted side reactions for high-performance Li-based batteries.⁴⁷⁶ In addition, different SEI formation processes with 0.8 M KPF₆-EC/EMC and potassium bis(fluorosulfonyl)imide (KFSI)-EMC (molar ratio of 1:2.5) electrolytes were investigated via *operando* XRD, revealing that the SEI mainly formed at high voltage in KFSI-based concentrated electrolyte, while the SEI mainly generated at low voltage in KPF₆ based dilute electrolyte.⁴⁷⁷ However, as a technique to monitor the bulk information of the electrode, it is difficult for XRD to distinguish specific interactions on the interphases. Recently, the synchrotron-based X-ray sources with much higher intensities and larger photon energies than laboratory equipment have been recognized as a powerful technique for *in situ/operando* investigations of battery systems, due to the benefits of fast period of measurement times, large penetration power, along with improved signal-to-noise ratios.⁴⁷⁷ Therefore, the synchrotron-based XRD is able to collect high-quality data for a trace amount of sample without significant radiation damage.⁴⁷⁸ In 2021, using synchrotron-based XRD and PDF analysis, Hu *et al.* identified and differentiated two elusive components, LiH and LiF, in the SEI components of Li metal anodes.⁵⁷⁴ As revealed from the synchrotron-based XRD, LiH existed as a face-centered-cubic (FCC) phase with a lattice parameter of 4.084 Å, which was further confirmed by the changes in XRD patterns due to its moisture sensitivity. The origins of LiH not being identified could be attributed to two main factors. Firstly, the typical XRD patterns of LiH and LiF were similar FCC structures with close lattice parameters (4.084 Å for LiH and 4.026 Å for LiF). Besides, owing to the high moisture sensitivity, LiH easily decomposed to make it undetectable. It was also found that the nanocrystalline LiF in SEI components is clearly different from that in the bulk phase, especially featuring a larger lattice parameter (~ 4.05 Å) along with a smaller particle size (<3 nm), which enables fast Li⁺ transport for higher CE and improved electrochemical performance. It should be noted that the beam may easily lead to the damage of battery materials during testing.

As a non-destructive imaging approach, *in situ* AFM can monitor the formation and properties of interphases through high-resolution topographical images, providing inter-topography information and mechanical properties. For instance, the elastic and plastic properties of the interphases can be evaluated in a quantitative way by analysis of the force-distance curves.⁵¹¹ In addition, to investigate the nanomechanics of interphases, AFM-nanoindentation was designed as illustrated in **Figure 23f**. Through converting the tip deflection into normal force F and analyzing indentation depth δ and the cantilever deflection Δd , the Young's modulus can be obtained as shown in the inset of **Figure 23f**, successfully quantifying the inhomogeneity of SEI in both morphological and mechanical properties.⁴⁶² Following this work, more systematic investigations of SEI information have been conducted, including the two-layered structure and the thickness of the SEI on graphite anodes,⁵⁷⁵ mechanical properties of the organic-inorganic mixed SEI on Si anode,⁵⁷⁵ the effects of electrolyte components, configurations and electrode face orientation on the

SEI morphology and thickness,^{463-465, 576} the deformation and mechanical failure mechanism of SEI,⁵¹² *etc.* Among these progresses, it is interesting to mention that the *in situ* AFM is powerful enough to distinguish the distributions of inorganic and organic species in the SEI at the nanometer level by probing the SEI in liquid electrolytes.

Unfortunately, the failure to unveil chemical information is a large limitation facing the AFM technique. To satisfy the nanometer spatial resolution required to disclose the correlation between the structure and function in the interphases, the tip-enhanced Raman spectroscopy (TERS) was developed.^{466, 514, 515} Through raster scanning the interphase, the chemical fingerprint of the interphases can be obtained. Besides, the TERS offers a spatial resolution at several nanometers or even on a sub-nanometer scale, which is attributed to the highly confined local electric field.⁴⁶⁷ Therefore, the TERS has been regarded as an effective technique for understanding the interphase as well as interfacial processes at the nanometer spatial resolution, eventually establishing the relationship between the structure and performance. Although with a high spatial resolution, the one-point foundation makes inherently weaker signals for TERS technique compared with Surface-enhanced Raman scattering (SERS), making it necessary to increase the efficiency of TERS on motivation and collection when used to probe the interphases. Besides, to monitor the dynamic evolutions of the interphase structures and further quantify the interphase compositions at the nanometer spatial resolution and the molecular level, the TERS should be developed into an *operando* technique.⁵⁷⁷

As a scattering technique, the NR measures the specular reflection of neutrons from the surface, which changes with the wave vector transfer perpendicular to the sample surface, following the equation $Q = [4\pi \sin(\theta)]/\lambda$ (θ represents the angle of incidence neutron beam with sample surface; λ denotes the wavelength of neutrons).^{578, 579} The thickness, roughness, as well as the layers' scattering length density (SLD) can be obtained by fitting the reflectivity via layered models, which is informative for determining layer compositions. Therefore, the NR has been growingly employed for probing interphasial properties of batteries.^{474, 516}

Particularly, the SLD depth profile yielded from fitting NR data in the surface normal direction can be used to detect the evolutions of the interphase structure during the charging/discharging process.⁴⁷³ By using the *in situ* NR and a novel designed electrochemical cell, Schmidt *et al.* detected the growth of a ~ 7 nm thick SEI layer during delithiation of Si electrode.⁵⁵⁰ Later on, the thickness and chemistry of the SEI on a Si anode were determined as a function of the state of charge during cycling. Based on the SLD results, the SEI thickness decreased from 25 nm to 18 nm ($\text{Li}_{3.7}\text{Si}$) after delithiation process. Besides, the SEI evolved with more LiF component during lithiation, while more Li-C-O-F like species was discovered during delithiation. More importantly, the SEI started to grow once the electrolyte was in contact with the Si electrode, even no electrical bias was applied.⁵⁸⁰ An opposite trend in SEI thickness was presented by Veith *et al.*, who investigated the SEI on Si anodes using the electrolyte of 0.1 M LiTFSI in deuterated dimethyl

perfluoroglutarate.⁵⁸¹ Based on the corresponding SLD profiles, they observed a decrease in the thickness of the SEI layer from 34 to 14 nm after lithiation process. Moreover, the *in situ* NR revealed the SEI formed on tungsten thin film electrodes was composed of a porous outer layer enriched in solvent-derived components and a compact inner layer with abundant inorganic species.⁴⁷⁴ Following this work, the tungsten oxide (*e.g.*, WO₃) was demonstrated to form SEI with three layers during the reduction process. An innermost layer (the evolving conversion electrode) was assigned to a mixture of W, Li₂O and incompletely reacted WO₃ or Li_xWO₃; a layer enriched in protons and/or Li, which tentatively consisted of LiOH or LiH (the inner SEI); an outermost layer adjacent to the electrolyte consisted of lower SLD species with solution-filled porosity or deuteron-rich species derived from the solvents (the outer and fragile SEI). A reverse of SEI evolution was observed during the oxidation process. These results were generally consistent with previous reports of SEI using other characterizations, indicating a bilayer structure of SEI with more inorganic species in the inner layer and more organic components in the outer layer.⁴⁷⁵

Overall, *in situ* NR sheds light on the study of the SEI generation mechanism by probing the evolution of interphase structure during battery operation. Unfortunately, its widespread application is significantly restricted by several factors, such as a long analysis time, an excessive choice of electrolyte solvents to enhance contrast, a flat specimen required to generate a strong signal, and very limited facilities to handle the produced neutrons outside the particle accelerator.⁴³⁷

To investigate various functional and morphological features of the interphases, other characterizations that can offer complementary information have also been developed. For instance, in contrast to the XRD providing information about the overall structure of a material, the XAS has been considered as an effective technique to probe the local atomic arrangement and electronic structure of a material. The XAS technology is based on X-ray photon induced electronic excitations from the core level to an empty electronic state for the detected element. Thanks to its element-resolved feature and high sensitivity to the local chemical bonds and solvent environments, the XAS measurement shows great potential for interphase characterizations.^{468-470, 582} Additionally, this technique can be used for determining amorphous phases as well as for small nanoparticles. Owing to the utilization of high-energy synchrotron radiation, data acquisition process is quite fast, which promotes the *in situ* analysis as well.^{583, 584} Although the XAS has been successfully used for analyzing the SEI compositions, the *in situ* XAS probing in a full-cell mode remains a big challenge, which requires a special electrochemical cell design.^{471, 472, 517-520}

The SECM is considered a powerful tool that can probe the surface characteristics of the interphases with nanoscale resolution. The SECM relies on the stark difference in activities between the electronically conductive electrode surface and the electronically insulating feature of SEI products.^{483, 484} The basic setup of SECM consists of four parts: a low current bipotentiostat, a 3D positioning system, an ultramicroelectrode tip, and a data acquisition system.⁴⁸⁵ The cell generally contains four electrodes,

including the tip, the reference electrode, the counter electrode, and the working electrode. The SECM tip probes the chemical changes occurring at the interphase and detects spatial information of electrochemical reactions taking place at selected areas.⁴⁸⁴ The SECM has attracted increasing attention in investigating the formation and evolution of SEI layers by employing the feedback mode.⁴⁸⁴ For instance, using the feedback mode of SECM with 2,5-di-tert-butyl-1,4-dimethoxy benzene (DBDMB) as the mediator, Wittstock *et al.* conducted *in situ* imaging of the spontaneous spatiotemporal changes for SEI layers formed on the graphite surface. The reduction in the mediator regeneration rate was accompanied by the SEI formation. Besides, the currents remained stable in some regions of the SEI-covered electrodes, while the currents in other regions changed drastically with time. These changes could be attributed to the volume evolutions during charging/discharging, dissolution of SEI, or gas formation. In addition, results show that deposition of metallic Li could take place upon charging and compromise battery safety, requiring the self-healing ability of SEI with incidental defects. Moreover, the re-passivation of damaged regions was detected *in situ*, which showed that it took several hours before these regions were susceptible to further short-term current fluctuation.⁴⁸⁶ Later, *operando* SECM was adopted by Schuhmann *et al.*, probing the electrically insulating feature of the Si surface during de-/lithiation process. Combined with AFM, the SECM results suggested that there were two types of cracks (*i.e.*, cracks partially covered by SEI and SEI-free cracks) during the initial cycle. The SEI-free cracks contributed to a discontinuity in the electrically insulating feature of the Si surface, further accelerating the electrolyte decomposition in the second cycle. More importantly, the *operando* SECM confirmed the electrically insulating feature of the SEI layer on the Si electrode, and the volume changes during the de-/lithiation process were the reason that caused the loss of “protecting” character of the SEI at the Si surface.⁵⁸⁵

In brief, to address fundamental questions regarding chemical composition, spatial distribution, and structure of fluorinated interphases, non-destructive and *in situ/operando* techniques are essential for real-time, dynamic, and intuitive analysis of interphase properties and their correlation with the battery performance. Taking cryo-TEM as an example, the combination of low electron dose and ultra-low temperature for sample frozen reveals atomic-level crystal details, which preserves delicate chemical and spatial features of interphases. For high-resolution imaging of interphasial evolution, dynamic *in situ* cell devices and sophisticated sample preparation techniques (*e.g.*, cryo-FIB) should be equipped. It should be kept in mind that each technique has its unique advantages and significant limitations, requiring the synergistic combination of various techniques, which yields multidimensional or multimodal information for elucidating structure-property relationships and guiding interphase design.

4. Fluorine Chemistry in Rechargeable Fluoride-Ion Batteries

4.1. Fluoride Electrode Materials

The electrode material for FIBs can release or absorb F^- ions while obtaining or losing electrons. Depending on the redox potential, the electrode materials for FIBs are utilized as cathodes with relatively high potential or anodes with relatively low potential. Due to the relatively light weight of the electrode materials in FIBs, the theoretical volumetric energy densities of FIBs can reach up to $5,000 \text{ Wh L}^{-1}$ based on the total volume of electrode materials³⁸, which makes FIBs a promising candidate for the next-generation high-energy rechargeable batteries. So far, the mechanism of F^- ions storage of electrodes in FIBs can be mainly classified into conversion-type and intercalation-type, which are further introduced below.

4.1.1. Conversion-Type Electrode Materials. The fluorination/defluorination process of conversion-type electrode materials (*e.g.*, metal/metal fluorides) is accompanied by continuous breaking or reforming of the metal-fluorine bond. Conversion-type electrode materials for FIBs possess high energy density because they are able to transport more than one F^- ion per redox-active metal species, and the active electrode materials typically possess lower molar masses.

Metal/metal fluorides (M/MF_x) are the most extensively studied conversion-type electrode materials for FIBs. The electrons and F^- ions transfer during the fluorination/defluorination between metal and metal fluorides. In 2011, M. Fichtner and M. Anji reported the feasibility of a series of metal fluorides (including SnF_2 , CuF_2 , KBiF_2 , and BiF_3) as cathode materials in an all-solid-state FIBs system with a F^- ion solid-state electrolyte $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ ($0 \leq x \leq 0.15$) at 150°C .⁴³ Cerium (Ce) metal was used as the anode due to the high F^- ion conductivity of its discharge product (cerium fluoride, CeF_3).⁵⁸⁶ The F^- ion full cell using BiF_3 as a cathode successfully realized reversible discharge and charge at $10 \mu\text{A cm}^{-2}$ with a discharge capacity of 190 mAh g^{-1} and an average voltage of 2.15 V . However, the irreversible volume changes, as a common problem of conversion-type electrode materials, limit the cycling performance of FIBs. Apart from Ce metal anode, M. Fichtner and co-workers investigated the application of other potential anode materials such as CaF_2 , MgF_2 , and $\text{Mg} + \text{MgF}_2$ (*i.e.*, the pre-mixed composite of metal and metal fluoride, $M + MF_x$) for all-solid-state FIBs in 2014.⁵⁸⁷ When paired with bismuth (Bi) cathode, the $\text{Mg} + \text{MgF}_2$ composite anode delivered an initial discharged specific capacity of about 80 mAh g^{-1} at 4 mA g^{-1} and 150°C (**Figure 24a**). It revealed that the $M + MF_x$ composite anode can effectively enhance cycling performances by improving interphase contacts between the reactive phases. In general, the low conductivity of metal fluorides and the extreme volume change during the fluorination/defluorination process of $M + MF_x$ electrodes cause the massive side reactions⁵⁸⁸ together with poor physical contact between active materials,⁵⁸⁹ electrolytes, and conductive carbon particles, both of which lead to rapid capacity decay of FIBs.

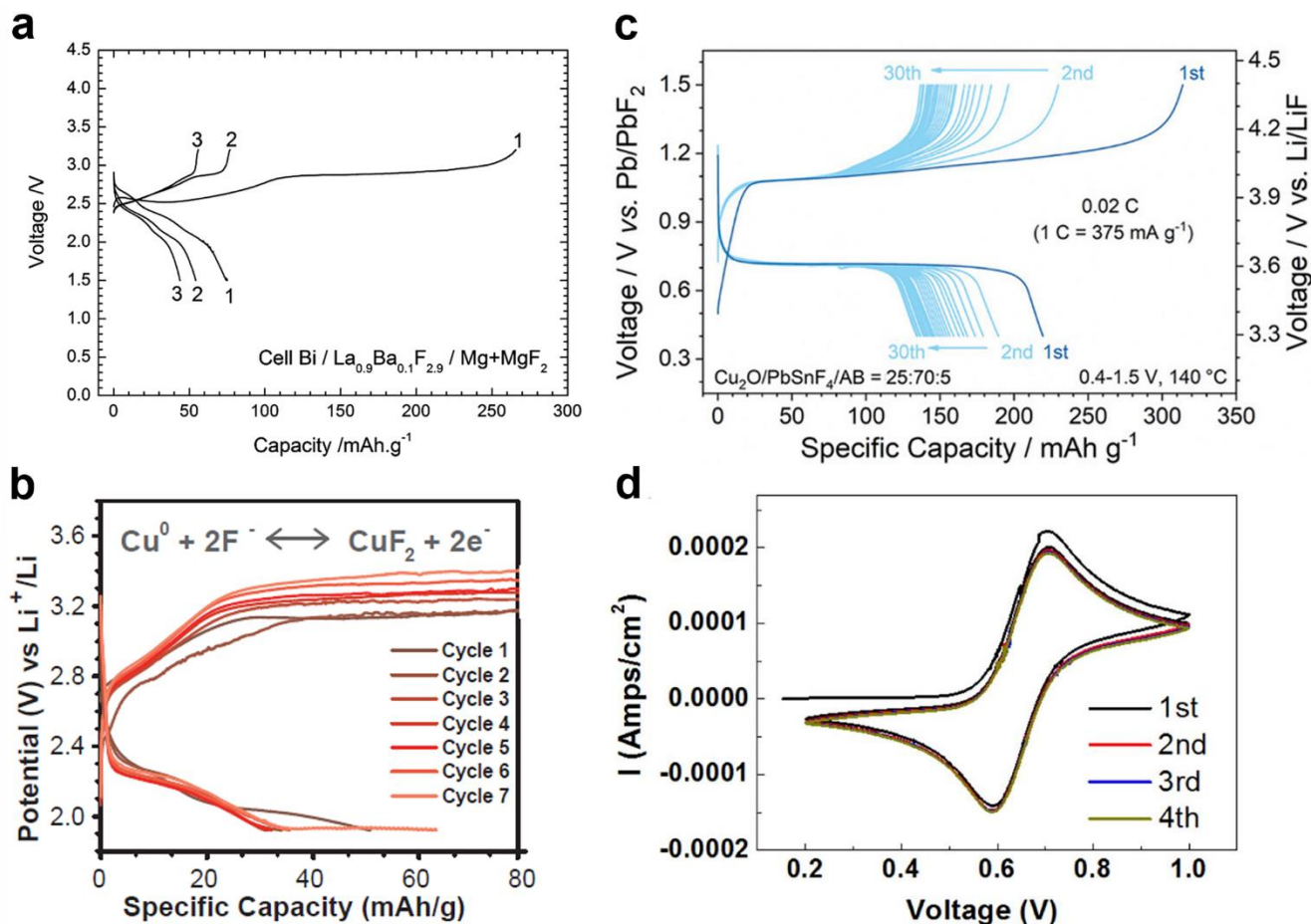


Figure 24. Conversion-type of electrode materials for FIBs. (a) Voltage-composition profiles for a FIB with the Bi cathode vs. Mg+MgF₂ anode in the three first cycles. The charge/discharge curves were obtained at 150 °C for a current density of *ca.* $\pm 4 \text{ mA g}^{-1}$. Reproduced with permission from ref ⁵⁸⁷. Copyright 2014 Royal Society of Chemistry. (b) Electrochemical charge and discharge curves for a three-electrode cell with Cu@LaF₃ cathode in 1 M N,N,N-trimethyl-N-neopentylammonium fluoride (Np₁F)- BTfE, cycled at 10 mA. Reproduced with permission from ref ⁵². Copyright 2018 The American Association for the Advancement of Science. (c) Charge/discharge profiles of Cu₂O cathode material for cycles 1–35 at 0.02 C and 140 °C. Reproduced with permission from ref ⁵⁹⁰. Copyright 2021 Wiley-VCH. (d) CV curves of 4-hydroxy-TEMPO in aqueous 0.8 M NaF electrolyte with glassy carbon as the working electrode, platinum as the counter electrode and the standard Ag/AgCl electrode as the reference electrode. Reproduced with permission from ref ⁵⁹¹. Copyright 2019 IOP Science.

M/MF_x has also been applied in liquid FIBs. Simon and co-workers reported room-temperature operable FIBs based on organic solvent-based electrolyte in 2018.⁵² In this system, a copper-lanthanum trifluoride core-shell cathode was developed, where the F⁻ ion conductive LaF₃ shell not only permitted F⁻ diffusion, but also inhibited the dissolution of the discharge product (CuF₂). The Cu@LaF₃ cathode achieved seven reversible cycles in liquid FIBs at room temperature in a three-electrode cell (**Figure 24b**).

Metal oxide-based electrodes have been developed as a new conversion-type electrode material. In 2021, Y. Uchimoto and co-workers reported the cuprous oxide (Cu₂O) cathode with Cu⁺/Cu²⁺ redox as a fast fluorination cathode material for all-solid-state FIBs.⁵⁹⁰ As shown in **Figure 24c**, the Pb/PbF₂|PbSnF₄|Cu₂O cell delivered an initial discharge specific capacity of 220 mAh g⁻¹ at 0.02 C (1 C = 375 mA g⁻¹) and

maintained stable after the stabilization of partially irreversible amorphization phase. The superior rate capability of Cu₂O cathode (110 mAh g⁻¹ at 1 C) surpassed the simple M/MF_x systems, which can be attributed to the fast F⁻ ion movement on the phase boundary.

An organic compound with radical groups has also been investigated as the electrode material for FIB. In 2019, F. Chen and co-workers reported the utilization of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (4-hydroxy-TEMPO) cathode in an aqueous rechargeable FIB.⁵⁹¹ The reaction mechanism of 4-hydroxy-TEMPO is as follows:



Where the electrostatic balance of 4-hydroxy-TEMPO was maintained by the transfer of the fluoride ions and electrons. The redox peak pairs at 0.706 V and 0.594 V in cyclic voltammetry (CV) curves (**Figure 24d**) can be distributed to the conversion between 4-hydroxy-TEMPO and 4-hydroxy-TEMPO⁺F⁻. When paired with a BiF₃ anode in a NaF water solution electrolyte and cycled between 0.0–1.4 V, this aqueous FIB delivered an initial discharge specific capacity of 145.3 mAh g⁻¹ at 1000 mA g⁻¹.

4.1.2. Intercalation-Type Electrode Materials. Different from the conversion-type electrodes, F⁻ ion can be reversibly stored in or released from the unoccupied interstitial sites or anion vacancies in the crystal structure of the intercalation-type electrodes for FIBs. Thus, the structural integrity of the intercalation-type electrode can be maintained due to the slight volume change during the intercalation/deintercalation of F⁻ ion, which ensures high-reversible cycling stability and good rate performance of FIBs.

Recently, F⁻ ion-intercalated CoFe layered double hydroxide (CoFe-F LDH) was reported as cathode materials for FIBs. Zhang and co-workers prepared the CoFe-F LDH through a facile co-precipitation approach combined with an ion-exchange method (**Figure 25a**) and successfully paired this material as a cathode with a Li metal anode in a CsF-based organic liquid electrolyte.⁵⁹² The Li||CoFe-F LDH cell delivered a stable specific capacity of 48.9 mAh g⁻¹ during 100 cycles at 10 mA g⁻¹ under room temperature (**Figure 25b**), owing to the unique topochemical transformation property and small volume change (~ 0.82%) of CoFe-F LDH materials accompanied by electrochemical intercalation/intercalation of F⁻ ions. Moreover, the good rate performances of CoFe-F LDH indicated that the mitigation of F⁻ ion in the layer spacing was facilitated by the weak electrostatic interaction between anions and host layers with a low diffusion barrier.

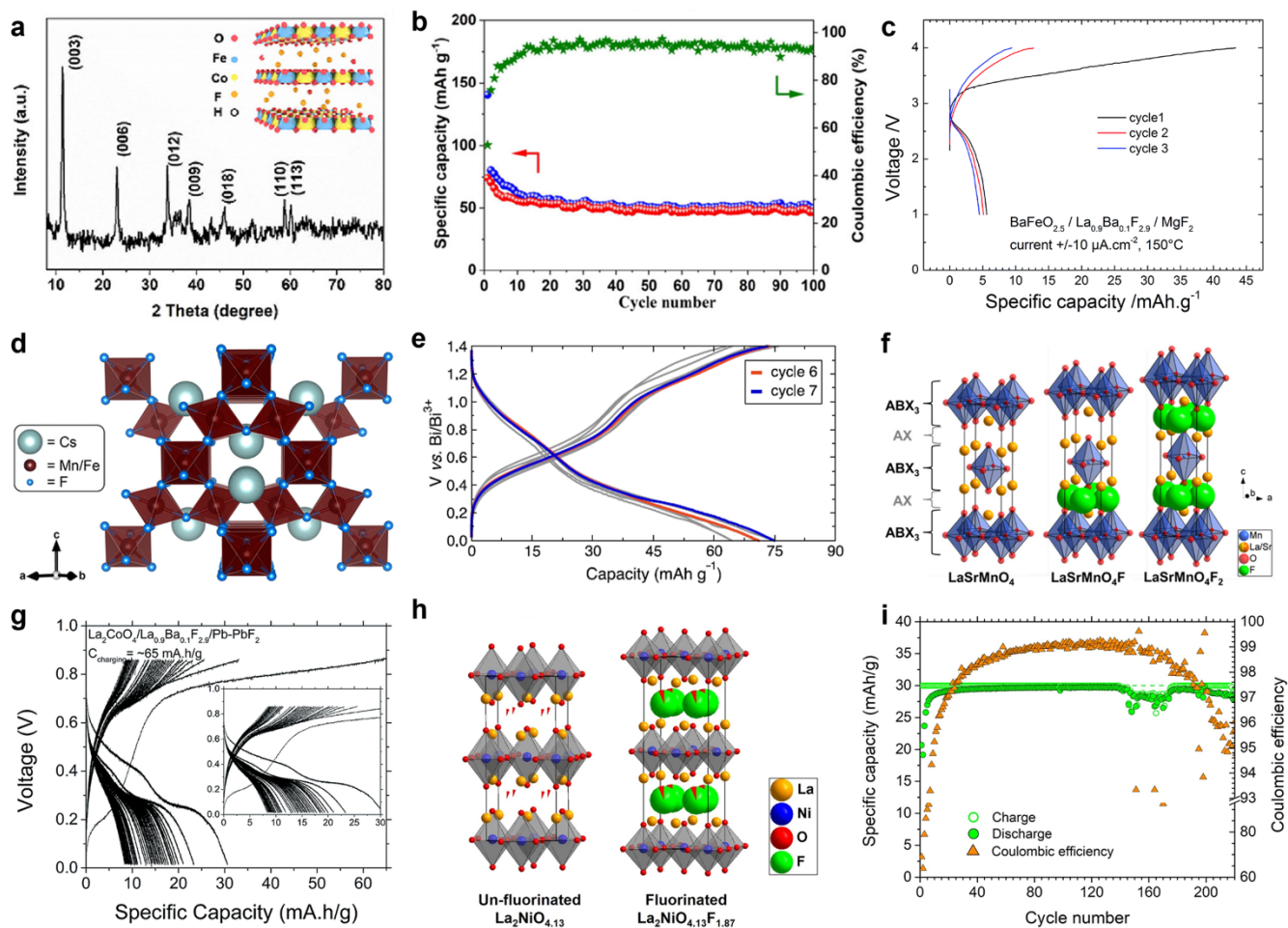


Figure 25. Interconversion-type of electrode materials for FIBs. (a) XRD pattern of CoFe-F LDH (inset: structural model). (b) Cycling performance and CE for the cell Li||CoFe-F LDH. Reproduced with permission from ref ⁵⁹². Copyright 2022 Wiley-VCH. (c) Voltage profiles measured during three charge/discharge cycles for the cell BaFeO_{2.5}/La_{0.9}Ba_{0.1}F_{2.9}/MgF₂ (current ±10 μA cm⁻² at 150 °C). Reproduced with permission from ref ⁵⁹³. Copyright 2014 Royal Society of Chemistry. (d) Crystal structure of the defect fluoride pyrochlore CsMnFeF₆, viewed down the [110] direction. (e) Cycles 4–9 from galvanostatic cycling of a F-ion cell, with a working electrode of mechanochemically synthesized CsMnFeF₆ and a Bi/BiF₃ composite counter electrode, cycled at room temperature at a rate of C/20 between 0.0 and 1.4 V vs Bi/BiF₃. Cycles six and seven are shown in orange and blue, respectively. Reproduced with permission from ref ⁵⁹⁴. Copyright 2022 American Chemical Society. (f) K₂NiF₄ type structure of LaSrMnO₄ (left) in comparison to partly fluorinated LaSrMnO₄F (middle) and fully fluorinated LaSrMnO₄F₂ (right). Reproduced with permission from ref ⁷². Copyright 2017 American Chemical Society. (g) Electrochemical charging and discharging of La₂CoO₄/La₂CoO₄F at 170 °C; I_{charging} = +10.0 μA, I_{discharging} = −1.0 μA. Reproduced with permission from ref ⁵⁹⁵. Copyright 2019 Wiley-VCH. (h) Schematic illustrations of the un-fluorinated La₂NiO_{4.13} (left) and the hypothetical fully fluorinated state La₂NiO_{4.13}F_{1.87} (right). Fractional occupancies are depicted for the interstitial anion site. (i) Charge/discharge capacities and CE against cycle number for the cells with the cutoff capacities of 30 mAh g⁻¹ at T = 170 °C, I_{charge} = +24 μA cm⁻², I_{discharge} = −12 μA cm⁻², and cutoff charge voltage = 2.3 V. Reproduced with permission from ref ⁵⁹⁶. Copyright 2020 Springer Nature.

The perovskite-type BaFeO₂ was reported as an intercalation-type electrode material for FIBs by Oliver and co-workers in 2014.⁵⁹³ At first, they demonstrated that BaFeO_{2.5} can be directly fluoridated by heating BaFeO_{2.5}F_{0.5} in F₂. The transformation of the monoclinic distorted phase to the cubic perovskite phase in the XRD pattern indicated the successful intercalation of the F⁻ ion into the sub-crystalline vacancies in BaFeO_{2.5}. Then, the MgF₂/La_{0.9}Ba_{0.1}F_{2.9}/BaFeO_{2.5} solid-state FIB was assembled and cycled between 3–4 V at 150 °C. As shown in **Figure 4c**, the long charge plateau at the initial cycle was attributed to the formation

of a Fe^{4+} containing phase fraction of a $\text{BaFeO}_{2.5}\text{F}_y$ compound, where the XRD pattern of electrochemical fluorination was consistent with that of the chemical fluorination result. However, the low reversible capacity in the following cycling suggested that the F^- ions were not fully deintercalated from the $\text{BaFeO}_{2.5}\text{F}_y$ cathode, which may be caused by the contact problems in the electrodes and side reactions of conductive carbon.

Likewise, CsMnFeF_6 was investigated as cathode materials for room temperature FIBs by Jessica and co-workers in 2022.⁵⁹⁴ CsMnFeF_6 in a defect pyrochlore structure with suitable particle size and phase purity was obtained through a mechanochemical method. The presence of Frenkel defects was required to endow F^- ion's diffusion through the network, so the defect pyrochlore $\text{CsMn}^{2+}\text{Fe}^{3+}\text{F}_6$ (**Figure 25d**) with the disorder in the MnFeF_6 substructure and ordered anionic vacancies became a suitable fluoride intercalation host allowing fast F^- ion transport at room temperature. After combined with an organic liquid electrolyte (1.0 M tetra-n-butylammonium fluoride (TBAF)-THF) and cell activation cycles, the half-cell delivered a reversible capacity of 70 mAh g^{-1} at room temperature with a high CE of 98% (**Figure 25e**), which almost approached the theoretical capacity for one fluoride ion transportation. *Ex situ* XRD and *ex situ* XAS revealed that the CsMnFeF_6 underwent a topotactic transformation from the original defect pyrochlore structure into a related polytype, meanwhile, the $\text{Fe}^{3+/2+}$ and $\text{Mn}^{3+/2+}$ redox couples both functioned during the cycling.

Oliver and Co-workers reported the investigation of LaSrMnO_4 with K_2NiF_4 type structure as an intercalation-based high voltage cathode material with high capacity for FIBs in 2017.⁷² As shown in **Figure 25f**, the structure of K_2NiF_4 type compounds (A_2BX_4) can be described as built up by alternating layers of ABX_3 perovskite-type subunits and AX rock salt subunits along the c-axis. The large interstitial sites that can store anions existed between the boundary of the rock salt and perovskite phase layers. The highest F^- ion occupied interstitial sites (Y) per formula unit was 2, which resulted in the composition of $\text{A}_2\text{BX}_4\text{Y}_2$. Pb-PbF_2 anode was paired with the $\text{LaSrMnO}_4\text{F}$ cathode with the $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$ solid-state electrolyte and the full cell was tested at $10 \mu\text{A}$ under 200°C . Combined with the results of electrochemical data, XRD spectra and DFT calculations, two charge voltage plateaus at 1 V and 2 V were confirmed as the first and the second steps of F^- ion intercalation ($\text{LaSrMnO}_4 \rightarrow \text{LaSrMnO}_4\text{F}$ and $\text{LaSrMnO}_4\text{F} \rightarrow \text{LaSrMnO}_4\text{F}_{2-x}$, $x \sim 0.2$). It is worth noting that the side reaction, fluorination of conductive carbon in cathode, along with the charging process resulted in an overcharge capacity of 800 mAh g^{-1} , which was much higher than the theoretical capacity (155 mAh g^{-1}) of two F^- ions transfer from $\text{LaSrMnO}_4 \rightarrow \text{LaSrMnO}_4\text{F}_2$. Moreover, the fluorination of conductive carbon also deteriorated electron transfer in the cathode, which then led to the low reversible discharge capacity of 20 mAh g^{-1} .

To overcome this side reaction issue, Oliver and co-workers replaced the redox pairs of $\text{Mn}^{3+}/\text{Mn}^{4+}$ with $\text{Co}^{2+}/\text{Co}^{3+}$ to reduce the oxidation potentials in the K_2NiF_4 type compounds.⁵⁹⁵ The obtained intercalation-

type cathode La_2CoO_4 showed a lower F^- ion interaction number of 1.2 per formula in the same battery system with LaSrMnO_4 . The unwanted side reactions in the cathode were effectively avoided by adjusting the charge cut-off capacity of 65 mAh g^{-1} , which delivered a better discharge capacity of 32 mAh g^{-1} with a capacity retention of $\sim 25\%$ for the initial discharge capacity after 50 cycles (**Figure 25g**). However, although the side reaction has been suppressed by a cut-off charge voltage of 1 V, the low discharge capacity of $\text{La}_2\text{CoO}_4\text{F}_{1.2}$ indicated that part of F^- ions were irreversibly fixed in the layered cathode, which was supported by the XRD structural analysis.

Then, Oliver and Co-workers developed a high voltage intercalation-type cathode ($\text{La}_2\text{NiO}_{4+d}$) and achieved an all-solid-state FIB with high cycling stability and a CE closed to 100%⁵⁹⁶. As shown in **Figure 25h**, the $\text{La}_2\text{NiO}_{4.13}$ was successfully synthesized by a solid-state method, which delivered a maximum theoretical capacity of 125 mAh g^{-1} after charging into $\text{La}_2\text{NiO}_{4.13}\text{F}_{1.87}$, where all empty interstitial anion sites were filled by F^- ions. When a charge cutoff capacity of 30 mAh g^{-1} was applied, the $\text{Zn}/\text{ZnF}_2|\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}|\text{La}_2\text{NiO}_{4+d}$ cell reached an average CE of 97.68% over 220 cycles (**Figure 25i**). Evidence from TEM images, automated diffraction tomography (ADT), EDX spectroscopy and XAS indicated that the interstitial sites in $\text{La}_2\text{NiO}_{4.13}$ cathode were nearly fully occupied by F^- ions, leading to the formation of high fluorine content phase of $\text{La}_2\text{NiO}_{4.13}\text{F}_{1.59}$. However, although the lower-reactive CNTs were used as conductors in the cathode, the side reaction did not stop in the charge process, as verified by the electrochemical impedance spectroscopy (EIS) and XPS test. Therefore, strategies aiming at improving the stability of interphase between active materials and carbon-based additives in electrode composites (*e.g.*, coating techniques or advanced engineering) should be further developed for the development of FIBs.

In general, the conversion-type materials degrade fast due to poor interphase contacts originating from the significant volume change, incomplete conversion reaction, electrode material dissolution, irreversible generation of oxyfluoride byproducts, while intercalation-type materials are limited by the relatively low capacity and low energy density. Moreover, side reactions between conductive carbons and fluorides in the electrode continuously degrade the performance of FIBs.

4.2. Fluoride Electrolytes

4.2.1. Solid-State Electrolytes. Since the pioneering work by Fichtner *et al.*, which demonstrated the first rechargeable FIBs employing $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$ solid electrolyte, there has been attracted extensive interest in the F^- -conducting solid-state electrolytes. Generally, the F^- -ion conducting solid electrolytes can be categorized into tysonite-type structure (rare-earth fluorides MF_3 , $\text{M} = \text{La, Ce, Pr, Nd}$), fluorite-type structure (alkaline-earth fluorides MF_2 , $\text{M} = \text{Ba, Ca, Sr}$) and their doped phases, displaying an ionic conductivity of $10^{-4} \text{ S cm}^{-1}$ at high temperature (*e.g.*, 150°C).⁴³ Thus, insufficient F^- -conductivity has been the restricting factor for the operation of solid-state FIBs at low or room temperature.

The F^- ion transport through solid electrolytes is typically facilitated by the Schottky and anti-Frenkel point defects via the vacancy mechanism, interstitial mechanism, and interstitial-substitutional exchange mechanism. Thus, the fast ionic conductivity can be achieved by creating new defects within the solid structure. However, the defect mechanism highly depends on the structure of the solid electrolyte. Given that the F^- interstitial site is relatively smaller (0.84 Å) compared to the F^- radius (1.19 Å), it is unlikely to be created in tysonite-type $R_{1-x}M_xF_{3-x}$ fluorides (where R denotes the rare-earth element while M represents the divalent element). In such instances, the formation of F^- vacancies has been demonstrated to be effective in improving the ionic conductivity of RF_3 fluorides.^{72, 586, 597-600} Doping the polycrystalline sintered CeF_3 with various difluorides including CaF_2 , SrF_2 , and BaF_2 (5 mol%), Takahashi and coworkers revealed that the conductivity of CeF_3 was significantly enhanced up to $1.0 \times 10^{-2} \text{ S cm}^{-1}$ at 200 °C (for $Ce_{0.95}Ca_{0.05}F_{2.95}$), which was attributed to the facile movement of vacancies.²⁷⁶ In addition, the structural features of solid electrolytes have critical impacts on the F^- mobility. In the case of the tysonite $Sm_{1-x}Ca_xF_{3-x}$ solid, as the Ca content increases, the distortion of the $F1(Sm, Ca)_4$ tetrahedral site diminished, leading to an exponentially reduced ionic conductivity and an increase in activation energy. Consequently, at room temperature, the highest conductivity of $10^{-4} \text{ S cm}^{-1}$ was achieved for the lowest Ca content or the smallest fluorine vacancy content in the $Sm_{0.95}Ca_{0.05}F_{2.95}$ tysonite.⁵⁹⁹ The F^- conduction mechanism for tysonite-type structure, however, was drastically different from that for fluorite-type solids. To reveal the conduction mechanism, Fichtner and coworkers prepared a series of $La_{1-y}Ba_yF_{3-y}$ ($0 \leq y \leq 0.15$) solid compounds using the ball-mill method, revealing that grain boundaries exert a detrimental effect on the F^- conduction of tysonite-type solids (**Figure 26a, b**). Sintering the compounds to reduce grain boundaries and improve grain growth contributed to higher ionic conductivities. Unfortunately, extending the sintering time beyond a certain threshold (20 h) did not further increase the ionic conductivity (compared to samples sintered for 2 h), due to the blocking effect of additional grain boundaries induced by oxides, silicates or fluorite-type phase.²⁷⁶

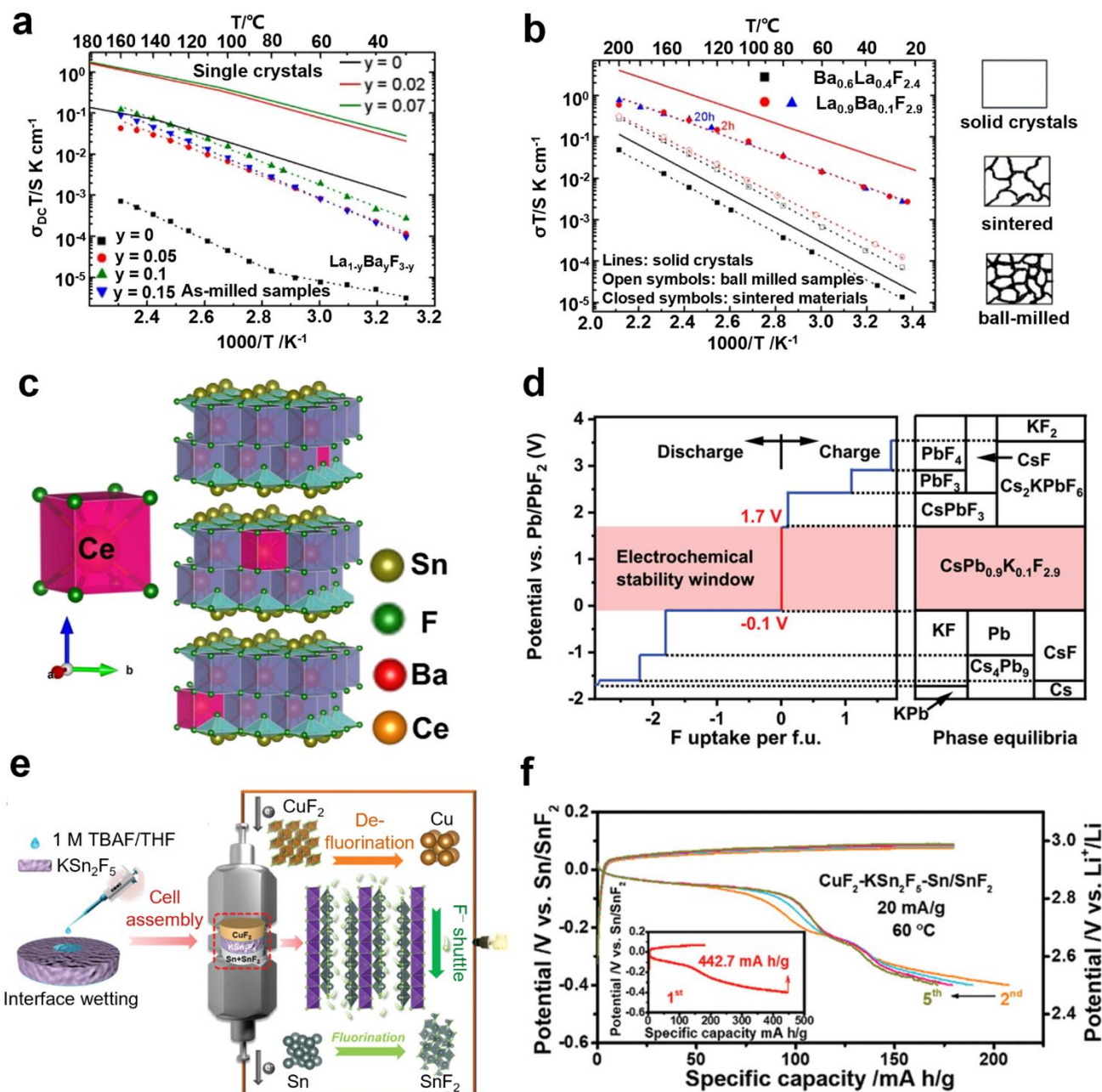


Figure 26. Developments of solid-state electrolytes for FIBs. (a) Arrhenius plot of the ionic conductivity for ball-milled $\text{La}_{1-y}\text{Ba}_y\text{F}_{3-y}$ electrolyte. (b) Arrhenius plots of the ionic conductivities for tysonite-type $\text{La}_{0.9}\text{Ba}_{0.1}\text{F}_{2.9}$ and fluorite-type $\text{Ba}_{0.6}\text{La}_{0.4}\text{F}_{2.4}$ prepared by ball-milling and sintering. Reproduced with permission from ref ²⁷⁶. Copyright 2014 American Chemical Society. (c) Crystal structures of the $\text{Ba}_{0.95}\text{Ce}_{0.05}\text{SnF}_{4.05}$ phase. Reproduced with permission from ref ⁶⁰¹. Copyright 2022 American Chemical Society. (d) ESW based on the calculated thermodynamic equilibrium voltage profiles and the phase equilibria for the $\text{CsPb}_{0.9}\text{K}_{0.1}\text{F}_{2.9}$ electrolyte. Reproduced with permission from ref ⁶⁰². Copyright 2022 Wiley-VCH. (e) Illustration of interphase wetting, cell assembly, and predicted reaction processes for Swagelok-cell-type $\text{CKC}|\text{KSr}_2\text{F}_5|\text{SSKC}$ FIB. (f) Voltage curves of the initial five cycles for $\text{SSKC}|\text{KSr}_2\text{F}_5|\text{CKC}$ battery. Reproduced with permission from ref ⁶⁰³. Copyright 2023 Wiley-VCH.

The abovementioned two mainstream fluorides have achieved substantial progress, yet they generally realize an ionic conductivity of $10^{-4} \text{ S cm}^{-1}$ at high temperatures around 150 °C.⁶⁰⁴ Their practical applications are still plagued by insufficient RT conductivity, prompting researchers to explore novel fluoride structures with faster transport of F ions at low temperature.^{43, 605-607} Sn(II)-based fluorides such as

BaSnF₄ compounds are anticipated to deliver high F⁻ conductivity since the polarizable lone pair of electrons on Sn²⁺ can reorient during moving, enabling the mobile F⁻ between Sn-Sn and Sn-Ba layers to take part in the ionic conduction process.⁶⁰⁸⁻⁶¹⁰ Unfortunately, the strong electrostatic interaction between Ba and F in the Ba-Ba layer considerably impedes the F ion migration. To eliminate this shielding effect, the introduction of point defects within BaSnF₄ solids has been adopted for realizing efficient F⁻ shuttling. By partially substituting Ba²⁺ by Ce³⁺, which has a similar atomic radius, point defects can be built in the tetragonal BaSnF₄ crystal (**Figure 26c**). Accordingly, the Ba-Ba 3D barrier was disrupted, broadening the pathways for F⁻ transport. The Ba_{0.95}Ce_{0.05}SnF_{4.05} displayed an enhanced RT conductivity of 5.2×10^{-4} S cm⁻¹ and a reduced activation energy of 0.15 eV, compared to 1.49×10^{-4} S cm⁻¹ and 0.15 eV for BaSnF₄ solid electrolyte, respectively. The assembled all-solid-state BiF₃|Ba_{0.95}Ce_{0.05}SnF_{4.05}|Sn FIB realized a high reversible specific capacity of 170.9 mA h g⁻¹ and a stable cyclability over 30 cycles at RT.⁶⁰¹ Clearly, constructing point defects in F⁻-conducting solid electrolytes is promising for efficient shuttling of F ions. Although the BaSnF₄ delivered high RT ionic conductivities comparable to those for solid electrolytes in LIBs,⁶¹¹ its narrow ESW restricted the selection of cathode and anode materials, which led to low average discharge voltage (usually less than 0.5 V).^{609, 612, 613} To fulfill the requirements of high conductivity (*e.g.*, 10^{-4} S cm⁻¹) at RT and an adequately broad ESW simultaneously, a solid electrolyte with the chemical formula of CsPb_{0.9}K_{0.1}F_{2.9} was designed. It was revealed that introducing F vacancies greatly facilitated the ionic transport of CsPb_{1-x}K_xF_{3-x}, with the F⁻ conductivity reaching the maximum of 1.23×10^{-3} S cm⁻¹ when x was increased to 0.1. Moreover, the redox reaction was found to proceed through the valence change of Pb rather than Sn, as indicated by the calculation result. The reduction of Pb occurred at -0.1 V (*vs.* Pb/PbF₂) while the oxidation to obtain high-valent Pb took place at 1.7 V, contributing to a wide ESW of 1.8 V for the CsPb_{0.9}K_{0.1}F_{2.9} electrolyte (**Figure 26d**). This result agreed well with LSV measurements, which showed a distinct oxidation started at 1.92 V and a reduction started at 0.11 V. Owing to these desirable features, a Pb/PbF₂|CsPb_{0.9}K_{0.1}F_{2.9}|Ag battery with high discharge voltage was constructed, maintaining high and stable specific capacity (~ 140 mAh g⁻¹) after 72 cycles (4581 h) at a current density of 5.2 mA g⁻¹.⁶⁰² Most recently, Li *et al.* introduced a new class of layered Sn(II)-based fluoride conductor (*i.e.*, KSn₂F₅) where F⁻ acted as charge carrier. The KSn₂F₅ solid electrolyte exhibited a higher ionic conductivity (10^{-4} S cm⁻¹ at 60 °C) compared to typical tysonite-type and fluorite-type fluorides, mainly due to the increased charge carrier concentration and more frequent jumping process. Integrating this solid conductor with a high potential CuF₂ cathode and a low potential Sn anode (**Figure 26e**), a high initial specific discharge capacity of 442 mAh g⁻¹ was achieved (**Figure 26f**), retaining a reversible specific capacity of ~ 150 mAh g⁻¹ for more than 70 cycles at 60 °C. It should be noted that the interphase wetting of the solid electrolyte by the TBAF favors the F⁻ transfer between the electrode and the electrolyte.⁶⁰³

4.2.2. Non-Aqueous Liquid Electrolytes. As discussed above, the physicochemical characteristics of F^- -conducting solid-state electrolytes have been studied for several decades. Nevertheless, the majority of solid electrolytes necessitate operation temperature above 150 °C for FIBs due to their low ionic conductivities at lower temperature. In contrast, liquid electrolytes are expected to exhibit superior F^- conductivities to enable RT FIBs. Besides, they demonstrate enhanced interphasial compatibility towards electrode materials, which is crucial for the commercialization of FIBs. Unfortunately, the developments of liquid electrolytes for RT FIBs has been largely constrained by two primary factors, *i.e.*, the low solubility of fluoride salts in the electrochemically stable aprotic organic solvents, and the strong chemical reactivity of F^- which is prone to create hydrofluoric acid (HF) in the presence of acidic hydrogen.^{9, 42} To establish liquid electrolytes for RT FIBs, several requirements should be satisfied, *e.g.*, abundant free fluoride species (F^- or F_2H^-) should exist in the electrolytes to support high ionic conductivity, sufficient electrochemical stability of the electrolytes to prevent decompositions during cycling, and high chemical stability of the electrolyte to prevent the dissolution of electrode active materials.⁴⁰ Thus, extensive attempts have been made to explore novel electrolytes for potential RT FIBs. However, initial efforts were disappointing due to the insolubility of most fluoride salts in organic solvents. Among these endeavors, a significant breakthrough was realized in 2018 by Jones *et al.*, who designed RT F^- -conducting electrolytes with high ionic conductivity, wide electrochemical stability window, as well as sufficient chemical stability, via dissolving tetraalkylammonium fluoride salts (*i.e.*, neopentyl (Np)-substituted alkylammonium fluorides) into ether solvents. The Np salt was chosen because the branched Np chain enhanced salt solubility while the absence of β -hydrogens inhibited HF_2^- generation. Results show that a high NpF salt concentration (> 2.2 M) could only be obtained when employing BTFE as the solvent without reacting with F^- (**Figure 27a**), exhibiting high ionic conductivity comparable to that of LIB electrolytes (within the range of 10^{-3} to 10^{-2} S cm^{-1} , **Figure 27b**). It is important to note that the electron-withdrawing groups on the BTFE molecule could strengthen the partial positive charges on α -CH₂, guaranteeing adequate F^- solvation. When paired with a Cu@LaF₃ core-shell nanostructure cathode, reversible electrochemical cycling with F^- shuttling was achieved at RT.⁵² Though the cycle stability was far from satisfactory for practical battery systems, this report represents the pioneering work in exploring high-energy devices beyond that of LIBs. To gain a deep understanding of the factors affecting F ion-solvent properties in liquid FIBs, these authors further investigated various organic solvents in combination with the Np₁F salt. They revealed that partially fluorinated solvents possessing partial charge distribution and conformational flexibility achieved the highest level of salt dissolution, with BTFE being particularly prominent for its large Np₁F salt dissolution. Besides, introducing amide as co-solvents promoted the ion dissociation between Np₁⁺ cations and F^- anions, thus enhancing the electrolyte ionic conductivity (**Figure 27c**).⁶¹⁴ Apart from organic fluoride salts, inorganic fluoride salts (*i.e.*, CsF, KF or NaF) have been successfully employed as fluoride sources in the

development of RT F^- -transporting liquid electrolytes, as demonstrated by the RISING project in Japan.⁶¹⁵⁻
⁶¹⁷ They introduced novel lactone (γ -butyrolactone, GBL)-based liquid electrolytes, which consist either of CsF or KF, through a solvent substitution method. Despite of the low F^- concentration of around 0.05 M, these electrolytes delivered high ionic conductivity of 0.8 mS cm^{-1} , enabling reversible metal/metal-fluoride transformations for a wide range of metal electrodes. Nevertheless, the electrolyte solvent showed poor anti-reductive stability with the anode, which was promoted by the presence of fluoride ions.⁶¹⁷ In another effort, when 4.5 M LiFSI and 0.45 M CsF salts were dissolved in tetraglyme (G4) solvent as the electrolyte, this project revealed the formation of a SEI on a MgF_2 anode, which resulted from the irreversible decomposition of the liquid electrolyte during the reduction process. However, the detected LiF within the SEI could exert a detrimental impact on the FIB performance, given the poor electronic and F^- conductivity of LiF.⁶¹⁵ Consequently, a thorough investigation of the SEI compositions and properties is warranted to optimize the FIB performance in future.

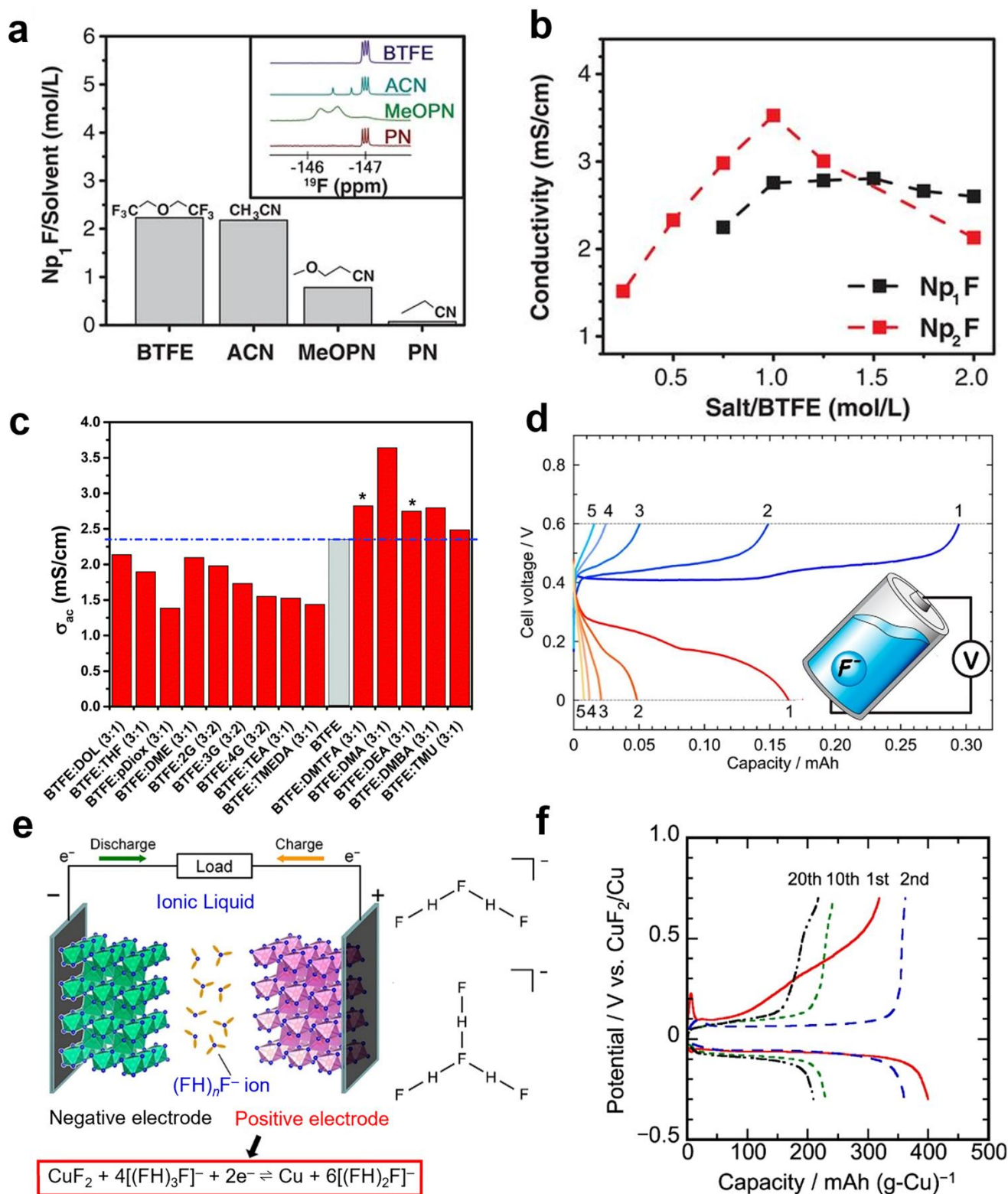


Figure 27. Room temperature F[−]-conducting non-aqueous liquid electrolytes for FIBs. (a) The solubility of Np₁F salt in BTFE, AN, 3-methoxypropionitrile (MeOPN), and propionitrile (PN) solvents. Inset displays the ¹⁹F (nuclear magnetic resonance) NMR spectra in the bifluoride region for Np₁F salt dissolved in each solvent. (b) The ionic conductivity of Np₁F and Np₂F in BTFE solvent as a function of salt concentration. Reproduced with permission from ref ⁵². Copyright 2018 American Association for the Advancement of Science. (c) Ionic conductivity of Np₁F salt (0.75 M) in the mixture of BTFE and co-solvent. Reproduced with permission from ref ⁶¹⁴. Copyright 2019 Royal Society of Chemistry. (d) Charge/discharge curves of the RT FIB based on a Bi cathode and a PbF₂/Pb anode in ~ 0.35 M MPPF/TMPA-TFSA at 20 μA cm^{−2}. Reproduced with permission from ref ⁶¹⁸. Copyright 2017 American Chemical Society. (e) Scheme illustration of FIB based on a fluorohydrogenate ionic liquid electrolyte and structures of fluorohydrogenate anions [(FH)_nF][−] when

n denotes 2 and 3, respectively). Reproduced with permission from ref ⁶¹⁹. Copyright 2019 American Chemical Society. (f) Voltage curves of the Cu electrode in the [C₂C₁pyrr][(FH)_{2.3}F] electrolyte at RT with a current rate of 0.05 C (= 42.2 mA (g-Cu)⁻¹). Reproduced with permission from ref ⁶²⁰. Copyright 2021 Elsevier.

Owing to their characteristic physicochemical properties, including high ionic conductivities, sufficient thermal and chemical stabilities, low volatilities, high non-flammability, and favorable solubility, RT (ionic liquids) ILs have been utilized for operating liquid FIBs. The first proof-of-principle RT FIB was presented by Darolles *et al.* in US patent 9166249, reporting an IL electrolyte consisting of tetramethylammonium fluoride (TMAF) in 1-methyl-1-propylpiperidinium bis(trifluoromethanesulfonyl) imide (MPPTFSI). An ionic conductivity of $\sim 10^{-3}$ S cm⁻¹ at RT and a stable voltage window > 4 V were realized, delivering an initial discharge specific capacity of 103 mAh g⁻¹ in a polyaniline (PANI)||PbF₂ battery.⁶²¹ Nevertheless, the extent of F⁻ shuttling contributed to the cyclability was not adequately verified, the possible influence of IL cations on the cycling process remained unsolved, and the redox reactions associated with the PANI cathode were not thoroughly investigated, as noted by Hörmann *et al.* Despite these shortcomings and very limited electrochemical performance, this patent remains seminal in the development of RTFIBs.⁴⁰ Subsequently, the RISING project in Japan has achieved notable progress in enhancing the ionic conductivity of ILs for the operation of RT FIBs. By dissolving the 1-methyl-1-propylpiperidinium fluoride (MPPF) in an IL, specifically N,N,N-trimethyl-N-propylammonium bis(trifluoromethanesulfonyl)amide (TPMA-TFSA), with a fluoride concentration of ~ 0.35 M, a high conductivity of 2.5 mS cm⁻¹ was realized. When paired with a Bi cathode and a PbF₂|Pb anode, the resulting liquid FIB exhibited distinct two-step plateaus in the initial charge/discharge profiles. However, some of the charged products (*e.g.*, BiF₃) was electrically detached from the Bi cathode through exfoliation, causing diminished charge-discharge efficiency and poor cycle stability (**Figure 27d**).⁶¹⁸ Notably, the possible generation of bifluoride ions from organic cations with β -hydrogens due to Hofmann elimination was not discussed in these IL-based electrolytes, presenting a significant challenge for the development of RT FIBs. To eliminate this issue, a novel liquid electrolyte based on fluorohydrogenate ionic liquids (FHILs) was designed by this project (**Figure 27e**), featuring the fluorohydrogenate anion ((FH)_nF⁻), which possesses high ionic conductivities (*e.g.*, 100 mS cm⁻¹ at RT for [C₂C₁im][(FH)_{2.3}F] (C₂C₁im = 1-ethyl-3-methylimidazolium)). When paired with this electrolyte, the CuF₂ cathode underwent reversible defluorination/fluorination, achieving 94.7% of the theoretical specific capacity (528 mAh (g-CuF₂)⁻¹) for the first cycle. However, a drastic capacity decay was observed upon subsequent cycling.⁶¹⁹ Afterwards, these authors developed an alternative FHILs, [C₂C₁pyrr][(FH)_{2.3}F] (C₂C₁pyrr = N-ethyl-N-methylpyrrolidinium), which, despite delivering reduced initial specific capacities (400 mAh (g-Cu)⁻¹), extended the cycle life to 20 cycles while maintaining the specific capacity (**Figure 27f**). The improved cyclability was attributed to the low CuF₂ solubility in [C₂C₁pyrr][(FH)_{2.3}F], which largely inhibits the aggregation of the Cu particles.⁶²⁰

Under acidic conditions, β -hydrogen elimination and/or other nucleophilic fluoride attacks towards atoms such as α -H, C=O, ChN, P, Si, *etc.* take place relatively easily. These reactions can be mitigated by enhancing the solvation of F^- through Lewis acidic solvating agents (*i.e.*, anion acceptors: AAs) such as organic compounds containing electropositive elements (*e.g.*, B, Si, P, *etc.*). Among them, boron-based AAs have been proven to be effective in promoting the dissolution of Li salt (*e.g.*, LiF, LiCl, Li₂O, Li₂O₂) by reducing the cation-anion interactions.⁶²²⁻⁶²⁶ Motivated by these findings, the RISING project in Japan undertook a series of research works to identify boron-containing compounds, including triphenylboroxine (TPhBX), triphenylborane (TPhB), fluorobis(2,4,6-trimethylphenyl) borane (FBTMPhB), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (DiOB-Py), *etc.*, as AAs to form complexes with anions, thereby providing sufficient F^- conductivity for operating RT FIBs.⁶²⁷⁻⁶³⁵ Typically, fluoride salts such as CsF are challenging to dissolve in organic solvent such as G4. Through DFT calculations, the optimized molecular structure of TPhBX- F^- was elucidated, revealing that the boron atom served as the most stable binding site for F^- . Besides, the introduction of 0.5 M TPhBX greatly increased the solubility of CsF in G4 solvent from 0.00017 to 0.51 M, experimentally validating the effectiveness of TPhBX as an AA. The resulting PbF₂ (mixed with carbon) electrode delivered a high discharge specific capacity approaching the theoretical value (219 mAh g⁻¹), which was sustained after the subsequent three cycles (**Figure 28a**).⁶²⁷ While the solubility of CsF in G4 could be enhanced by AAs, it was found that the AA also led to the severe dissolution of the electrode active material, causing fast capacity degradation during cycling.⁶³³ Subsequently, these researchers demonstrated that both the type of AA and the concentration of CsF can be optimized to balance the AA- F^- interaction and the electrode dissolution. It was revealed that though the BiF₃ electrode could be discharged/charged normally in both electrolytes, the cycling performance with CsF (saturated)-TPhBX (0.50 M)-G4 electrolyte was higher than that with CsF (0.45 M)-TPhBX (0.50 M)-G4, attributed to the reduced dissolution of BiF₃ active material (**Figure 28b**). Additionally, it was proposed that the CsF/TPhBX ratio would significantly affect the formation state of Bi as well as the electrolyte decomposition products during the discharge process.⁶³⁶

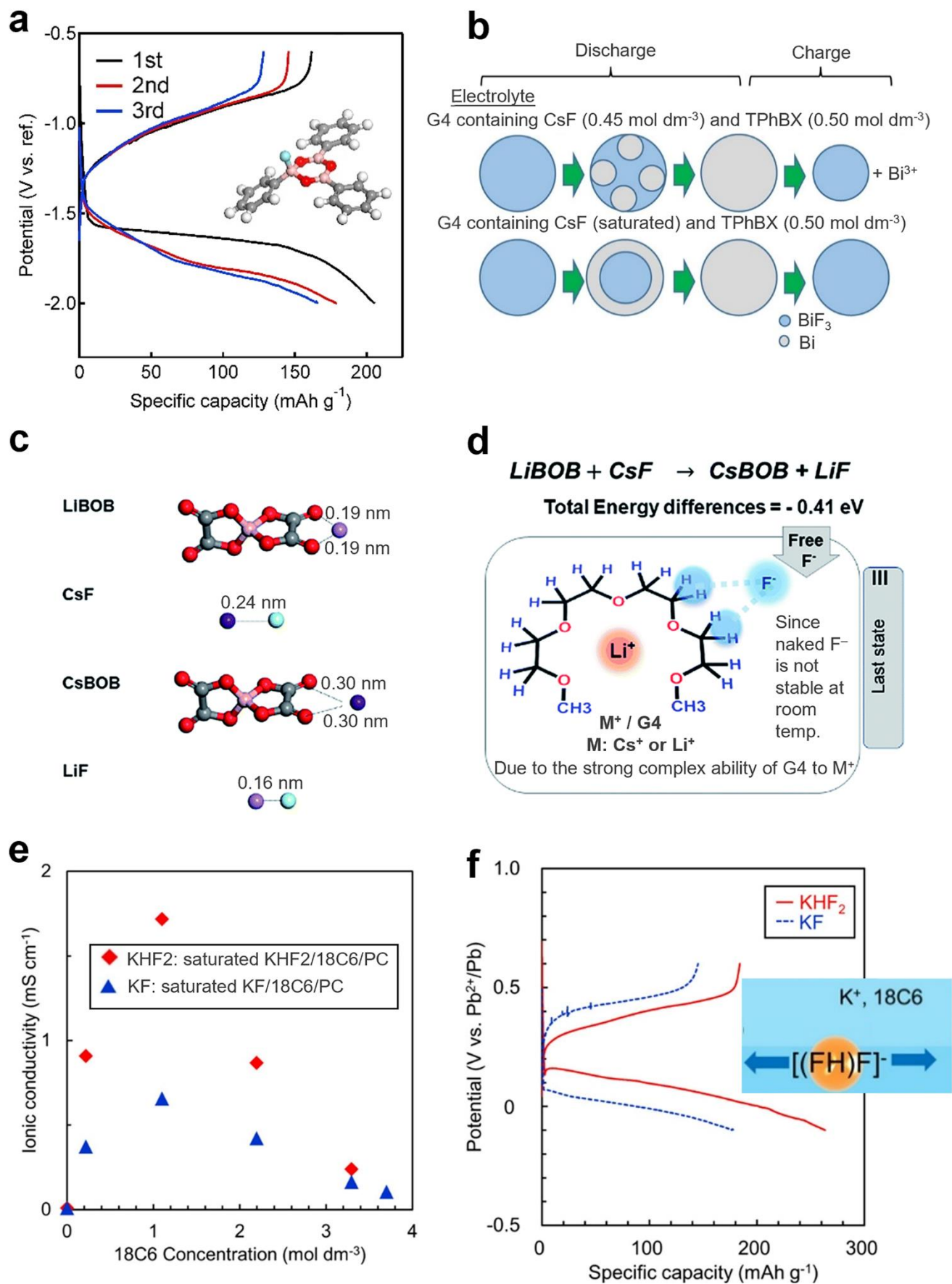


Figure 28. Employing anion acceptors and cation acceptors to improve the F^- conductivity for FIB electrolytes. (a) Discharge/charge curves of the PbF_2 (C) electrodes (vs. Ag/Ag^+) at 0.025 C ($1 \text{ C} = 219 \text{ mA g}^{-1}$). Inset shows the optimized molecular structure of TPhBX-F^- . Reproduced with permission from ref ⁶²⁷. Copyright 2019 Elsevier. (b) Scheme

illustrating effects of electrolyte concentrations (CsF: 0.45 mol dm⁻³ or saturated) on the BiF₃ dissolution during cycling. Reproduced with permission from ref ⁶³⁶. Copyright 2019 American Chemical Society. (c) The most stable structures of lithium bis(oxalato)borate (LiBOB), CsF, CsBOB, and LiF, respectively. (d) Possible interactions in the LiBOB_{0.25}/CsF/G4 electrolyte system. Reproduced with permission from ref ⁶³⁷. Copyright 2019 Royal Society of Chemistry. (e) Relationship between the 18C6 concentration and the ionic conductivity. (f) Charge/discharge curve of BiF₃ electrodes at 0.02C (1 C=302 mA g⁻¹; KHF₂ represents the saturated KHF₂/18C6/PC electrolyte, KF denotes the saturated KF/18C6/PC electrolyte, while 18C6 concentration is 1.10 M). Inset shows the [(FH)F]⁻ shuttling between two electrodes during charge/discharge. Reproduced with permission from ref ⁶³⁸. Copyright 2022 American Chemical Society.

Besides the AAs, another type of additive called cation acceptors (CAs) can also improve the conductivity of F⁻ by promoting the dissolution of F salt in electrolytes. Unlike the AAs discussed above, CAs interact with cations instead of anions from the salts. As an extensively investigated salt additive to mitigate the cathode material dissolution/diffusion in LIBs, lithium bis(oxalato)borate (LiBOB) has exhibited great potential as a CA in liquid FIBs.^{637, 639-643} This is attributed to the strong interactions between BOB ions and alkali metal ions (such as Na⁺ and Li⁺).⁶⁴⁴⁻⁶⁴⁶ Kucuk *et al.* found that the optimum BOB⁻ content to promote CsF dissolution in G4 was 0.25 M. Results revealed that BOB⁻ addition not only reduced active material loss, but also improved the electrolyte electrochemical stability during redox reactions, via the interactions between BOB⁻ and Cs⁺ as well as between fluoride and the CH₂ group of G4 solvent (**Figure 28c,d**).⁶³⁷ More recently, instead of using CsF salt, a widely available potassium salt, potassium bifluoride (KHF₂), was employed as the F⁻ source. To increase the salt disassociation, the 18-crown-6 ether (18C6) was introduced as a CA to interact with potassium ions, significantly boosting the mobility of fluoride ions with an ionic conductivity of 1.72 mS cm⁻¹ (**Figure 28e**). As depicted in **Figure 28f**, the consequent BiF₃ electrode achieved a discharge specific and a charge specific capacity of 263 mAh g⁻¹ and 184 mAh g⁻¹, respectively. In contrast, a higher voltage polarization was observed for the KF salt-based electrolyte, with a reversible specific capacity below 140 mAh g⁻¹. It is interesting to note that the fluoride ions existed in the form of [(FH)F]⁻, shuttling between the two electrodes during cycling. In addition, the HF generated from the equilibration reactions of [(FH)F]⁻ was considered to dissolve metal fluorides, further enhancing the fluorination/defluorination reactivity of metal fluorides.⁶³⁸ Based on these results, the AA (or CA) type, as well as fluoride salt/AA (or CA) ratio, should be carefully regulated to achieve high mobility of fluoride ions and to suppress the loss of active material. Furthermore, other types of supporting fluoride salts with higher dissociation levels (compared to the common CsF) should be explored. However, it should be noted that ultimately, after enhancing the fluoride ion solvation, the reactivity of fluoride ions may probably be suppressed due to the high de-solvation energy of fluoride ions on the electrode surface, which can affect the electrochemical storage/release of F⁻ during cycling.

4.2.3. Aqueous Electrolytes. Compared with other electrolyte systems, aqueous solutions typically possess outstanding merits of high ionic conductivity, low cost, and environmental benignity, which have

gained attention for developing liquid RT FIBs. In 2019, Chen and co-workers applied an aqueous NaF salt solution to operate a rechargeable FIB based on a TEMPO cathode and a BiF₃ anode. To prevent side effects of insoluble compounds from both electrodes, an anion exchange membrane was placed to ensure only F⁻ transported between cathode and anode during cycling. This FIB delivered a discharge capacity of 89.5 mAh g⁻¹ (based on the mass of BiF₃) after 85 cycles at 1000 mA g⁻¹, as well as good rate capability.⁵⁹¹ However, the voltage polarization was notably larger (~ 1.0 V) compared to that observed in LIBs. Additionally, the possibility of creating HF or bifluoride in the aqueous electrolyte, and the electrolyte compatibility toward electrode materials were not examined. Besides NaF salt, KF, which boasts a high solubility of 16 m in an aqueous solution has recently attracted great interest for FIBs. As demonstrated by Ji *et al.*, a “water-in-salt” electrolyte of 16 m KF (KF·3.47H₂O) facilitated the reversible F⁻ storage process of commercial Cu powder, mitigating the dissolution associated with the active material for the reversible conversion between Cu and CuF₂ (the charged product of Cu). Furthermore, the KF solid embedded into the Cu electrode acted as part of the active material, contributing to a higher specific capacity of 222 mA h g⁻¹ (based on the Cu mass) in the initial cycle. It was observed that the cathodic peaks shifted to a higher potential to reduce the electrochemical polarization, which aligned with the voltage curves. **(Figure 29a, b).**⁶⁴⁷ Soon after, a “water-in-salt” aqueous electrolyte composed of 7.5 M KF and 1.5 M KOH was designed, expanding the electrolyte stability window to ~2.1 V. Taking advantage of this electrolyte, a Zn||Cu battery based on the F⁻ shuttling was constructed, realizing an improved discharge platform of 1.9 V and a steady operation over 1600 cycles.⁶⁴⁸ This finding combined the advantages of the high conversion voltage of metal fluoride and the low-cost, environmental friendliness of Zn||Cu batteries. Most recently, the ESW of aqueous electrolytes was significantly increased to 3.1 V by dissolving 25 m CsF in water. As reflected in the ¹⁷O NMR spectroscopy and MD simulation, the 25 m CsF electrolyte displayed an increased fraction of ion pairs and aggregates, in addition to the elimination of free water molecules (compared with 1 m CsF), which confirmed the mechanism behind the expanded ESW **(Figure 29c, d)**. More significantly, the chemical stability of fluorides was investigated through ¹⁹F NMR coupled with pH measurements, demonstrating that the HF formation was almost completely suppressed **(Figure 29e, f)**. Therefore, the dissolution of active materials from electrodes such as Pb|PbF₂ and CuF₂ was inhibited, offering improved cycle stabilities.⁶⁴⁹

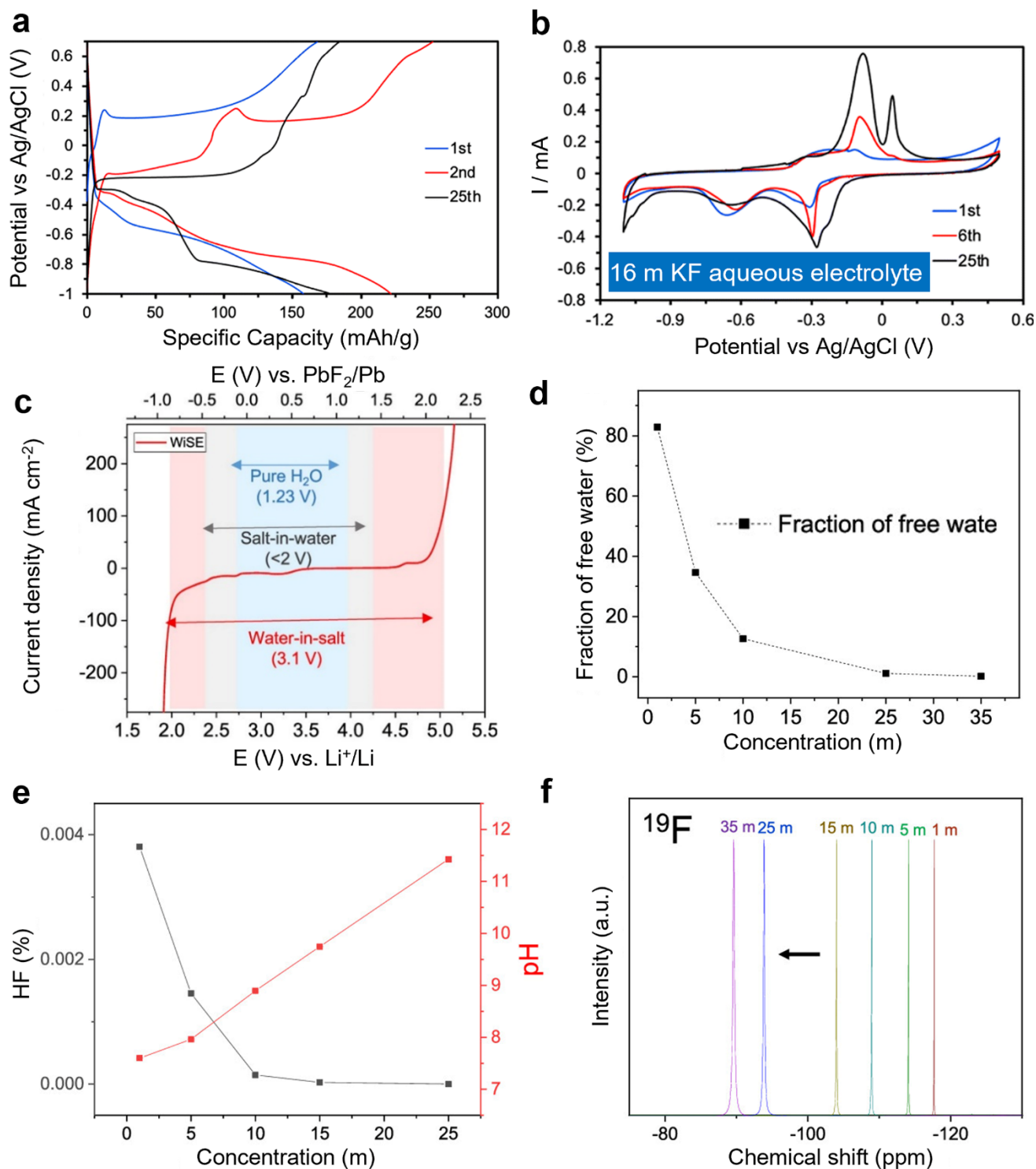


Figure 29. Developments of “water-in-salt” aqueous electrolytes in FIBs. (a) Charge-discharge curves of the Cu electrode in 16 m KF aqueous electrolyte at 500 mA h^{-1} . (b) CV results for different cycles at a scan rate of 1 mV s^{-1} . Reproduced with permission from ref ⁶⁴⁷. Copyright 2022 Royal Society of Chemistry. (c) ESW expansion using 25 m CsF aqueous electrolyte compared to pure water and other aqueous electrolytes. (d) The fraction of free water molecules calculated from the MD simulation. Fluoride ion chemical species and electronic environment: (e) pH as a function of concentration, suggesting a decrease in the HF content, and (f) ^{19}F NMR spectroscopy. Reproduced with permission from ref ⁶⁴⁹. Copyright 2023 American Chemical Society.

To conclude, in terms of solid-state electrolytes, the high operating temperature (*e.g.*, > 150 °C), low ionic transport capability, and poor interfacial contact remain challenging for most of the fluorite-type and tysonite-type solid-state electrolytes. Novel fluoride structures and modification strategies are urgently needed to promote the development of F[−]-conducting solid-state electrolytes. Liquid electrolytes permit FIBs to operate at ambient temperature with minimal internal resistance. Nevertheless, several issues persisted, as outlined in **Table 4**. The majority of fluoride salts exhibit limited solubility in organic solvents, leading to low ionic conductivity. Besides, the narrow ESW strongly constrains the selection of active materials, thus lowering the energy density of FIBs. Dissolution issues related with active material are another main concern that cause unsatisfactory cycle stability. Notably, due to the high chemical reactivity of F[−] ions, most liquid electrolytes are corrosive and toxic towards cell components. To achieve high ionic conductivities and simultaneously inhibit nucleophilic β-hydrogen elimination and/or other nucleophilic fluoride attacks, novel fluoride salts (other than the common CsF) and/or suitable solvents should be explored. Besides, suitable anion acceptors acting via forming complex with F anion or cation acceptors interacting with cations can be employed for promoting the dissociation of fluoride salts. It should be noted that the anion acceptors may also facilitate the loss of active materials. For a more comprehensive overview of electrolyte advancements in rechargeable FIBs, readers are encouraged to refer to several excellent reviews.^{41, 276}

Table 4. Comparisons of the electrochemical performance and remaining issues of liquid electrolytes for RT FIBs discussed in this section.

Electrolyte	Anode Cathode	Ionic conductivity (mS cm ^{−1})	Electrolyte stability window (V)	Retained capacity (mAh g ^{−1})/cycles	Remaining issues	Ref.
1 M Np ₁ F-BTfE	Cu@LaF ₃ (vs. Li ⁺ /Li)	2 to 3	4.1	65/7 th	Poor cycle stability and large electrochemical polarization	⁵²
0.05 M CsF- γ-butyrolactone	Zn Ag	0.8	/	~ 0.068 mAh cm ^{−2} /24 th	Irreversible reductive reactions of the solvent restricted the negative potential to ~ −1.5 V vs. SHE	⁶¹⁷
6.3 mM KF+ 0.5 M DiOB-Py-G4	BiF ₃ /C (vs. REF (0.587 V vs. SHE))	1.02 × 10 ^{−2}	~ 3.2	316/1 st	Although dissolution of the active material was very low, fast capacity fading still existed	⁶¹⁶
TMAF-MPPTFSI	PANI PbF ₂	~ 1	> 4	103/1 st	The contribution of F [−] shuttling to the cyclability was not verified, the possible influence of IL cations on the cycling process remained unclear	⁶²¹
~ 0.35 M MPPF-TMPA/TFSA	PbF ₂ Pb Bi	2.5	/	< 0.01 mAh/5 th	Some charged products were electrically detached from the cathode by exfoliation, causing poor	⁶¹⁸

					cycle stability, probably generated bifluoride ions	
C ₂ C ₁ im][$(\text{FH})_{2.3}\text{F}$	CuF ₂ (vs. CuF ₂ /Cu)	100	/	264 mAh (g-CuF ₂) ⁻¹ /10 th	Possible chemical dissolution of the CuF ₂ produced during charging and its re-precipitation on the electrode surface	619
C ₂ C ₁ pyrr][$(\text{FH})_{2.3}\text{F}$	Cu (vs. CuF ₂ /Cu)	/	/	210 mAh (g-Cu) ⁻¹ /20 th	The electrochemical dissolution of Cu metal and chemical dissolution of CuF ₂ still existed	620
0.51 dm ⁻³ CsF-tetraglyme + 0.5 dm ⁻³ TPhBX	PbF ₂ @C (vs. Ag/Ag ⁺)	/	4.2	~ 170/3 rd	The TPhBX caused severe dissolution of the electrode active material	627
Saturated CsF-tetraglyme + 0.5 dm ⁻³ TPhBX	BiF ₃ (vs. REF (0.587 V vs. SHE))	/	/	~ 100/3 rd	The electrochemical reaction mechanism and performance were dependent on the CsF/TPhBX ratio	636
0.5 M CsF-tetraglyme + 0.25 M LiBOB	BiF ₃ @C (vs. REF (0.587 V vs. SHE))	~ 1.6	~ 2.7	~ 125/1 st	The electrochemical polarization was large for redox reactions	637
Saturated KHF ₂ -PC + 18C6	BiF ₃ (vs. Pb ²⁺ /Pb)	1.72	3.7	184/1 st	The fluoride ions of the reactive species bond with protons, probably creating hydrogen during reduction at low potentials	638
0.8 M NaF-H ₂ O	BiF ₃ TEMPO	/	/	89.5/85 th	The possibility of creating HF or bifluoride in the aqueous electrolyte, the electrolyte compatibility toward electrode materials were unclear	591
16 m KF-H ₂ O	Cu (vs. Ag/Ag ⁺)	/	/	50/300 th	Uncontrolled KF precipitation on the electrode surface and the unregulated volumetric changes	647
7.5 M KF + 1.5 M KOH-H ₂ O	Zn Cu	/	~ 2.1 V	0.11 mAh cm ⁻¹ /1600 th	Low reversible capacity for F ⁻ storage reaction	648
25 m CsF-H ₂ O	Symmetric Pb PbF ₂	152	3.1 V	~ 65/50 th	The dissolution of active material still existed	649

REF: a silver rod immersed in acetonitrile with 0.1 M silver nitrate and 0.1 M tetraethylammonium perchlorate as reference electrode.

5. Fluorine Chemistry in Other Rechargeable Batteries

5.1. Na- and K-Based Batteries

5.1.1. Fluorine-Containing Electrode Materials in Na-Based Batteries. As mentioned above, fluorine is the most electronegative element with $\chi = 3.98$ compared to 3.44 for oxygen on the Pauling scale, contributing to more ionic M-X bonds in fluorides and thus higher redox potentials of transition-metal ions

than oxygen ions (**Figure 30a, b**).^{54, 650} In addition, in contrast to polyanions such as PO_4^{3-} , SO_4^{2-} , the lighter molecular weight of F^- is favorable for enhanced specific capacity. Generally, F-based inorganic or organic compounds are more stable against oxidation. Therefore, F-containing compounds ($\text{Na}_x\text{M}_y\text{F}_z$) can combine the benefits of the large gravimetric energy density of layered Na_xMO_2 with the high structural stability of polyanions, which has been proposed as promising cathode materials for SIBs.⁵⁴ A summary of the main characteristics of fluorinated materials as the cathode materials of SIBs has been thoroughly reviewed by Maisonneuve *et al.*,⁶⁵¹; readers are encouraged to refer to this review dedicated solely to fluorinated cathodes based on the material structures and other related reviews focused on transition metal oxyfluorides, transition metal fluorides, *etc.*^{113, 652} Here, we mainly discuss some representative cathode materials of SIBs with best overall performance, especially for 3D materials, analyzing the structure characteristics for further improving highly reversible/stable Na^+ uptake/release.

The metal difluorides (MF_2) synthesized from the decomposition of metal trifluoroacetates, were first employed in SIBs in 2014. Different from the direct conversion reaction with Li, the FeF_2 reacted with Na by the direct conversion at the surface region; then, it reacted heterogeneously with Na to convert to Fe^{3+} and Fe^0 .⁶⁵³ This work proved the disproportionation reaction mechanism in the conversion system, which guided to understand the nanoscale sodiation in metal difluorides. Sun *et al.* prepared a FeF_2 -reduced graphene oxide nanocomposite. When associated with a PAA (poly(acrylic acid)) binder, the reversible capacity of the nanocomposite was greatly improved from 100 to 175 mAh g^{-1} , and the high-rate capability was also achieved with a capacity of 78 mAh g^{-1} at 10 A g^{-1} .⁶⁵⁴

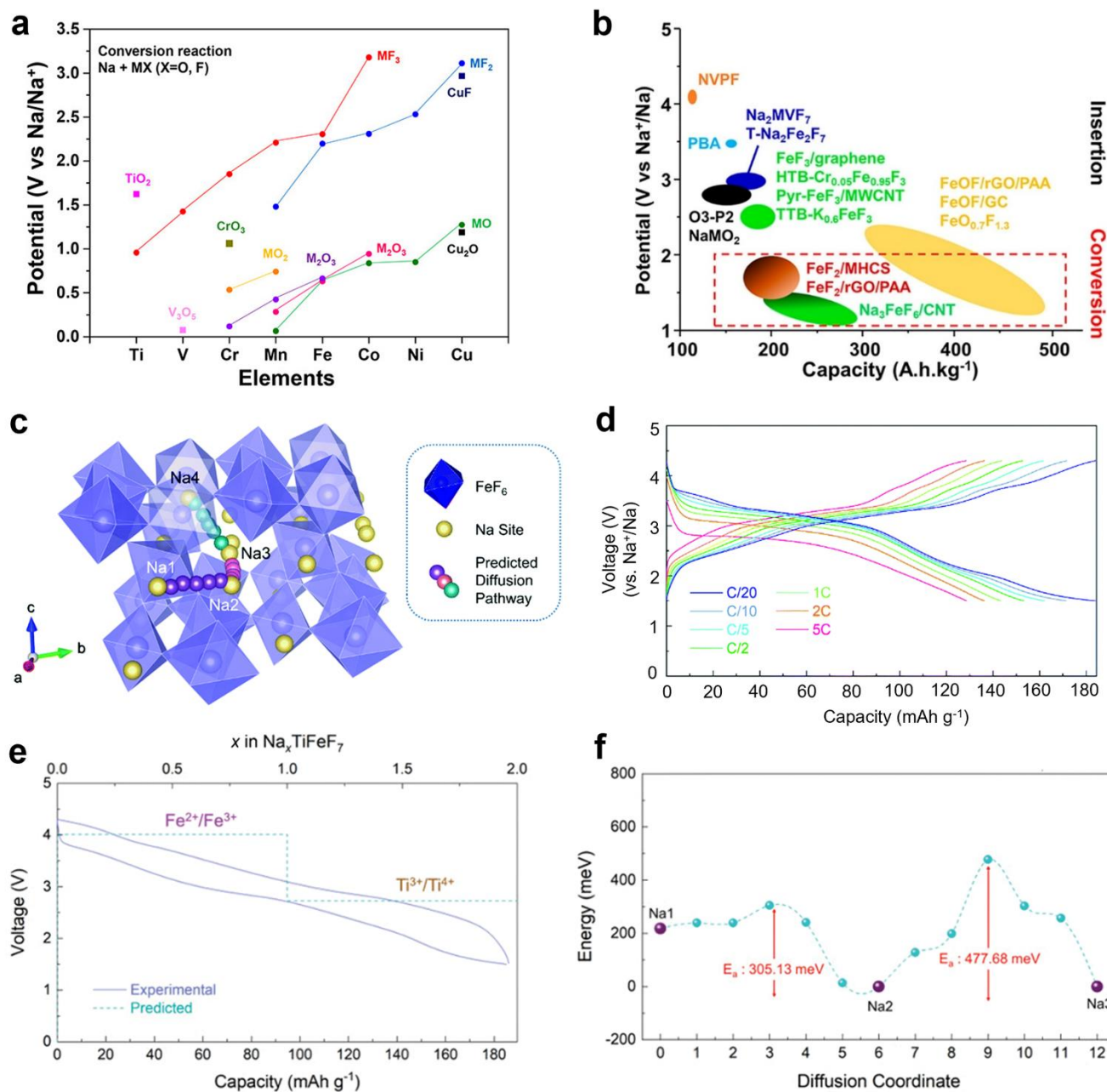


Figure 30. Fluorine-containing electrode materials for SIBs. (a) Calculated potentials for conversion reactions between transition metal oxides or fluorides with Na. (b) Voltage vs. capacity of SIB electrodes fluorinated materials. Reproduced with permission from ref ⁶⁵⁵. Copyright 2011 Elsevier. (c) 3D Na^+ migration pathways with energy landscape predicted by the NEB method in the $\text{Na}_x\text{Fe}_2\text{F}_7$ structure. (d) Voltage curves of the $\text{Na}_2\text{Fe}_2\text{F}_7$ cathode within the range of 1.5–4.3 V at a charge current rate of C/20 while various discharge current rates. Reproduced with permission from ref ⁵⁴. Copyright 2021 Elsevier. (e) Comparison of predicted redox potential of $\text{Na}_x\text{TiFeF}_7$ and its experimentally tested charge/discharge curves. (f) The energy landscape determined by the NEB method in $\text{Na}_2\text{TiFeF}_7$ structure. Reproduced with permission from ref ⁶⁵⁶. Copyright 2022 Wiley-VCH.

To increase the capacity based on conversion reactions, the oxyfluoride FeOF has also been employed in SIBs. The FeOF was studied by Deng *et al.* for insertion-conversion reactions in SIBs, which was prepared through a facial alcohol-assisted solvothermal method. The obtained FeOF nanorods delivered a high reversible capacity of $\sim 250 \text{ mAh g}^{-1}$ after 20 cycles at 10 mA g^{-1} .⁶⁵⁷ Afterwards, $\text{FeO}_{0.7}\text{F}_{1.3}/\text{C}$

nanocomposite was synthesized via a solution process for Na storage. This cathode material displayed a high initial discharge capacity of 496 mAh g⁻¹, a reversible capacity of 388 mAh g⁻¹ at 50 °C, as well as satisfactory capacity retention of 92.8% after 50 cycles. Furthermore, it was elucidated that the reaction mechanism of FeO_{0.7}F_{1.3}/C included a hybridized mechanism of both intercalation and conversion reactions. The initial discharged products were NaF, Fe nanoparticles and a newly formed rock salt phase (Na_{1.4}FeO_{1.4}F_{0.6}). Then, the phase separation was observed during recharging, inducing huge irreversible capacity loss in the first cycle. As the competitive reactions involved the rock salt phase and rutile components could improve the cycling stability of nanosized electrode materials,⁶⁵⁸ the authors then proposed that the phase separation could stabilize the de-sodiation reactions during subsequent cycles.

Apart from the above-mentioned potential high gravimetric energy densities, most Na_xM_yF_z materials exhibit excellent structural stability in the Na-deficient phase compared with layered Na_xMO₂, attributing to their three dimensionally framework. Using a similar solvothermal method for the preparation of NaFeF₄ except at elevated temperature (230 °C), NaF was introduced into the one-dimensional (1D)-FeF₃·3H₂O host to stabilize the lattice structure, and therefore obtaining the novel weberite Na₂Fe₂F₇ (via the Fe²⁺/Fe³⁺ redox reaction). A high insertion voltage of 3.25 V vs. Na⁺/Na was achieved, but the Na₂Fe₂F₇ cathode delivered rather low discharge capacity of 58 mAh g⁻¹ and poor cyclability.⁶⁵⁹ A more recent report by Kim *et al.* demonstrated the Na_xFe₂F₇ cathode material with the crystal structure composed of point-shared FeF₆ octahedra could deliver a high capacity of 184 mA h g⁻¹ at C/20 (1 C = 184 mA g⁻¹), attributed to a single-phase reaction without phase transition and negligible volume change during Na⁺ extraction/insertion.. The activation barrier energies for Na⁺ ions migration in Na_xFe₂F₇ were theoretically predicted by the nudged elastic band (NEB) according to first-principles calculations (**Figure 30c**), revealing the low activation barrier energies for efficient Na⁺ diffusion along 3D pathways. This structure characteristics favor a long-term cycle span of over 1000 cycles at 2 C with ~88% capacity retention and an outstanding rate capability, as shown in **Figure 30d**.⁵⁴ Although Na₂Fe₂F₇ remained the best reported performances for weberite cathode, the relationships between the structures and the properties remained unclear. To investigate the structure features and electrochemical behavior of the Na₂Fe₂F₇ weberite cathode in detail, experimental-computational approach was adopted by Foley *et al.*⁶⁶⁰ Results showed that Na₂Fe₂F₇ was metastable with a mixture of polymorphs (*e.g.*, the orthorhombic (2O), trigonal (3T), and monoclinic (4M) weberite polymorphs). As the Na₂Fe₂F₇ phases preferred to transform to the more stable NaFeF₃ perovskite, the cathode experienced a capacity fading upon cycling. Interestingly, these various polymorphs would not exert large impact on the Na storage behavior, as indicated from the first-principle investigations. Further comprehensive investigations on regulating the weberite polymorphism and phase stability for advanced SIB cathodes are needed.

Except for $\text{Na}_2\text{Fe}_2\text{F}_7$, the weberite structure contains a large family of materials featuring the chemical formula of $\text{Na}_2\text{M}^{\text{II}}\text{M}^{\text{III}}\text{F}_7$ (*e.g.*, $\text{M}^{\text{II}} = \text{Mg, Fe, Mn, Co, Ni, etc.}$, $\text{M}^{\text{III}} = \text{Al, Fe, Mn, V, Cr}$),^{661, 662} which have not been employed as cathode material for SIBs. Zhou *et al.* synthesized three vanadium-based weberite-type fluorides, Na_2MVF_7 (M denotes Mn, Fe, and Co), through polytetrafluoroethylene-assisted fluorination process. Based on the redox reactions of $\text{Fe}^{2+}/\text{Fe}^{3+}$ and $\text{V}^{3+}/\text{V}^{4+}$, a reversible capacity of $146.5 \text{ mA h g}^{-1}$ was obtained for the optimal Na_2FeVF_7 cathode. Furthermore, 95% capacity was retained after 200 cycles, owing to the robust crystal structure during repeated Na^+ de-/intercalation.⁶⁶³ More recently, a novel $\text{Fe}^{2+}/\text{Ti}^{3+}$ -based fluoride, $\text{Na}_2\text{TiFeF}_7$, was prepared as a SIB cathode materials. The Fe^{2+} and Ti^{3+} ions in the $\text{Na}_2\text{TiFeF}_7$ structure enabled the full utilization of $\text{Ti}^{3+}/\text{Ti}^{4+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couples for a high specific capacity of $\sim 185 \text{ mAh g}^{-1}$ at C/20 ($1 \text{ C} = 189 \text{ mA g}^{-1}$). Moreover, the high $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox potential ($\sim 3.75 \text{ V vs Na}^+/\text{Na}$) increased the average operating voltage of the cathode to 3.37 V (**Figure 30e**). Notably, the $\text{Na}_2\text{TiFeF}_7$ cathode still delivered a specific capacity of $\sim 136 \text{ mAh g}^{-1}$ even at 5 C, which was associated with the low activation energy barriers ($\sim 477.68 \text{ meV}$, **Figure 30f**) and low band-gap energy ($\sim 1.83 \text{ eV}$) for high power SIB applications.⁶⁵⁶

MX_3 -typed fluorides, in particular FeF_3 , have been widely studied for SIBs. Among its three allotropic varieties (ReO_3 , hexagonal tungsten bronze (HTB), and pyrochlore), the hydrated $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ HTB has gained visibly increasing interest in recent years due to its high average voltage ($\sim 2.74 \text{ V vs. Na/Na}^+$), high theoretical specific capacity, non-toxicity, and low-cost.^{664, 665} The presence of cavities could remove water molecules from the [001] hexagonal channels and insert Na^+ ions. In 2013, an HTB-type $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ was synthesized through a solid-solid transformation, where thermally vulnerable channels in $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ were expanded into more robust ones. At the same time, the micro-sized precursor underwent particle nanosizing. During this process, the characteristic Fe-based octahedral chains isolated in $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$ precursor were preserved, mainly due to the infiltration and capping of IL (1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF_4)), followed by the alleviated release of hydration H_2O from $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$. Beneficial from the well-suited Na-insertable cavities, this HTB-type $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ electrode (wired by 10 wt.% single-wall CNT (SWCNTs)) delivered a high discharge capacity of 130 mAh g^{-1} in the first cycle and good capacity retention (74 mAh g^{-1}) after 50 cycles.⁶⁶⁶ Despite these advantages, the low electronic and ionic conductivities of $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$, induced by the highly ionic character of the Fe-F bond, strongly hinder the practical application of SIBs. To improve the electrochemical performance, the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ nanoparticles were packaged into 3D order mesoporous carbons (3D-OMCs) to serve as a SIB cathode material, where the 3D-OMCs as carbon source facilitated the electron transfer and shortened the Na^+ diffusion path, meanwhile improving the structural stability and suppressed nanoparticle aggregation upon the Na^+ de-/intercalation. Besides, 3D-OMCs provided a large surface area for high mass loading, as well as increased contact area of the electrode|electrolyte interphase. Consequently, the $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}@\text{3D-}$

OMCs nanocomposite exhibited a high 1st discharge capacity of 386 mAh g⁻¹ with a steady capacity of 238.0 mAh g⁻¹ over 100 cycles at 20 mA g⁻¹. This nanocomposite cathode also demonstrated remarkable rate performance with a reversible capacity of 201 mAh g⁻¹ even at 100 mA g⁻¹.⁶⁶⁵ Although the electrochemical properties were enhanced, the intrinsic conductivity of FeF₃·0.33H₂O was still the same. Previous studies revealed that the band gap of this material could be decreased through ion doping, thus improving the intrinsic conductivities of FeF₃·0.33H₂O.⁶⁶⁷⁻⁶⁷⁰ For instance, with a smaller ionic radius (0.0615 nm) than that of Fe³⁺ (0.0645 nm), Cr³⁺ is easier to enter into the lattice of FeF₃·0.33H₂O. According to the DFT calculation results, Cr³⁺ doping could redistribute the charge of FeF₃·0.33H₂O, which reduced the band gap from 0.88 to 0.49 eV to improve its intrinsic conductivity. The optimized Fe_{0.95}Cr_{0.05}F₃·0.33H₂O cathode delivered a reversible capacity of 194.02 mAh g⁻¹ at 0.1 C, which is much larger than that obtained with FeF₃·0.33H₂O cathode (136.47 mAh g⁻¹). In addition, this doping cathode displayed much lower impedances than that of FeF₃·0.33H₂O cathode, further proving the increased electronic conductivity of the cathode material after Cr³⁺ doping.⁶⁷¹ In brief, these findings suggest that the thermodynamically stable phases of the fluoride-based cathodes are promising to achieve excellent electrochemical performances in SIBs, especially in terms of power-capability and cycle durability.

Although great progress has been achieved, fluoride-based cathode material has been limited to a small number of candidates. In addition, pre-sodiation is required for some of these developed fluoride-based cathodes to utilize their high theoretical capacities. More notably, owing to the large band-gap energies and low electronic conductivities, fluoride-based cathode materials typically suffer from poor electrochemical kinetics, which further causes rapid capacity deterioration, especially at high charging rates, significantly restricting their applications in SIBs.

5.1.2. Fluorinated Electrolytes in Na-Based Batteries. Similar to Li-based batteries, the battery performance of SIBs is largely determined by the selection of electrolytes.⁶⁷²⁻⁶⁷⁴ Especially, the stability of the electrolytes toward the high electrochemical polarization of both the cathode and anode. The ability to form passivation layers on the electrode surfaces must be considered for the stable operation of SIBs. Encouraged by the positive results obtained from Li-based battery systems, the effect of FEC on the performance of SIBs was first examined in 2011, revealing an improved reversibility insertion/extraction of Na⁺ ions for the hard carbon (HC) anode and the NaNi_{1/2}Mn_{1/2}O₂ cathode. Besides, FEC benefited the passivation of Na metal anode for suppressing undesirable reactions, thus enhancing the deposition/dissolution of metallic Na with higher reversibility.⁶⁷⁵ The favorable role of FEC toward both the anode (*e.g.*, hard carbon, Na metal) and cathode (*e.g.*, Na_{0.44}MnO₂) material was further verified by researchers, demonstrating the formation of a desirable passivation layer with FEC for improving the cycle stability and of SIBs.⁶⁷⁶⁻⁶⁷⁹

Very recently, a unique SEI was designed via *in situ* pre-implantation of F atoms rooted in Na metal.⁶⁸⁰ As a fluorine booster, the soluble functional molecule, amide molecule bis(trifluoroacetamide) (ECDA), can be anchored onto the Na metal. Owing to the strong induction effect and electrostatic repulsion of Na toward ECDA, abundant FEC-decomposed F atoms were driven to penetrate deeply into the Na metal from the outside inwards, which resulted in a desired functional rooted interphase (**Figure 31a**). Afterward, this interphase promoted the generation of a multilayer, inorganic-rich (*e.g.*, NaF, Na_xN, and Na₂O) SEI with a concentration gradient, ultimately enabling a high CE of 97.3% with an extended Na plating/stripping lifetime (1700 h) at 1 mA cm⁻². In addition, the 4.5 V Prussian Blue||Na@Cu battery delivered a high capacity retention of 86% over 200 cycles with a limited amount of Na.⁶⁸⁰ Unfortunately, these strategies failed to satisfy the wide temperature applications of SIBs. Generally, unwanted electrolyte decomposition on the cathode surface aggravates rapidly with increasing temperature, where the unstable CEI layer is commonly accompanied by continuous electrolyte decomposition, surface reconstruction, and capacity fading.⁶⁸¹⁻⁶⁸³ In addition, the defects of uncontrollable CEI would be further aggravated with high voltage and high temperature conditions.⁶⁸⁴ Recently, Chou and coworkers introduced an anion receptor tris(pentafluorophenyl)borane (TPFPB) containing an electron-deficient B center, which preferentially oxidized for constructing the NaF-rich CEI layer. The strong interactions between the ClO₄⁻ anion and the TPFPB additive effectively reduced the involvement of ClO₄⁻ in the first solvation sheath and contributed to facilitated coordination capability between organic solvents and Na⁺ cations, which greatly enhanced the anti-oxidative stability (**Figure 31b,c**). With the TPFPB-containing electrolyte, the resulting Na₃V₂(PO₄)₃ cathode delivered a capacity retention of 86.9% over 100 cycles, when operated with a high cut-off voltage of 4.2 V (*vs.* Na⁺/Na) and at a high operating temperature of 60 °C. This electrolyte also exhibited promising performance over a wide temperature range from -30 to 60 °C, highlighting the significance of tailoring the solvation chemistry for high-voltage and high-temperature SIBs.⁶⁸⁵

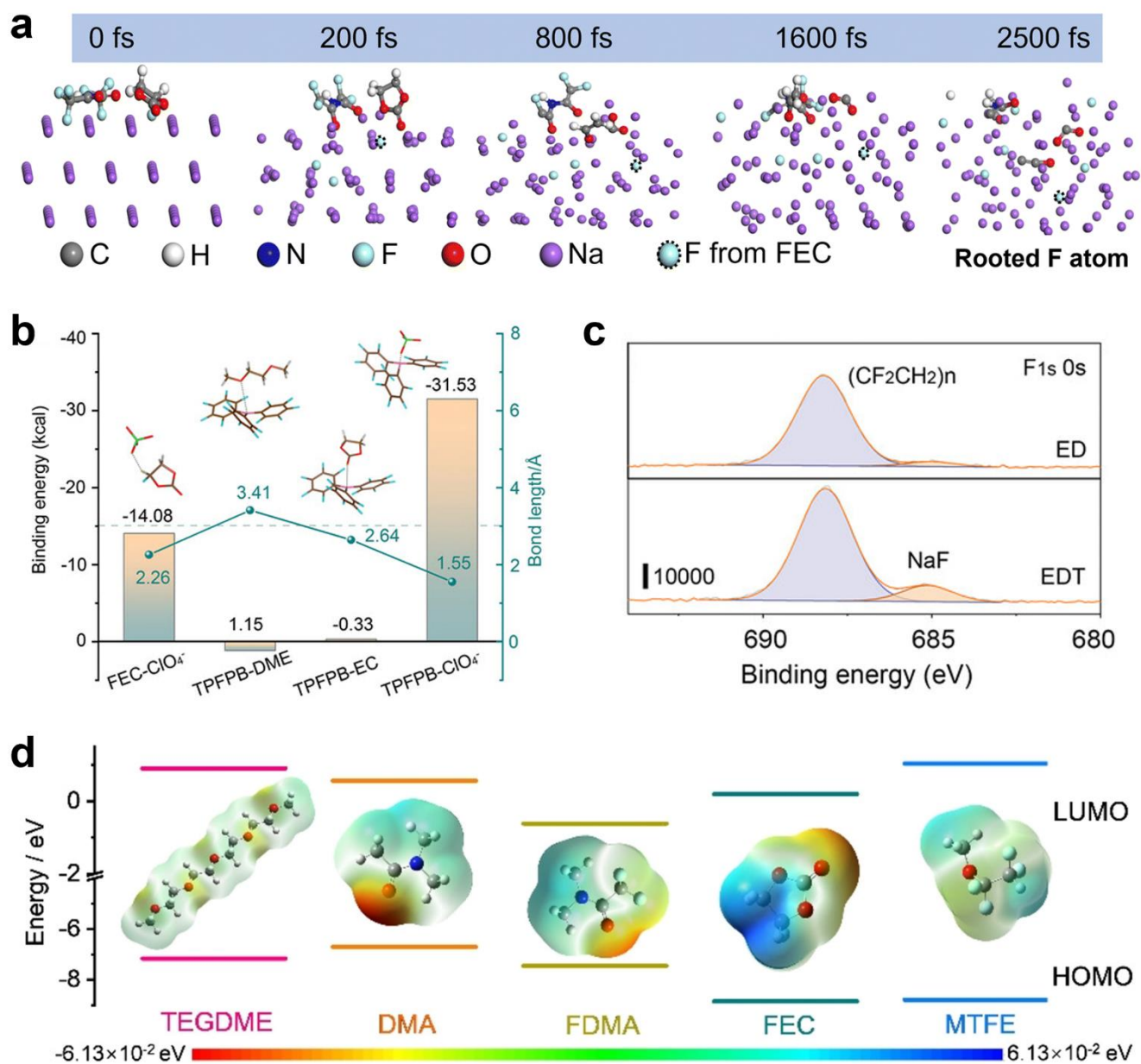


Figure 31. F-containing additives and (co-)solvents for stable operation of Na-based batteries. (a) AIMD simulations with ECDA and FEC. Reproduced with permission from ref ⁶⁸⁰. Copyright 2023 Elsevier. (b) Binding energy and bond length of FEC-C104⁻, TFPB-DME, TFPB-EC, and TFPB-C104⁻ through H-O, B-O, B-O, and B-O interactions, respectively. (c) XPS spectra of F 1s using electrolytes without and with TFPB additive. Reproduced with permission from ref ⁶⁸⁵. Copyright 2023 Wiley-VCH. (d) LUMO and HOMO energy values of electrolyte components. Inset shows the electrostatic potential mapping of these components. Reproduced with permission from ref ⁶⁸⁶. Copyright 2022 Wiley-VCH.

Learning from the Li-based battery electrolyte systems, fluorinated “inert” diluents have been successfully employed in SIBs for tuning the solvation structure and the related electrochemical behavior. In 2018, Zhang *et al.* designed a LHCE in SIBs by introducing a hydrofluoroether diluent (*i.e.*, BTFE) to decrease the concentration of NaFSI-DME electrolyte to less than 1.5 M. ⁶⁸⁷ Taking advantage of the “inert” nature of the fluorinated diluent, the interphasial reaction kinetics and interphasial stability of the Na metal anode was largely improved, which was attributed to the formation of a F-enriched protective SEI layer.

Consequently, a dendrite-free Na deposition process, along with a stable cycling (90.8% capacity retention over 40000 cycles) and a fast charging (20 C) were achieved in Na||Na₃V₂(PO₄)₃ battery. Afterward, the authors reported a nonflammable LHCE composed of NaFSI- triethyl phosphate (TEP)/TTE (1:1.5:2 in molar ratio) for highly reversible SIBs. This electrolyte stabilized the interphases on both the layered NaCu_{1/9}Ni_{2/9}Fe_{1/3}Mn_{1/3}O₂ (Na-NCFM) cathodes and the HC anodes, enabling high CE and long-term cyclability for the HC||Na-NCFM full cells.⁶⁸⁸

More interestingly, fluorine chemistry has also been utilized in designing novel salts for SIBs. Despite high ionic conductivity, NaPF₆ is susceptible to undergoing hydrolysis, leading to toxic species such as HF and POF₃ and posing severe safety concerns.^{689, 690} Meanwhile, alternative Na salts suffer from poor electrochemical performance, severe safety concerns or high cost. Borate anions with various attractive features have gained interest as electrolyte salts recently, especially when possessing varying degrees of fluorination for greater ESW. Wright *et al.* prepared a series of Na borate salts with varying steric and electronic properties, where Na[B(hfip)₄]. DME (hfip = hexafluoroisopropoxy, OⁱPr^F) and Na[B(pp)₂] (pp = perfluorinated pinacolato, O₂C₂(CF₃)₄) stood out with increased oxidative stability as well as excellent electrochemical performance.⁶⁹¹

Combining the Na anode with abundant, non-toxic and high-capacity (1675 mAh g⁻¹) sulfur cathode, the sodium-sulfur (Na-S) batteries have been technologically attractive for grid-scale energy storage. High-temperature Na-S batteries have been commercialized since 2002 with a high efficiency of ~ 100 % as well as a theoretical energy density of 760 Wh kg⁻¹ (based on both the Na anode and the sulfur cathode), the safety concerns and additional maintenance costs brought by the high operating temperature (300–350 °C) still remains unsolved. Besides, the capacity utilization of the sulfur cathode is only ~ 1/3 of the theoretical value, which is ascribed to the incomplete sulfur conversion reactions. Motivated by these issues, increasing efforts have been focused on RT Na-S batteries, which operate through a complete sulfur conversion with sodium sulfide (Na₂S) as the final discharge product instead of Na polysulfides, improving the theoretical energy density to 1274 Wh kg⁻¹. Nevertheless, RT Na-S batteries are strongly restricted by low reversible capacity, serious self-discharge and insufficient cycle stability, which are mainly attributed to the incompatible electrolyte systems towards the electrodes. By introducing FEC as the electrolyte cosolvent, Wang *et al.* discovered the solubility of Na polysulfides in the electrolyte was successfully inhibited, due to the low binding energy between FEC and Na polysulfides. Meanwhile, a stable and robust F-rich SEI was generated on the anode, protecting the Na metal from dendrite growth.⁶⁹² Recently, their continuous work demonstrated highly reversible long-term Na-S batteries through developing an all-fluorinated electrolyte, consisting of 2,2,2-trifluoro-N,N-dimethylacetamide (FDMA) as solvent, 1,1,2,2-tetrafluoroethyl methyl ether (MTFE) as anti-solvent and FEC as additive. The MTFE with a reduced HOMO value would strengthen the electrolyte anti-oxidative stability. Besides, the decreased negative

charge density of the FDMA-MTFE system could suppress the dissolution of polar polysulfide, and also lead to weak solvation of Na salts, which contributed to anions-dominated SEI construction (**Figure 31d**). It was also demonstrated that the FDMA solvent and FEC additive controllably reacted with Na polysulfides to form a NaF- and Na₃N-rich CEI, enabling a “quasi-solid-phase” Na-S conversion. As a consequence, the RT Na-S batteries delivered a high reversible capacity of 1114 mAh g⁻¹ (based on the mass of sulfur) along with an extended lifespan.⁶⁸⁶

5.1.3. Fluorine-Containing Electrode Materials in K-Based Batteries. Typically, the larger radius of K⁺ (1.38 Å) than Li⁺ (0.76 Å) and Na⁺ (1.02 Å) causes sluggish intercalation kinetics, which further leads to low storage capacity, unsatisfactory rate capability, and poor cycle stability of PIBs. Thus, exploring appropriate host materials for high-performance PIBs is urgently needed.⁶⁹³ In PIBs, polyanion compounds possessing 3D open-framework structures have been extensively explored as cathode materials due to the fast K⁺ diffusion kinetics and high redox voltages, among which fluorophosphates and fluorosulfates have attracted great interest.⁶⁹⁴⁻⁷⁰⁰ As early as 2012, the family of potassium fluorosulfates, KMSO₄F (M = Fe, Co and Ni), has been explored for the insertion/extraction of various alkali ions including Li⁺, Na⁺, or K⁺. KFeSO₄F crystalizes in an orthorhombic unit cell (space group *Pna2*₁), and its structure consists of chains of FeO₄F₂ octahedra linked via F⁻ ions. With the removal of K⁺ from KFeSO₄F (**Figure 32a**), no obvious structural change was observed for the K_{0.55}MSO₄F composition. Further removal of K⁺ (x<0.5) leads to a new oxidized phase with a formula of “FeSO₄F”. Notably, this new phase with large and empty channels displayed excellent versatility as reversible hosts for a variety of alkali guests.⁷⁰¹ Afterwards, a mechanistic investigation for the K⁺ removal from the KFeSO₄F cathode was conducted. Based on the first-principles calculations, the mechanism that induced this phase transition upon K⁺ extraction was studied at the atomic scale. It was unveiled that the crystal structure was stable for the phase transition from KFeSO₄F to K_{0.5}FeSO₄F, where only neighboring Fe²⁺-Fe³⁺ pairs were formed through selective oxidation. The continuous removal of K⁺ (x<0.5) would cause Fe³⁺-Fe³⁺ pairs with strong electrostatic repulsion, thus triggering a structure transition to a more ordered “FeSO₄F” phase (enlarge the Fe³⁺-Fe³⁺ distance). Apart from the structural stability, such strong electrostatic repulsion also played a critical role in the voltage curve of the cathode, with multiple voltage plateaus from x = 1 to x = 0.5 and just a single plateau when x<0.5 (**Figure 32b**).⁷⁰² Nevertheless, the electronic conductivities of these KMSO₄F compounds were insufficient for achieving high electrochemical performance. To tackle this issue, Chen *et al.* synthesized a graphene-decorated KFeSO₄F (KFSF@G) submicron particles.⁷⁰⁰ The ball-milling treatment facilitated a tight wrap of graphene to the KFeSO₄F particle for efficient electron and K⁺ transport, meanwhile largely reducing the particle size to increase reaction sites. The obtained KFSF@G not only displayed a reversible capacity of 111.5 mAh g⁻¹ with a high average operating voltage of 3.55 V, but also exhibited excellent

rate capability with a discharge capacity of 82.8 mAh g^{-1} at 5 C ($1 \text{ C} = 128 \text{ mA h g}^{-1}$). Unfortunately, all these efforts have not achieved a satisfactory long-term lifespan of the KFeSO_4F -based PIBs.

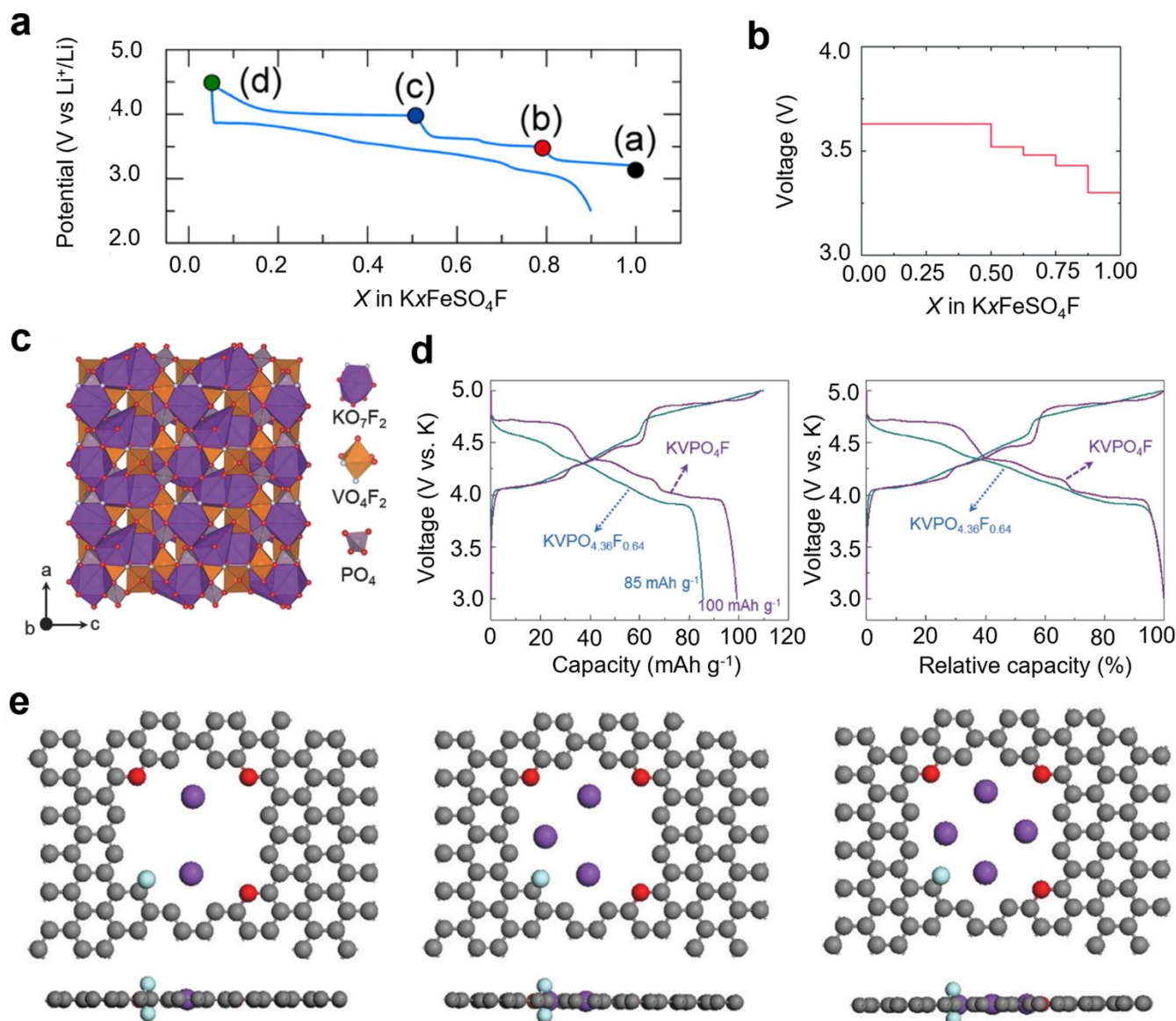


Figure 32. The effect of fluorine on improving the electrochemical performance of polyanion cathode or carbonaceous anode materials in PIBs. (a) Voltage curve of the $\text{Li}||\text{KFeSO}_4\text{F}$ cell started with charging process. Reproduced with permission from ref ⁷⁰¹. Copyright 2012 American Chemical Society. (b) Voltage curve predicted for the extraction of K^+ from KFeSO_4F cathode material. Reproduced with permission from ref ⁷⁰². Copyright 2013 Royal Society of Chemistry. (c) Crystal structure of KVPO_4F cathode material. (d) Charge/discharge curves of KVPO_4F and $\text{KVPO}_{4.36}\text{F}_{0.64}$ in the second cycle at a current rate of 5 mA g^{-1} . Reproduced with permission from ref ⁶⁹⁹ Copyright 2018 Wiley-VCH. (e) The optimized mode after absorbing two, three, and four K atoms in the O/F dual-doped carbon, respectively (viewed from top and side). Reproduced with permission from ref ⁷¹. Copyright 2019 Wiley-VCH.

Compared with the above-mentioned fluorosulfates, V-based polyanion compounds with enhanced cycle stability have attracted great interest in recent years. In 2017, KVPO_4F was investigated as a high-voltage cathode material for PIBs, displaying a reversible capacity of 92 mAh g^{-1} and a high average

working voltage above 4.0 V (vs. K/K⁺) in 1 M KPF₆-EC/PC electrolyte. Notably, the lattice volume of the cathode material shrank only 5.8% after charging to 5 V, which was promising for applying as the high voltage cathodes in PIBs.⁶⁹⁵ In these fluorophosphates, F⁻ could be substituted by some O²⁻ (oxygenation), thus reducing the average working voltage and reversible capacity. To illustrate the effects of the fluorine, a stoichiometric KVPO₄F synthesized via a two-step reaction was evaluated by Ceder *et al.*⁶⁹⁹ Such KVPO₄F cathode achieved a reversible capacity of ~ 105 mAh g⁻¹ along with a high average voltage of ~ 4.33 V (**Figure 32c, d**), corresponding to a promising energy density of ~ 454 Wh kg⁻¹. In addition, they revealed that intermediate phases at x = 0.75, 0.625, and 0.5 for the K_xVPO₄F cathode were formed upon cycling. The oxygenation of KVPO₄F not only caused a disordered structure to suppress the K⁺/vacancy formation, but also reduced the reversible K⁺ storage capacity and the operating voltage. To improve the cycle stability of the KVPO₄F cathode, Chen *et al.* prepared KVPO₄F through flower-like carbon-coated VPO₄, and then enveloped these primary particles in carbon frameworks (KVPO₄F/C). The carbon framework enhanced the electronic conductivity and acted as a reducing agent to control the F content in KVPO₄F. It was elucidated that with a higher carbon content in the KVPO₄F/C material, the oxidation of V and the desorption of F could be suppressed. The optimized KVPO₄F/C manifested a reversible capacity of 103 mAh g⁻¹ at 20 mA g⁻¹ and a stable cycle life of 900 cycles at 1 A g⁻¹. Such cathode also exhibited superior discharging capability with a reversible capacity of 87.6 mAh g⁻¹ at 5 A g⁻¹. More promisingly, a full cell based on this KVPO₄F/C cathode and a VPO₄ anode demonstrated a long lifespan of over 2000 cycles, an excellent capacity retention of 86.8%, and an average CE of 99.5% (at 1 A g⁻¹).⁶⁹⁷

As regards the anode materials, since the first report on the successful electrochemical K⁺ insertion into graphite by Ji *et al.* in 2015,⁷⁰³ carbonaceous materials have become the spotlight for PIB anodes because of their low cost, high electronic conductivity, and environmental friendliness. Unfortunately, these carbonaceous anodes such as graphite suffer from low specific capacity with a theoretical capacity of only 279 mA h g⁻¹ with the formation of KC₈ after discharging, along with poor cycle stability and huge volume change (61%) upon potassiation. To enhance electrochemical properties of this anode material, heteroatom-doping was adopted by Chen *et al.*⁷¹ The F-doping was reported to improve the surface disorder of the carbonaceous material, which could create large amounts of surface defects to facilitate K⁺ adsorption. In addition, the O-doping decreased the inert surface area and generated abundant active sites as well. The co-doping of O/F into the porous carbon framework regulated the electronic structure of the carbon atoms and enhanced the adsorption of K⁺, as suggested by the structural integrity after absorbing a number of K atoms (**Figure 32e**). Consequently, the O/F co-doped anode material achieved a high reversible capacity of 481 mA h g⁻¹ at 0.05 A g⁻¹ and excellent cycle performance, with 92% capacity retained over 2000 cycles at 1 A g⁻¹. Even at a current density of 10 A g⁻¹, an ultra-long lifespan of 5000 cycles can be enabled with a retained capacity of 111 mAh g⁻¹. In brief, structure modification, carbon coating, and heteroatom-doping

are effective strategies to enhance the overall electrochemical performance of polyanion (*e.g.*, KVPO₄F and KFeSO₄F) cathode or carbonaceous anode materials.

5.1.4. Fluorinated Electrolytes in K-Based Batteries. As within LIBs, electrolytes play a critical role in deciding the performance of K-based batteries.⁷⁰⁴ With regard to the electrolyte salts, since the electron-withdrawing feature of F atoms favors high solubility in organic aprotic solvents, most K salts contain fluorinated anions.⁷⁰⁵ Wu *et al.* investigated various electrolyte formulations based on KPF₆, potassium bis(trifluoromethylsulfonyl)imide (KTFSI) and KFSI salts, demonstrating that only KFSI/DME electrolyte enabled a reversible/stable plating/stripping behavior for K metal.⁷⁰⁶ This result was attributed to the cleavage of weak S-F bonds in FSI⁻, forming a stable KF-rich SEI layer. Besides chemical compositions, the choice of electrolyte salts also affects the structure, mechanical property, and electrical property of the SEI layer.⁷⁰⁷⁻⁷¹¹ As revealed by Guo *et al.*, a thinner SEI with higher viscoelasticity was formed with the KFSI-based electrolyte instead of the KPF₆-based electrolyte, largely alleviating the stress induced by volume changes during plating/stripping of K metal.⁷¹⁰ Besides, compared with the KPF₆-based electrolyte, the SEI constructed in KFSI-based electrolyte exhibited an improved thermal stability with more thermodynamic inorganic species, as evidenced by the decomposition reaction occurred at ~ 117 °C.⁷¹² Afterwards, DFT and MD calculations were conducted to reveal the underlining mechanism for different salts. Both the KFSI and KFSI-solvent complexes exhibited lower LUMO energy levels compared with the corresponding KPF₆ and KPF₆-solvent complexes. The solvation energy of K⁺ was higher in KFSI-based electrolyte than that in KPF₆-based electrolyte. These findings suggested that the SEI layer constructed with KFSI electrolytes was salt anion-dominated while the layer with KPF₆ was derived from solvent decomposition.⁷¹³

Based on KFSI as the conducting salt and the flame-retardant TEP as the sole solvent, an intrinsically non-flammable electrolyte was demonstrated for K-based batteries.⁷¹⁴ Compared with the requirements of highly concentrated phosphate electrolytes in LIBs and SIBs, a rather dilute electrolyte with a concentration of 0.9 M was sufficient to run the K-based battery system. Further optimizing the concentration of the KFSI-TEP electrolyte to 2.0 M, a uniform and robust anion-derived SEI layer was constructed along with the synergistic merits of low cost, low viscosity, and high ionic conductivity of the optimized electrolyte (**Figure 33a**), significantly suppressing the solvent decomposition and allowing a high CE of 99.6% for K-metal plating/stripping without dendrites. This advanced electrolyte was superior to conventional carbonate electrolytes, offering a new avenue for designing non-flammable electrolytes with high safety.

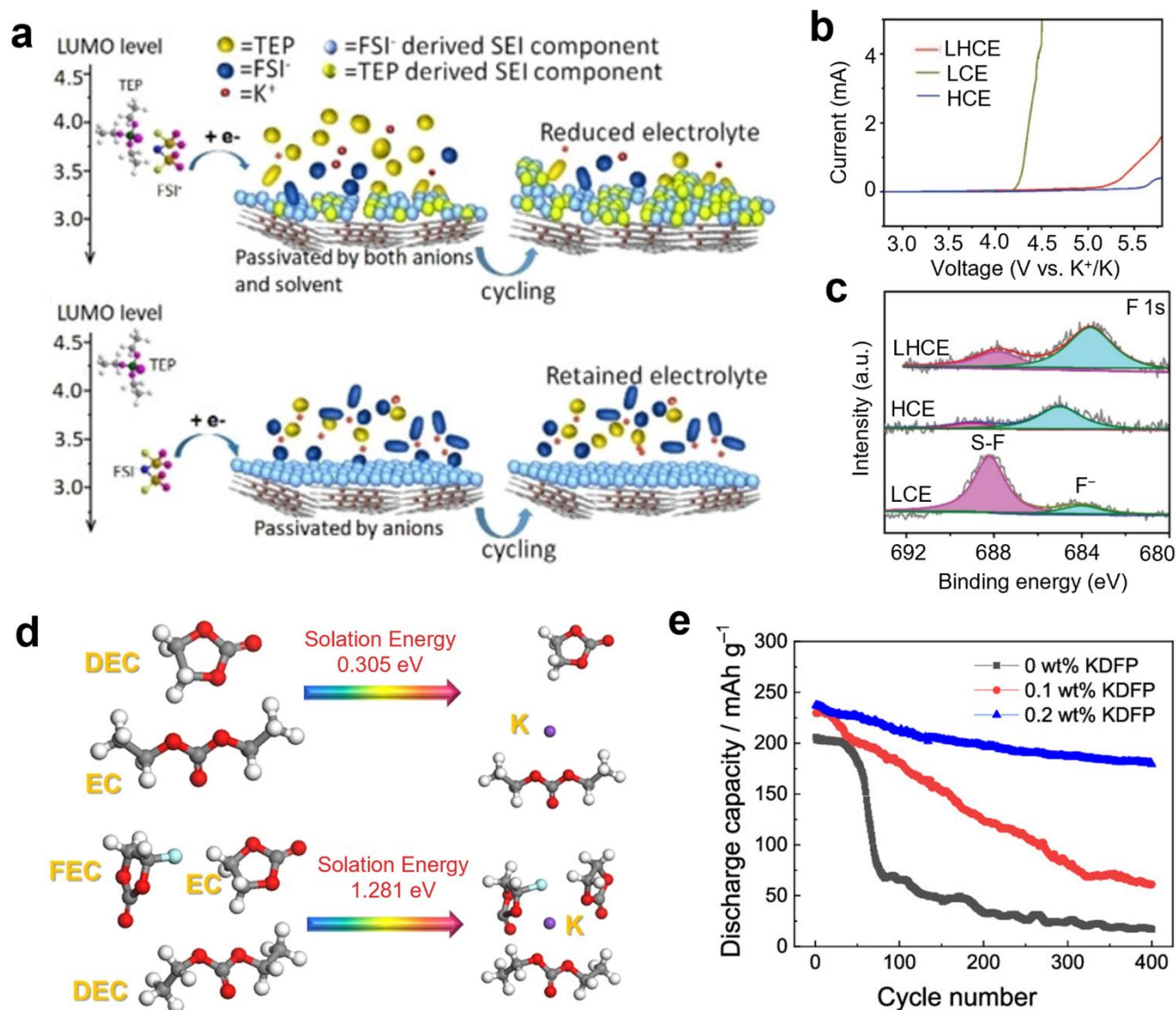


Figure 33. Fluorine-containing salts and electrolyte additives explored in PIBs. (a) Schematic illustration of the SEI constructed with 0.9 M-KFSI/TEP and 2 M-KFSI/TEP electrolytes. Reproduced with permission from ref ⁷¹⁴. Copyright 2020 Wiley-VCH. (b) LSV measurements of low concentration electrolyte (LCE), HCE and LHCE. (c) XPS F 1s spectra of the NCP anode with different electrolytes. Reproduced with permission from ref ⁷¹⁵. Copyright 2023 Wiley-VCH. (d) DFT calculations for the solvation energies estimated from the binding energy of the clusters. Reproduced with permission from ref ⁷⁰⁷. Copyright 2018 Elsevier. (e) Cycle stability of the graphite anode in 0.5 M KPF₆-EC/DEC electrolyte containing 0, 0.1, and 0.2 wt.% of KDFP, respectively at 1/3C (1C = 279 mA g⁻¹). Reproduced with permission from ref ⁷¹⁶. Copyright 2020 American Chemical Society.

Following the design of LHCEs in LIBs discussed in section 3.2., a low-polarity diluent that does not dissolve K salts was introduced to enhance the performance of LHCEs in K-based batteries. The first attempt adopted the highly fluorinated HFE as a diluent based on the concentrated KFSI-DME electrolyte, forming a LHCE with the molar ratio of 1:1.90:0.95 for KFSI: DME: HFE components. Such a LHCE displayed higher anti-oxidation stability, lower flammability, and higher ionic conductivity than the concentrated KFSI-DME electrolyte. In addition, with a durable KF-rich SEI layer constructed on the surface of graphite, the graphite anode with a high mass loading of ~8 mg cm⁻² survived for more than 300

cycles with a reversible capacity of 200 mA h g^{-1} , along with a high CE of 99.5%.⁷¹⁷ This report employed LHCE to achieve highly reversible graphite anodes. However, the influence of “inert” diluent molecules on the K^+ solvation structure and the local coordination environment is still ambiguous. Later, a fire-retardant electrolyte was developed by blending concentrated KFSI-TEP electrolyte with TTE as an “inert” diluent. Results revealed that such LHCE retained a relatively weakened anion-coordinated solvation environment, and the TTE diluent was non-solvated. Combining the synergistic effects of the KFI^- anions and the highly fluorinated diluent, a SEI film containing well-balanced inorganic/organic species was tailored *in situ* on the graphite anode, protecting the graphite anode from continuous side reactions and meanwhile facilitating the K-ion transport. Consequently, the graphite anode retained 92.4% capacity retention after 1400 cycles at 0.1 A g^{-1} .¹⁵⁵ Apart from the effects on graphite anodes, LHCEs were also designed to improve the compatibility between electrolytes and carbon-based anode materials in PIBs. Very recently, a LHCE was designed by introducing the non-solvent TTE into the concentrated KFSI-DME electrolyte. This LHCE broke the interconnected 3D K^+ solvated shell while maintaining the original individual K^+ solvated structure, thus improving the ionic conductivity and ensuring sufficient oxidation resistance of the electrolyte (**Figure 33b**). More promisingly, a uniform and durable KF-rich SEI layer was formed on the carbonous (nitrogen-doped carbon spheres, NCP) anode (**Figure 33c**), delivering a high reversible capacity of 232.5 mAh g^{-1} along with 78.7% capacity retention over 200 cycles.⁷¹⁵ These reports discovered the significance of “inert” diluents combined with salts and solvents for the design of LHCE systems for enhanced K-based batteries.

Besides the fluorine-containing salts, appropriate electrolyte additives can also stabilize the electrode|electrolyte interphase and further enhance the battery performance, which has been widely applied in LIBs and SIBs. Among them, as a widely applied film-forming additive, FEC has demonstrated excellent capability to solve the interfacial incompatibility of electrolytes towards reactive metal anodes. Owing to the anti-oxidative ability of the F-containing group, FEC additive was adopted to reduce side reactions of the Prussian blue analog (PBA) cathodes in PIBs, thus increasing the CE and cycle stability of the $\text{K}||\text{PBA}$ half cell.^{718, 719} However, the FEC additive sometimes worsened the electrochemical performance of full cells, especially when intercalation-based or alloy-based anode materials were used. This may be related to the excessive reduction of FEC that induces undesirable SEI formation during repeated cycling.⁷²⁰ Through DFT calculation, Guo *et al.* verified that the electrolyte with FEC increased the solvation energy from 0.305 eV to 1.281 eV (**Figure 33d**), pointing out a larger resistance for the K^+ diffusion and desolvation in the FEC-containing electrolyte, thus leading to poor performance.⁷⁰⁷ Similarly, the addition of FEC exerted negative influence on the electrochemical performance of Sn_4P_3 anode with fast capacity decay at high current rates. The FEC additive generated more components with carbonyl groups and K-F bonds in an unstable SEI layer that failed to suppress continuous side reactions, resulting in the quick resistance increase

and rapid capacity degradation.⁷⁰⁸ Later, such excessive SEI layer induced by FEC additive was further observed by Mai *et al.*, displaying a lower initial CE of 58%. In addition, FEC stimulated a large amount of electrolyte decomposition, which inevitably led to an increase in cell resistance and a decrease in capacity.⁷⁰⁹ Contrary to the unfavorable role of FEC additive on these anodes, by employing potassium difluorophosphate (KDFP) as additive to the KPF₆-EC/DEC electrolyte, Matsumoto *et al.* successfully constructed a stable K⁺-conducting SEI (enriched in KF and PO_x species) on the graphite anode, which promoted a highly reversible capacity of 274 mAh g⁻¹ with the formation of a suitable potassium-graphite intercalation compound (K-GIC, KC₈).⁷¹⁶ The KDFP electrolyte enabled a fast de-/potassiation kinetic process, an increased cyclability with 76.8% capacity retention, and a high average CE of ~ 99.9% over 400 cycles (**Figure 33e**). To briefly summarize, compared with the favorable effects of FEC additive on forming stable and robust SEI layers in LIBs and SIBs, the role of FEC in PIBs remains unclear and needs further investigations. Other effective functional F-containing additives should be explored to avoid undesired reactions between the anode materials and the electrolytes. It is noteworthy that the full cell performance, including both the cathode and the anode, should be implemented to reveal the real functions of these additives.

Overall, fluorinated electrode materials are of great interest to SIBs, where F⁻ anions (compared with large polyanions such as PO₄³⁻, SO₄²⁻) can improve the specific capacity, and fluorinated compounds are relatively stable against oxidation. The research is currently focusing on 3D fluorinated phases such as cubic perovskite fluorides due to their high-power capability and 3D network stability, but further investigation is needed to regulate polymorphism and phase transition during Na⁺ storage. Furthermore, establishing structure-performance relationships of these materials can reduce activation energy barriers and lower band-gap energy for efficient Na⁺ diffusion. For PIBs, though 3D open-framework polyanion compounds (*e.g.*, potassium fluorophosphates and fluorosulfates) can enable fast K⁺ diffusion and high redox potential, the low electronic conductivity of these materials requires surface modifications. Meanwhile, V-based fluorosulfates offer high working voltages when used as cathodes, but the fluorine to oxygen ratio should be controlled to prevent disordered fluorosulfate structures. Analogous to Li-based batteries, fluorine substitution in co-/solvents and additives can address critical issues in SIBs and PIBs, including interphasial instability, flammability, and capacity decay under fast charging or wide temperature ranges. Notably, strategies from fluorinated electrolytes in Li-based cannot be directly applied to SIBs and PIBs, for instance, FEC exhibits negative influence on certain anodes by stimulating electrolyte decomposition and forming unstable interphases. The current understanding of fluorinated electrolytes and corresponding interphases in SIBs and PIBs are still in the primary stage, and efforts should concentrate on these aspects.

5.2. Multivalent Metal-Based Batteries

5.2.1. Aqueous Multivalent Metal-Based Batteries. Aqueous multivalent metal-based batteries, such as the aqueous ZIBs, have become a research hotspot owing to the merit of high safety, high specific capacity, low cost and abundant distribution in the earth's crust. Zn metal is considered an ideal anode due to its high theoretical specific capacity (820 mAh g^{-1}), low electrode potential (-0.76 V vs. standard hydrogen electrode), abundant distribution, and low toxicity. However, when applied in aqueous electrolytes, Zn metal anodes still face serious issues such as corrosion reactions, hydrogen evolution, and uncontrolled dendrite formation.⁷²¹ These problems lead to low CE, poor cycle life, continuous electrolyte consumption, and even internal short-circuits.

Fluoride plays an important role in constructing highly reversible Zn metal anodes. In 2021, Li *et al.* devised a novel approach to create durable Zn metal anodes protected by a 3D ZnF_2 matrix, effectively preventing dendrite formation and extending the lifespan.⁷²² In their study, a 3D interconnected ZnF_2 matrix was engineered onto the surface of the Zn foil, denoted as Zn@ZnF_2 , using a rapid and straightforward anodic growth technique. This Zn@ZnF_2 electrode served as a versatile protective layer, facilitating the redistribution of Zn^{2+} ions and significantly reducing the desolvation active energy, resulting in stable and efficient Zn deposition. The findings demonstrated that the Zn@ZnF_2 electrode effectively suppressed dendrite growth, mitigated hydrogen evolution reactions, and exhibited outstanding plating/stripping of Zn^{2+}/Zn . In addition, the authors used *in situ* optical microscopy to capture the dynamic Zn plating process within 20 min, revealing the growth of Zn dendrites and large hydrogen bubbles on the pristine Zn electrode. In contrast, the smooth Zn deposition was observed on the surface of the Zn@ZnF_2 electrode without dendrites or gas bubbles (**Figure 34a**). Consequently, the Zn@ZnF_2 electrode displayed an impressive cycle life, exceeding 800 h at a current density of 1 mA cm^{-2} in a symmetrical cell test (**Figure 34b**). This excellent performance was also confirmed in $\text{Zn@ZnF}_2\|\text{MnO}_2$ and $\text{Zn@ZnF}_2\|\text{V}_2\text{O}_5$ full cells. Notably, a hybrid Zn ion capacitor employing the $\text{Zn@ZnF}_2\|\text{active carbon (AC)}$ configuration demonstrated exceptional durability, maintaining a high-capacity retention of 92.8% over 5000 cycles at an ultrahigh current density of approximately 60 mA cm^{-2} .

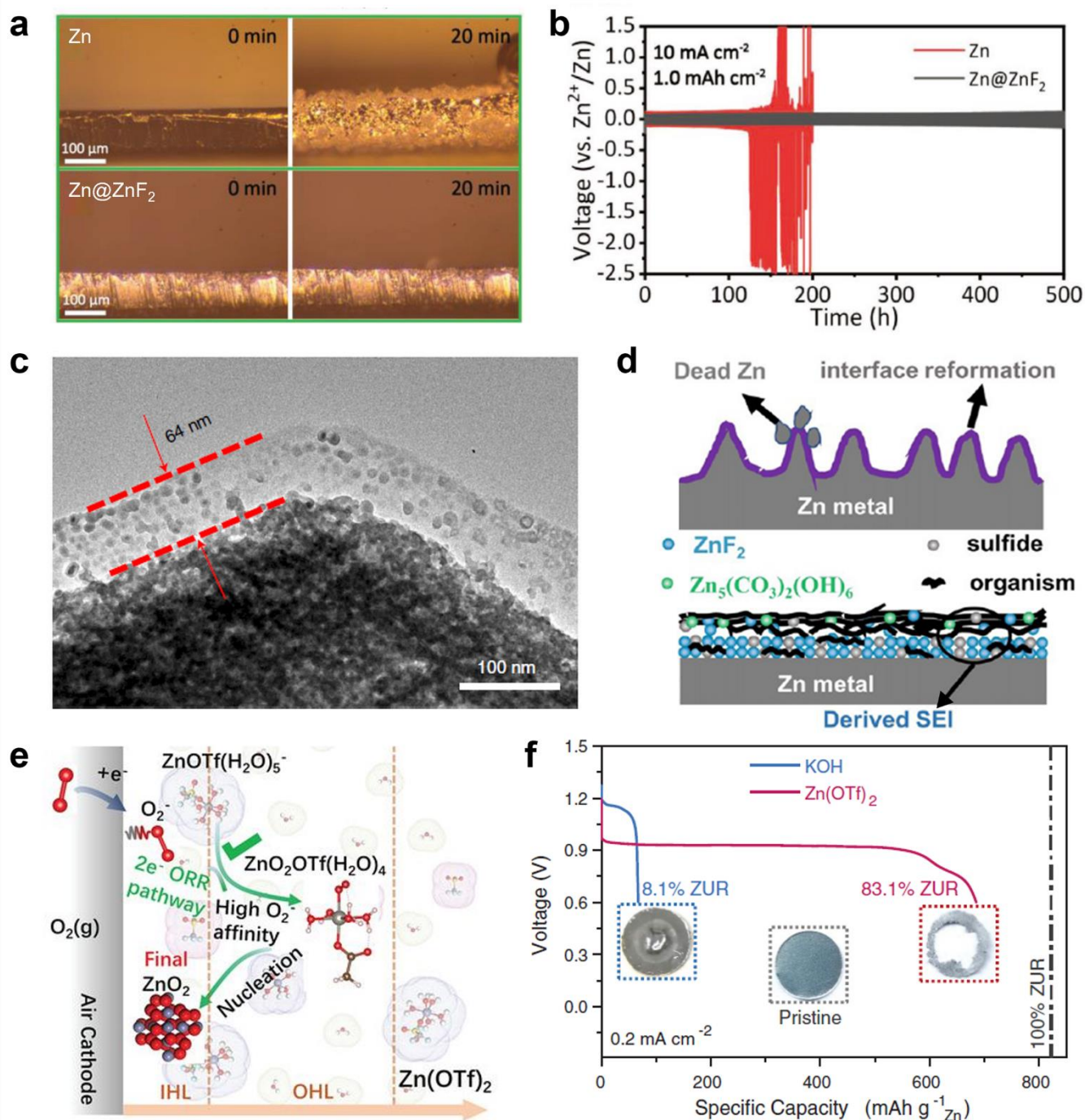


Figure 34. Fluorine chemistry in aqueous multivalent metal-based batteries. (a) Time-voltage curves for Zn||Zn and Zn@ZnF₂||Zn@ZnF₂ symmetrical cells at 10 mA cm⁻¹ with a plating/stripping capacity of 1 mAh cm⁻². (b) *In situ* optical observation results of the Zn deposition morphologies on the Zn foil and Zn@ZnF₂ electrode at a current density of 10 mA cm⁻² for 20 min. Reproduced with permission from ref ⁷²². Copyright 2021 Wiley-VCH. (c) TEM images of the cycled Zn anode surface in 4 m Zn(OTf)₂ + 0.5 m Me₃EtNOTF. Reproduced with permission from ref ⁷²³. Copyright 2021 Springer Nature. (d) Illustration of surface evolution mechanism. Upper panel: Zn dendrite growth in aqueous electrolytes. The water-passivation-induced porous ZnO layer (purple) constantly breaks and reforms, leading to non-uniform Zn electrodeposition, dendrite formation, and dead Zn during Zn plating/stripping. Lower panel: Formation mechanism of ZnF₂-Zn₅(CO₃)₂(OH)₆-organic SEI. The presence of NO₃⁻ promotes the formation of an electrically and ionically insulating Zn₅(OH)₈(NO₃)₂ · 2 H₂O layer (red), which subsequently transforms into an electrically insulating but ionically conductive SEI in which the ZnF₂-Zn₅(CO₃)₂(OH)₆ inner part is coated by the organic outer part. Reproduced with permission from ref ⁷²⁴. Copyright 2021 Wiley-VCH. (e) Galvanostatic discharge profiles of Zn-air cells in KOH (blue) and Zn(OTf)₂ (red) electrolytes at 0.2 mA cm⁻² (cutoff voltage: 0.6 V). The corresponding ZURs are indexed for

comparison. Insets are photographs of the pristine Zn anode (middle), the Zn anode after discharge in KOH (left), and Zn(OTf)₂ (right) electrolytes. (f) Schematic illustration of reaction processes in the IHL and outer Helmholtz layer (OHL) at the surface of the air cathode in Zn(OTf)₂ and ZnSO₄ electrolytes, respectively. Reproduced with permission from ref ⁷²⁵. Copyright 2021 The American Association for the Advancement of Science.

Fluorine chemistry is widely used in aqueous electrolytes and interface control. Wang *et al.* reported the development of an aqueous Zn metal battery.⁷²³ They utilized a dilute and acidic aqueous electrolyte containing 4 m zinc trifluoromethanesulfonate (Zn(OTf)₂) and an alkylammonium salt (trimethylethyl ammonium trifluoromethanesulfonate, Me₃EtNOTF) as the additive to facilitate the creation of a robust, Zn²⁺-conducting, and waterproof SEI. The TEM analysis revealed the presence of a 64 nm thick ZnF₂-rich interphase on the deposited Zn surface when Me₃EtNOTF was introduced (**Figure 34c**). This SEI acted as an electron barrier, preventing the reduction of water while allowing the migration of Zn²⁺. The presence of this SEI led to outstanding performance, including dendrite-free Zn plating and stripping, a remarkable 99.9% CE over 1000 cycles in a Ti||Zn asymmetric cell, stable cycling behavior for 6000 cycles (equivalent to 6000 hours) in a Zn||Zn symmetric cell, and impressive energy densities in full cells with limited Zn source (e.g. 136 Wh kg⁻¹ in a Zn||VOPO₄ full cell with 88.7% capacity retention over 6000 cycles; 218 Wh kg⁻¹ in a Zn||MnO₂ full cell with 88.5% capacity retention over 1000 cycles. Furthermore, the electrolyte is conducive to SEI formation, allowing the reversible operation of an anode-free pouch cell. The Ti||Zn_xVOPO₄ full cell can be cycled at 100% depth of discharge for 100 cycles, enabling aqueous Zn-based batteries as practical and viable energy storage systems for various applications. Wang *et al.* also reported the development of a Zn-ion conductive, water-resistant and ZnF₂-rich SEI on the Zn anode.⁷²⁴ A designed low-concentration aqueous electrolyte composed of fluorine-containing Zn(OTf)₂ and Zn(NO₃)₂ was developed. This electrolyte facilitated the *in situ* formation of a robust SEI with an inorganic inner layer made of ZnF₂ and Zn₅(CO₃)₂(OH)₆ to enhance Zn-ion diffusion, and an organic outer layer acted as a barrier against water infiltration. Their research revealed that the initial layer formed on the Zn anode surface was an insulating Zn₅(OH)₈(NO₃)₂ · 2H₂O, resulting from a self-terminated chemical reaction involving NO₃³⁻, Zn²⁺, and OH⁻ generated through the hydrogen evolution reaction (HER). Subsequently, this inorganic layer transformed into Zn-ion conducting Zn₅(CO₃)₂(OH)₆, promoting the formation of ZnF₂ as the inner layer (**Figure 34d**). The organic-dominated outer layer was established through the reduction of OTf⁻. This *in situ* formed SEI exhibited remarkable performance, achieving a high CE of 99.8% over 200 h in Ti||Zn half cells and maintaining a high energy density of 168 Wh kg⁻¹ in Zn||MnO₂ full cells with 96.5% capacity retention after 700 cycles, even with a N/P ratio of 2:1.

Rechargeable Zn-air batteries hold the promise of delivering both high energy density and safety. However, they encounter huge challenges due to the sluggish 4-electron (e⁻)/oxygen (O₂) reaction that relies

on water participation. The electrochemical reversibility stems from unwanted side reactions driven by the harsh electrolytes and atmospheric carbon dioxide. In 2021, Winter *et al.* reported a breakthrough result in the form of a Zn-O₂/zinc peroxide (ZnO₂) chemistry, which was operated *via* a 2-e⁻/O₂ reaction in non-alkaline aqueous electrolytes.⁷²⁵ The new reaction mechanism facilitated highly reversible redox reactions for Zn-air batteries. The success of this ZnO₂-based chemistry can be attributed to the formation of a water-scarce and Zn²⁺-rich inner Helmholtz layer (IHZ) on the air cathode, induced by the hydrophobic trifluoromethanesulfonate anions (**Figure 34e**). In a non-alkaline electrolyte containing 1 mol kg⁻¹ Zn(OTf)₂, the Zn-air battery exhibited a well-defined discharge plateau at approximately 1.0 V, boasting an areal capacity of 52 mAh cm⁻², corresponding to a specific capacity of 684 mAh g⁻¹ (based on the weight of Zn anode). Additionally, as shown in **Figure 34f**, it achieved a remarkable Zn utilization ratio (ZUR) of 83.1%. In contrast, the Zn-air battery with an alkaline electrolyte composed of 6 mol kg⁻¹ KOH only achieved a ZUR of 8.1%. The photographic evidence of pristine and cycled Zn anodes immersed in different electrolytes confirmed the superior ZUR in the Zn(OTf)₂ electrolyte, where most of the Zn foil dissolves. As a result, the non-alkaline Zn-air battery not only maintained stable performance in ambient air, but also demonstrated significantly improved reversibility compared to its alkaline counterpart. Similar fluorine chemistry-involved electrolyte engineering strategies can be promisingly extended to other aqueous multi-valent ion systems (*e.g.*, Mg-ion, Ca-ion and Al-ion batteries).

Moreover, F-containing materials have also been applied as cathodes in aqueous multi-valent ion batteries. In 2021, Gregorio *et al.* developed a trigonal Na₅V(PO₄)₂F₂ as the cathode for Mg-ion batteries.⁷²⁶ Beneficial from the multi-electron transfer redox couples of V⁴⁺/V³⁺ and V⁵⁺/V⁴⁺, the Mg|0.5M magnesium bis(trifluoromethanesulfonyl)imide (Mg(TFSI)₂)-DME+0.4 M H₂O|Na₅V(PO₄)₂F₂ cell delivered a reversible specific capacity of 136 mA h g⁻¹, achieving a high energy density of 190 W h kg⁻¹ with the average discharge voltage of 1.4 V. It should be noted that the regulation of F⁻/O²⁻ ratio in sodium-vanadium fluorophosphate directly affected the content of V³⁺/V⁴⁺ and changed the specific capacity of the cathode materials.

5.2.2. Non-Aqueous Multivalent Metal-Based Batteries. F-related chemistry also plays an important role in the development of non-aqueous multivalent metal-ion batteries (*e.g.*, Mg-ion batteries, Ca-ion batteries and Al-ion batteries) as promising energy storage systems, owing to the high energy densities and low cost. The multielectron redox capability contributes to the high energy density, and the abundant distribution of these multivalent metal ions in Earth's crust ensures the low manufacturing costs. However, the larger ionic radii and greater charge density of multivalent metal ions bring significant challenges

associated with slow ion transport, large polarization and low reversibility, making them less competitive than Li-based batteries in the race towards ever-rising energy density targets.⁷²⁷

Strategy aiming at balancing the protection and passivation effect of the F-containing layer on the anode surface is widely applied to realize the high-performance multivalent-metal ion batteries. For instance, Mg-based batteries often face several challenges, such as low power density and limited cycle life, primarily due to the issue of severe passivation of the Mg anode. Although using nucleophilic electrolytes can effectively stabilize the Mg anode, their high chemical reactivity prevents the use of organic and conversion cathodes. To solve this issue, Lu *et al.* introduced a non-passivating anion additive known as reduced perylene diimide-ethylene diamine (rPDI). This additive has been proven effective in facilitating rapid and reversible Mg deposition/dissolution in a straightforward Mg(TFSI)₂-MgCl₂-based electrolyte with only a minimal addition of 0.2 mM rPDI. The ability of rPDI to selectively adhere to Mg anode is the key factor for the enhanced performance, thus repelling TFSI⁻ anions from the surface of Mg anode. This prevented TFSI⁻ decomposition and the subsequent Mg passivation (**Figure 35a**). Leveraging rPDI's mM-level solubility in the electrolyte, it was employed as an electrolyte additive in both symmetric cells and full cells. With the addition of only 0.2 mM rPDI as the electrolyte additive, Mg symmetric cells with the electrolyte of 0.25 M Mg(TFSI)₂-2MgCl₂/DME demonstrated impressive results, achieving highly reversible cycling performance for 300 h at 1.0 mA cm⁻². More importantly, the protective effect of rPDI persisted even when the electrolyte was exposed to air, which remarkably extended the cycling stability. Furthermore, the researchers showcased the performance of a Mg-organic full cell, demonstrating fast and reversible Mg²⁺ storage at 50 C (6.4 A g⁻¹). This configuration achieved a superior specific power density of 8.78 kW kg⁻¹ and a stable cycle life exceeding 1000 cycles at 15 C. Exceptional areal power density (2.0 mW cm⁻²) and energy density (1.6 mWh cm⁻²) were attained at 1 C, along with the highest reported areal capacity of 1.0 mAh cm⁻² and a stable cycle life extending beyond 200 cycles (**Figure 35b**). In another case, Zhao *et al.* effectively synthesized magnesium tetrakis(hexafluoroisopropoxy)borate, denoted as Mg[B(hfip)₄]₂, showcasing its exceptional characteristics as a viable and efficient electrolyte for prospective high-energy Mg-based batteries.⁷²⁸

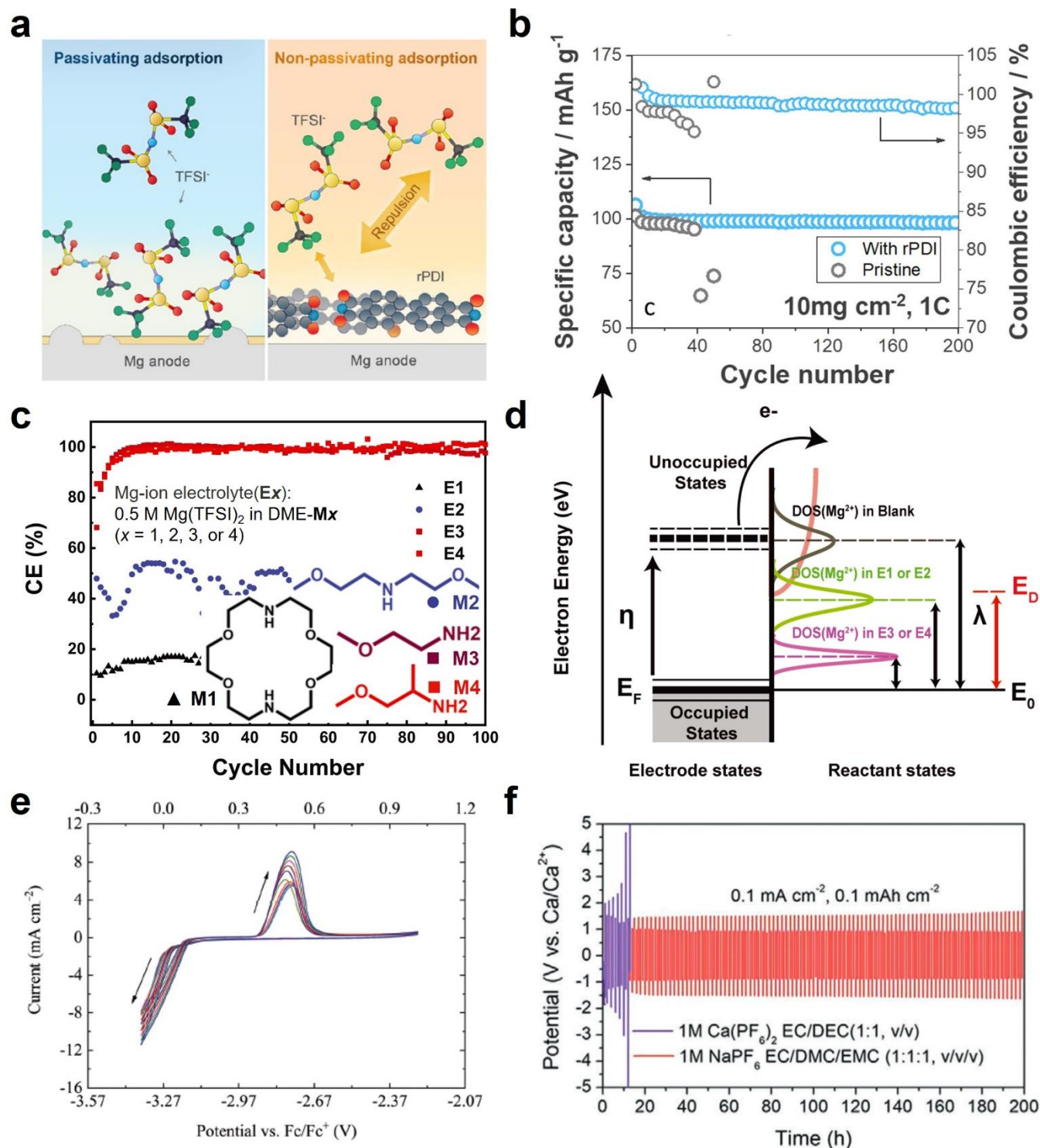


Figure 35. Fluorine Chemistry in non-aqueous multivalent metal-based batteries. (a) Schematic illustration of passivating adsorption and non-passivating adsorption. Left panel: passivating anions (TFSI⁻) adsorb on the Mg anode and form the passivation layer. Right panel: non-passivating anions (rPDI) with higher adsorption energy repel TFSI⁻ away to prevent Mg anode passivation. (b) Cycling stability of Mg-PDI full cells with pristine (gray) and rPDI (blue) electrolyte at 15 °C under 1 mg cm⁻² (1 C = 128 mA g⁻¹). Reproduced with permission from ref ⁷²⁹. Copyright 2021 American Chemical Society. (c) CEs for Mg plating and stripping in **Ex** in Mg||SS cells cycled at 0.1 mA cm⁻². Mg-ion electrolyte (**Ex**): 0.5 M Mg(TFSI)₂-DME/**Mx** (x = 1, 2, 3, or 4). (d) Marcus-Gierischer diagram of electron transfer at the metal electrode/electrolyte interphase. E_F refers to the Fermi level of the metal electrode, and E_0 refers to the energy level of the electrolyte and electrode at equilibrium. Red, green, and black Gaussians represent the DOS of Mg²⁺ in the electrolyte. The orange curve represents the DOSs of other electrolyte components, and E_D refers to the onset potential of the electrolyte decomposition. Reproduced with permission from ref ⁷³⁰. Copyright 2021 The American Association for the Advancement of Science. (e)

CVs of Ca plating/stripping in the electrolyte containing Fc as the internal reference with a three-electrode configuration using Pt, Ag, and Ca as a working electrode, reference electrode and counter electrode, respectively, at a scan rate of 80 mV s⁻¹. Reproduced with permission from ref ⁷³¹. Copyright 2019 Royal Society of Chemistry. (f) Cycling stability of voltage-time curves with a capacity of ~ 0.1 mAh cm⁻² at 0.1 mA cm⁻² of Ca||Ca symmetrical batteries. Reproduced with permission from ref ⁷³². Copyright 2020 Wiley-VCH.

Similar to Mg-based batteries, rechargeable Ca-based batteries show great promise as alternatives to LIBs due to the abundant resource of Ca element in the Earth's crust and the high theoretical specific capacity. However, these batteries face significant challenges related to slow reaction kinetics and unwanted side reactions. Wang *et al.* developed a significant breakthrough by demonstrating that multidentate methoxyethyl-amine chelates [-(CH₂OCH₂CH₂N)_{*n*}], located in the first solvation sheath of Mg²⁺ and Ca²⁺, facilitate both highly reversible reactions on Mg and Ca anodes as well as high-voltage layered oxide cathodes.⁷³⁰ Specifically, 0.5 M Mg(TFSI)₂-DME was selected as baseline electrolyte. Four types of multidentate chelates (**Mx**, *x* = 1, 2, 3, or 4) were added to the baseline electrolyte to form the electrolytes **Ex** (*x* = 1, 2, 3, or 4), respectively. The overpotentials during Mg plating and stripping processes were significantly reduced from 2.0 V (blank) to below 0.1 V (**E4**) with a high CE of 99.5% (**Figure 35c**). The solvation sheath analysis demonstrated that the solvation sheath became less compact and more polarizable, leading to a decrease in solvation sheath reorganization energy (λ) for electron transfer (**Figure 35d**). This, in turn, lowered overpotential by preventing electrolyte decomposition and facilitating stable Mg and Ca plating and stripping. Calcium tetrakis(hexafluoroisopropoxy)borate, known as Ca[B(hfip)₄]₂, was developed as a prospective electrolyte for room-temperature rechargeable Ca batteries, which demonstrated room temperature reversible Ca plating and stripping (**Figure 35e**), exceptional oxidative stability up to 4.5 V, and a high ionic conductivity exceeding 8 mS cm⁻¹.⁷³¹

Wang *et al.* showcased that a hybrid Na/Ca-based SEI surpassed a purely Ca-based SEI in achieving stable Ca plating and stripping processes.⁷³² In the case of fluorine-based electrolytes like calcium hexafluorophosphate (Ca(PF₆)₂) and calcium tetrafluoroborate (Ca(BF₄)₂) ethers and esters solutions, Ca metal underwent passivation with a SEI primarily composed of CaF₂ (pure Ca SEI). This CaF₂ layer served as both an ionic and electronic insulating barrier. Conversely, when using NaPF₆ in an electrolyte composed of EC/DMC /EMC in a 1:1:1 ratio by vol., an *in situ* evolution of a hybrid Na/Ca-based SEI occurred. These hybrid SEIs exhibited excellent ion conductivity for both Ca²⁺ and Na⁺ ions, simultaneously preventing anions from deeply penetrating and averting uncontrolled decomposition of the electrolyte upon the freshly deposited Ca. Consequently, long-term Ca plating and stripping (lasting over 1000 hours with minimal polarization shift) can be reliably achieved by utilizing Ca metal itself as the current collector (**Figure 35f**). Furthermore, Ca metal safeguarded by the hybrid Na/Ca-based SEIs also maintains impressive high-voltage stability, extending up to 4.5 V when used in full cells.

Aluminum, the third most abundant element in the Earth's crust with an oxidation state of 3+, endows the construction of cost-effective and high-energy-density batteries, boosting the high specific capacity in the form of Al metal anodes and enhanced safety due to its air-stable passive surface layer compared to Li metal. In 2017, Masashi *et al.* reported a fluoropolymer-supported Al³⁺-conducting solid-state electrolyte.⁷³³ By tuning the ratio of PVDF and AlCl₃ (F/Al ratio), the optimized Al³⁺ conductivity at room temperature reached $4.4 \times 10^{-4} \text{ S cm}^{-1}$ with a F/Al ratio of 8. This Al³⁺-conducting solid-state electrolyte also showed a stable electrochemical window of 0~2.4 V vs. Al³⁺/Al, fulfilling the redox potential of the reported cathode materials of Al-ion batteries. This fluoropolymer-based solid-state electrolyte is promising to eliminate the safety issues such as the leakage of highly corrosive liquid electrolytes in conventional aluminum-ion batteries.

The cathode materials of non-aqueous multivalent metal-based batteries also benefit from fluorine chemistry. In 2021, Xu and colleagues applied a polyanion fluoride (Na_{1.5}VPO_{4.8}F_{0.7}, NVPF) as the cathode material for a non-aqueous Ca-ion battery and achieved a high reversible performance of over 500 cycles with a low capacity fading of 0.02% per cycle.⁷³⁴ A variety of characterizations revealed that the volume change relating to the insertion/extraction of Ca²⁺, the diffusion resistances and the activation of large Ca²⁺ ion barriers were successfully suppressed, owing to the rigid open framework of VPO_{4.8}F_{0.7}.

In general, for aqueous multivalent metal-based systems (*e.g.*, ZIBs), the strategy of constructing fluoride-rich anode|electrolyte interphases can effectively suppress the anode dendrite growth and electrolyte decomposition. Moreover, the sluggish plating kinetics of anode in non-aqueous multivalent metal-based systems (*e.g.*, Mg-ion and Ca-ion batteries) can be improved by the solvation structure modification via the introduction of fluorinated salts, solvents and additives. All these fluorine chemistry-involving strategies are accelerating the real-world application of multivalent metal-based batteries.

5.3. Dual-Ion Batteries and Beyond

In DIBs, anion insertion is considered as the most important reaction on the cathode side, whereas various inserted anions with F-containing groups were intensively investigated, such as PF₆⁻,⁷⁸⁻⁸¹ TFSI⁻,^{82, 735} FSI⁻,⁸³⁻⁸⁶ FTFSI⁻,^{87, 88} BF₄⁻,⁷³⁶ DFOB⁻,⁹¹ CF₃SO₃⁻⁹², AlF₄⁻⁹³, tris(pentafluoroethyl) trifluorophosphate [(C₂F₅)₃PF₃]⁻⁷³⁷ and BETI⁻.⁸⁷ To improve the performance of Al||graphite DIBs, Tang *et al.* developed an electrolyte of 7.5 m LiFSI-EC/DMC (1:1 v/v), which not only elongated the cycle stability of the graphite cathode during repeated de-/intercalation of FSI⁻ anions, but also enhanced the structural stability of Al anode via constructing a LiF-rich SEI layer.⁷³⁸ Motivated by this Al-graphite electrochemistry, Chen *et al.* developed an EMC/DMC carbonate electrolyte with binary salts of LiPF₆ and AlF₃. It was revealed that the Al anode was protected from dissolving after adding AlF₃ into the electrolyte. More notably, AlF₄⁻ complex anions were formed via the combination of the dissolved Al³⁺ and F⁻ in the electrolyte, which de-

/intercalated from/into the graphite during discharging/charging together with PF_6^- . Based on this electrochemistry, the battery exhibited a high average working voltage of 4.0-4.5 V, and a high reversible capacity of $\sim 100 \text{ mAh g}^{-1}$, along with a high CE of $\sim 99\%$ over 600 cycles.⁹³ Besides the Al anode, Ca^{2+}/Ca redox chemistry shows promising prospects for rechargeable batteries due to its low polarization and low reduction potential (-2.87 V vs. SHE). Unfortunately, Ca-based batteries experience critical issues, including unsuitable electrode materials for reversible Ca^{2+} storage, low working voltages ($< 2 \text{ V}$), and poor cycle stability, especially at RT. To tackle these issues, Tang *et al.* designed a new battery configuration by employing graphite as the cathode material and Sn foil as both the anode material and current collector. With an electrolyte consisting of $0.8 \text{ M Ca}(\text{PF}_6)_2$ in mixed solvents (EC: PC: DMC: EMC = 2:2:3:3 by vol.), highly reversible redox reactions incorporating the de-/intercalation of PF_6^- anion at the cathode and the de-/alloying of Ca^{2+} ions at the metal anode were achieved. The resulting DIBs yielded a high discharge voltage of up to 4.45 V and high cycling stability (95% capacity retention over 350 cycles), as displayed in **Figure 36a and b**.⁷³⁹

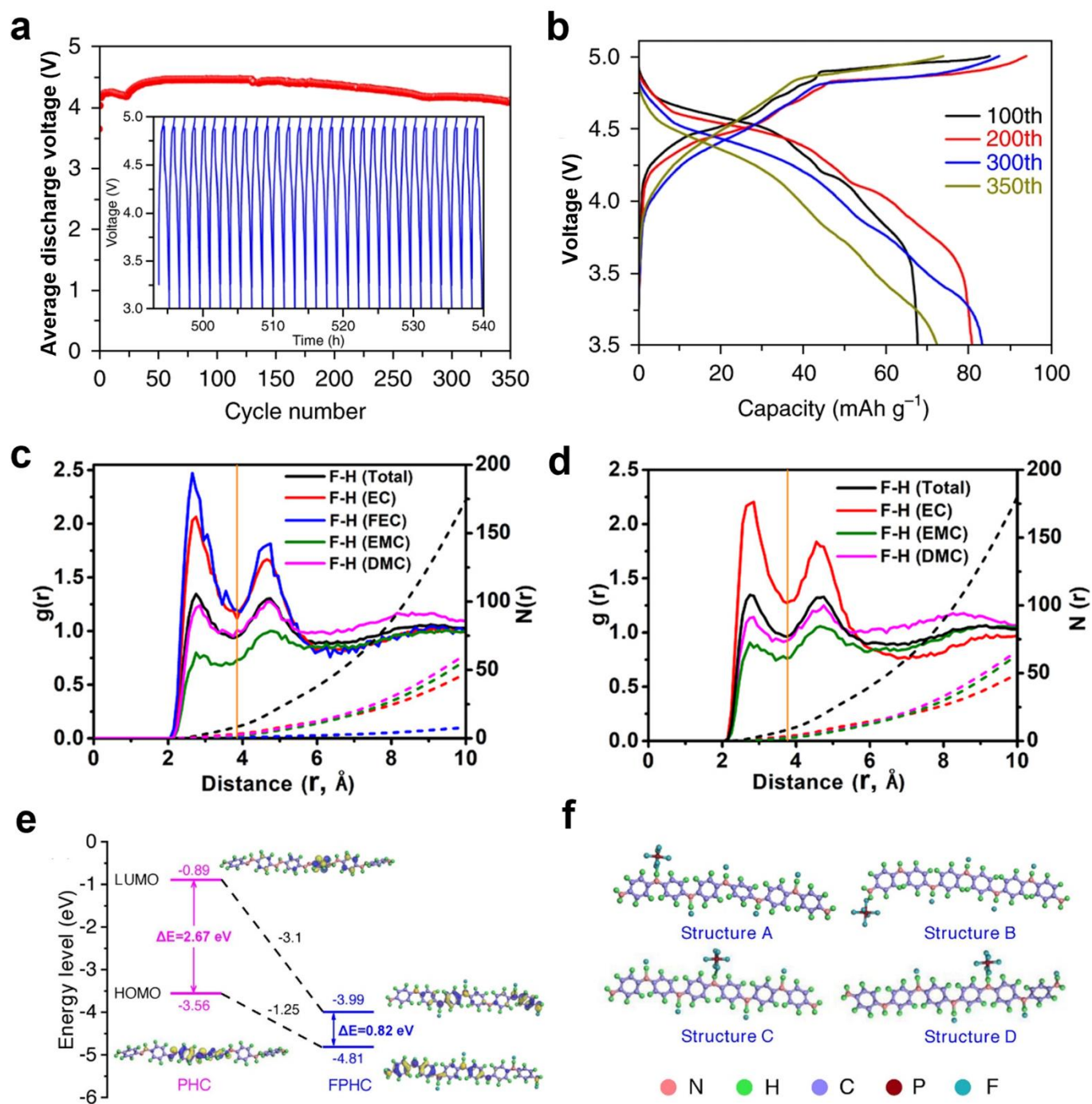


Figure 36. Fluorine-containing electrolytes or electrodes for high-performance DIBs. (a) Average discharge voltage and (b) corresponding charge-discharge profiles of the Ca||graphite DIB at a current density of 100 mA g^{-1} . Inset of (a) shows the enlarged curves for the final 30 cycles. Reproduced with permission from ref ⁷³⁹. Copyright 2018 Springer Nature. MD simulation for the RDFs $g(r)$ (solid lines) and coordination number $N(r)$ (dashed lines) of F-H interactions in 1.0 M NaPF₆-EC/DMC/EMC (1:1:1 by vol.) electrolytes with (c) 10 wt.% FEC and (d) without FEC additive. Reproduced with permission from ref ⁷⁴⁰. Copyright 2021 American Chemical Society. (e) HOMO-LUMO energy and energy gap of PHC and FPHC molecules. (f) Four optimized models of PF₆-FPHC with PF₆⁻ at near-end group, PF₆⁻ at end group, PF₆⁻ at the middle group and PF₆⁻ at the near-middle group, respectively. Reproduced with permission from ref ⁷⁴¹. Copyright 2022 Wiley-VCH.

Apart from the F-containing salts, fluorination treatment of other electrolyte components also endows DIBs with unique features such as wide working windows, wide temperature range, non-flammability and

enhanced electrode|electrolyte compatibility. Read *et al.* employed a fluorinated solvent and additive in DIBs. The designed 1.7 M LiPF₆-FEC/EMC electrolyte with 5 mM tris(hexafluoro-isopropyl) phosphate (HFIP) as the additive supported a graphite||graphite cell with a charge voltage up to 5.2 V, enabling the accommodation of PF₆⁻ and Li⁺ at the graphite cathode and the graphite anode simultaneously with a high CE of 97%.⁷⁴² Thereafter, the role of FEC on the anion solvation status and the anion insertion/extraction behaviors in DIBs was carefully evaluated by Yang *et al.*⁷⁴⁰ It was revealed that FEC tuned the solvation structures of both Na⁺ and PF₆⁻ by replacing part of the original EMC solvent in the solvation shell (**Figure 36c,d**), inducing the formation of a fluorinated CEI film to resist the electrolyte side reactions at high voltages and suppress the expansion of graphitic layers in the cathodes during long-term cycling. The CEI layer on cathodes can also be modified by different salts as additives, as evidenced by the work conducted by Yu *et al.*⁷⁴³ With the addition of ~ 0.5 wt.% LiDFOB (with)in the electrolyte, a less-resistive Li_xBO_yF_z enriched CEI layer was constructed on the cathode surface. The LiDFOB salt has a higher HOMO energy level than that of the baseline solvent (EMC), inducing the preferential decomposition of LiDFOB. This robust and durable CEI enabled fast electrode reaction kinetics and achieved an ultra-fast charging capability within 2 min. Later, the authors designed an all-fluorinated electrolyte (1 M LiPF₆-FEC/FEMC) that synergistically guaranteed a highly stable operation of the DIB up to 5.2 V by generating robust and ion-conductive passivation films on both electrodes to reduce undesired side reactions. More significantly, this fluorinated electrolyte facilitated fast reaction kinetics of PF₆⁻ and Li⁺ at low temperatures, delivering 97.8% reversible capacity at RT, together with ~ 100% capacity retention over 3000 cycles at 500 mA g⁻¹.⁷⁴⁴ The all-fluorinated electrolyte system endows DIBs as a promising choice for wide-temperature applications. In addition to a wide operational temperature range, safety concerns (*e.g.*, fire, explosion, and leakage of toxic electrolyte components) should be given sufficient consideration. Based on the all-fluorinated electrolyte (1 M LiPF₆-FEC/FEMC/THE, 1: 6: 3 by vol.), Wang *et al.* prepared a GPE via *in situ* polymerization of diethyl allyl phosphate (DAP) monomer and pentaerythritol tetraacrylate (PETEA) crosslinker.³⁵³ This GPE with 3D polymer matrix showcased high safety features (*e.g.*, nonflammability), sufficient ionic conductivity (1.99 mS cm⁻¹), superior stability up to 5.5 V (vs. Li/Li⁺), and high compatibility towards both electrodes.

To tackle concerns of cost, eco-friendliness, and safety caused by organic electrolytes, aqueous or hybrid aqueous/nonaqueous electrolytes have emerged as a highly interesting alternative for promoting practical applications of DIBs. Particularly, the pioneer work from Xu *et al.* proposed the concept “water-in-salt” (WiS) electrolyte, which significantly enlarged the ESW of aqueous electrolytes from 1.23 V to ~ 4.9 V.^{135, 745} Encouraged by this widely adopted strategy in aqueous metal-ion batteries, especially in LIBs, a WiS electrolyte formulated with 21 M LiTFSI in aqueous electrolyte H₂O was combined with 9.25 M LiTFSI-DMC (mass ratio 1:1) nonaqueous electrolyte by Placke *et al.*⁷⁴⁶ This hybrid electrolyte not only guaranteed

adequate safety with the nonflammable feature from the WiS aqueous electrolyte, but also protected the anode from side reactions by forming a stable SEI with the assistant of the nonaqueous component. Therefore, a stage-2 graphite intercalation compound (GIC) for TFSI⁻ intercalation was achieved in aqueous-based electrolytes. Afterwards, an aqueous WiS consisting of 20 m NaFSI and 0.5 m Zn(TFSI)₂ was developed by Placke *et al.* in a Zn||graphite DIB.⁷⁴⁷ The role of the high concentration NaFSI salt was to reduce the free water molecules in the WiS electrolyte and to suppress the occurrence of oxygen evolution reaction (OER). It was interesting to note that instead of the co-intercalation of FSI⁻ and TFSI⁻, TFSI⁻ anions were proved to predominantly the intercalation process into the graphite layers, which was associated to its lower intercalation barrier. Benefiting from this advanced electrolyte design, the consequent Zn||graphite DIB exhibited a high working voltage of ~ 2.3–2.5 V and a high reversible capacity of ~ 110 mAh g⁻¹ with > 80% capacity retention after 200 cycles.

Besides its beneficial effects on electrolyte optimization, fluorine element can also be introduced to the cathode material to boost and stabilize anion intercalations. It is generally known that with strong electronegativity, low van der Waals radius, and low polarizability properties, F is considered to have the ability to tune the photoelectric properties of conducting conjugated polymers such as PANI.⁷⁴¹ Based on these merits, a novel fluoridized-polyaniline-H⁺/CNT composite (FPHC) has been developed as the cathode material for DIBs. The introduction of F effectively reduced the energy gap between HOMO and LUMO (**Figure 36e**), thus enabling a highly efficient storage of anions in the FPHC cathode. This result was further reflected by the higher electronic conductivity of 0.162 S cm⁻¹ compared with the non-fluorinated PHC cathode (0.138 S cm⁻¹). In addition, the combinative formation of PF₆⁻ anion in FPHC cathode was verified, suggesting that F⁻ of the PF₆⁻ anion tended to form a stable covalent bond with -NH in FPHC, and thus exhibiting a symmetric structure of the whole PF₆⁻-FPHC molecular, as shown in **Figure 36f**. This fluoridized treatment guaranteed a stable cycling of 2000 times at 2 A g⁻¹ with a retained discharge capacity of 73 mAh g⁻¹, along with a high power density of 7720 W kg⁻¹ at an energy density of 310 Wh kg⁻¹.⁷⁴¹

In addition to the abovementioned DIBs, another emerging battery system also based on both cations and anions as charge carriers for electrochemical reactions is called RDIBs, except that the sequence of the anion- and cation-storage chemistries is flipped between the cathode and the anodes. Till now, the RDIB chemistries have been only realized in aqueous electrolytes. In 2018, Hou *et al.* developed a novel RDIB relying on F⁻ anion and Na⁺ cation electrochemistry, which comprised 0.8 M NaF aqueous solution as the electrolyte, Na_{0.44}MnO₂ as the cathode material, and BiF₃ as the anode material.⁷⁴⁸ During the charge process, the BiF₃ anode released F⁻ ions and the Na_{0.44}MnO₂ cathode deintercalated Na⁺ ions to the aqueous electrolyte simultaneously. During the discharge process, the F⁻ ions in the electrolyte were captured by the anode to obtain BiF₃, and the Na⁺ ions were intercalated into the cathode material as well (**Figure 37a**). This RDIB delivered a high discharge capacity of ~123 mAh g⁻¹ at the current density of 100 mA g⁻¹ based

on the mass of BiF₃ anode materials. However, the capacity deteriorated very rapidly to 47.28 mAh g⁻¹ over just 40 cycles, which was probably due to the instability of the anode material. An obvious volume change of the anode material was observed during cycling, *i.e.*, 57.3% volume contraction for the phase transition from BiF₃ into Bi, and a large volume expansion of 134.0% for the reverse transition from Bi to BiF₃. Therefore, strategies such as structure modifications or surface coatings should be explored to enhance the cycling stability of the Bi/BiF₃ electrode. Afterward, another RDIB was designed by Li *et al.* (**Figure 37b**), utilizing KF aqueous electrolyte, Prussian blue (PB) cathode material and BiF₃@Bi₇F₁₁O₅@reduced graphene oxide (BFO) anode material.⁵⁸⁹ It was elucidated the low electrolyte concentration improved the cycle stability of the BFO||PB RDIB despite the reduced discharge capacity. The reduction of F⁻ ions in the dilute electrolytes suppresses the dissolution of Bi³⁺ ions generated upon the discharge process, reducing the deposition of the side products on the electrode surface. In addition, this Bi³⁺ dissolution phenomenon can also be mitigated by the graphene coating on the surface of the BFO anode material. The resulting F/K-based RDIB achieved a high discharge capacity of 218 mAh g⁻¹ at 1 A g⁻¹, as well as fast rate capability with a capacity retention of 47% at a high current density of 5 A g⁻¹, which were calculated based on the weight of the BFO anode material.

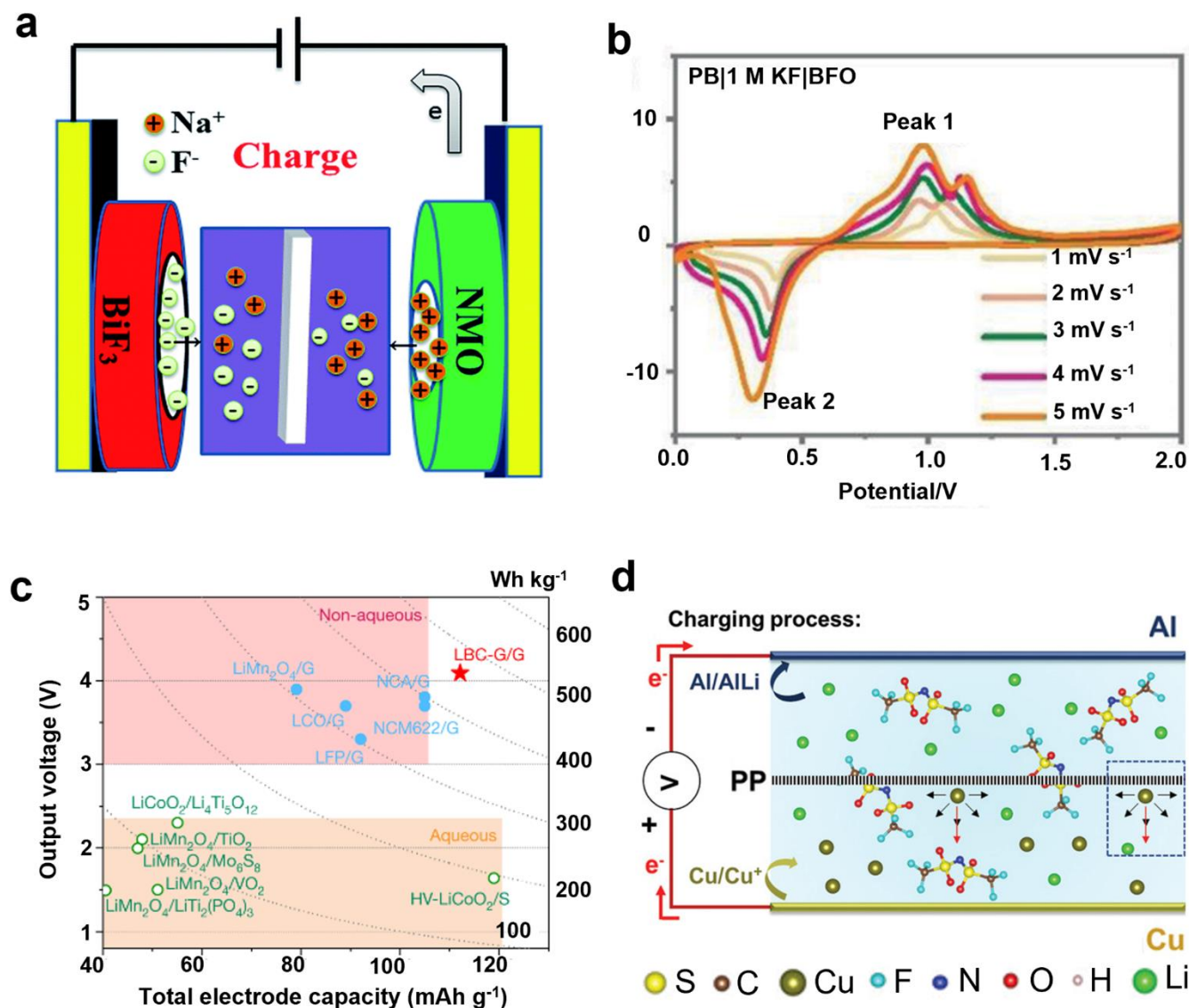


Figure 37. Beneficial effects of fluorine on the RDIB and beyond battery chemistries. (a) Schematics of the aqueous $\text{BiF}_3\text{Na}_{0.44}||\text{MnO}_2$ RDIB based on the F^- anion and Na^+ cation electrochemistry during charging process. Reproduced with permission from ref ⁷⁴⁸. Copyright 2018 Royal Society of Chemistry. (b) Voltage curves of the RDIB with BF and modified BFO anode material at 1 A g^{-1} . Reproduced with permission from ref ⁵⁸⁹. Copyright 2021 Wiley-VCH. (c) Energy density of the highly fluorinated HFE/PEO protected graphite||(LiBr) $_{0.5}$ (LiCl) $_{0.5}$ C $_{\sim 3.7}$ full cell with an aqueous gel electrolyte, compared with various state-of-the-art commercial and experimental Li-ion chemistries using non-aqueous (blue circles) and aqueous (green circles) electrolytes. Note: all energy densities were converted using the total weight of the cathode and the anode. Reproduced with permission from ref ⁷⁴⁹. Copyright 2019 Springer Nature. (d) Schematic diagram of the 3 V Al||Cu battery in 3M LiTFSI-FEC electrolyte with a PP membrane. Reproduced with permission from ref ⁷⁵⁰. Copyright 2020 Wiley-VCH.

Interestingly, Wang *et al.* demonstrated a novel conversion-intercalation chemistry, based on the sequential intercalation of Br^- and Cl^- into a composite cathode consisting of $(\text{LiBr})_{0.5}(\text{LiCl})_{0.5}\text{C}_{\sim 3.7}$ (LBC-G), using a highly concentrated “water-in-bisalt” aqueous gel electrolyte. Benefiting from the formed hydrated LiBr/LiCl layer ($\text{LiBr} \cdot 0.34\text{H}_2\text{O} - \text{LiCl} \cdot 0.34\text{H}_2\text{O}$) by extracting water from the electrolyte, the LBC-G surface was separated from the electrolyte accordingly. Upon charging, the Br^- within the hydration layer was first oxidized to Br_0 and then intercalated into the graphite. As the charging process continued, the

oxidation and intercalation of Cl^- occurred, leading to a mixed intercalation compound. This unique mechanism contributed to a stage-1 GIC, which accounted for a high reversible capacity of 243 mAh g^{-1} at a high average voltage of $4.2 \text{ V vs. Li}^+/\text{Li}$. When coupled with a highly fluorinated ether (i.e., HFE)/PEO-protected graphite anode, the 4 V-class full cell achieved a high energy density of 460 Wh kg^{-1} (calculated based on the total weight of the cathode and anode, **Figure 37c**), along with CE of $\sim 100\%$.⁷⁴⁹

It can be reasonably concluded that anion-hosting cathode materials generally provide limited theoretical capacities, requiring the exploration of new cathode chemistry to enhance the energy density of the battery systems.⁷⁵¹ Along this line, Yu *et al.* proposed a novel metal-metal system that uses Cu and Al metal foils directly as the cathode and anode, respectively.⁷⁵⁰ The electrochemical reactions proceed via the stripping/plating of Cu at the cathode and the alloying/de-alloying of AlLi at the anode (**Figure 37d**). However, the Cu^+ ions inevitably shuttled from the cathode to the anode, causing severe self-discharge and low CE during cycling. By utilizing 3 M LiTFSI-FEC electrolyte, they disclosed that Cu^+ were bound by FEC and TFSI $^-$ to form the solvation complex, which prevented Cu^+ ions from transporting through the PP membrane due to high interfacial tension between FEC molecules and the membrane. The blocking effect by FEC contributed to a stable operation of the 3 V Al||Cu battery for more than 1000 cycles. For comparison, a Li||Cu battery was designed by Ji *et al.* with a different operation mechanism.⁷⁵¹ Upon charging, Cu was oxidized to Cu^{2+} to precipitate as copper(II) bis(trifluoromethane sulfonyl)imide ($\text{Cu}(\text{TFSI})_2$) on the cathode, meanwhile Li^+ was plated on the Li anode. During the discharge process, Cu^{2+} was first reduced to Cu^+ and continuously reduced to Cu, while the anode strips into Li^+ . An anion exchange membrane was placed between the two electrodes to prohibit the crossover of cations during charging. Besides, the catholyte//anolyte concentration was regulated to 2 m//6 m for mitigating the negative concentration gradient of TFSI $^-$, and therefore, maximum utilizing the Cu capacity and suppressing $\text{Cu}^{2+}/\text{Cu}^+$ crossover. Although a high reversible capacity of 762 mAh g^{-1} was enabled at an average discharge voltage of $3.2 \text{ V vs. Li}^+/\text{Li}$, the solubility of charged-product $\text{Cu}(\text{TFSI})_2$ leads to unsatisfactory reversibility, the heavy TFSI $^-$ as counter ions limits the battery energy density, and the usage of AEM increases the cost of the battery system.

Overall, anion insertion with F-containing groups is crucial for DIB/RDIB performance, whereas no existing anion is ideal for satisfying high energy density, fast charging rate, long lifespan and low cost simultaneously. Further research should explore novel anions towards higher theoretical specific capacity and energy density of DIBs and RDIBs. Besides, fluorination of electrolyte components can endow DIBs with broad ESW, wide temperature range, non-flammability, and improved electrode|electrolyte compatibility. Moreover, though RDIB chemistry can be realized in KF and NaF aqueous electrolytes, the rapid capacity deterioration associated with incompatible electrode materials remains a significant obstacle,

requiring further exploration of F-containing salts and novel organic electrolytes to construct protective and robust interphases.

6. Conclusions and Outlook

Taking advantage of the extraordinary electronegativity, low atomic weight, small ionic size, natural abundance, and low-cost of fluorine, fluorine chemistry has significantly advanced rechargeable battery technology. However, atomic-level insights into fluorine chemistry remains underexplored, especially under extreme conditions, are not fully understood. This review summarized the state-of-the-art research and technical achievements in fluorine-containing materials/interphases for metal ion-batteries, FIBs, DIBs, and beyond (**Figure 38a**). Specifically, fluorine chemistry can address challenges in various battery materials, including poor intrinsic conductivity and severe structure deterioration during conversion reactions, large volume change and low redox potential during intercalation reactions, safety issues related with anode materials, insufficient chemical/electrochemical stability and/or low ionic conductivity for electrolytes, and performance restrictions of other battery components. This review highlights the pivotal role of fluorinated interphases, material structure-performance relationships, and cutting-edge techniques for probing fluorine chemistry. From a fundamental and practical perspective, the promising research directions to enhance the benefits of fluorine chemistry in rechargeable batteries can be identified as the following five aspects.

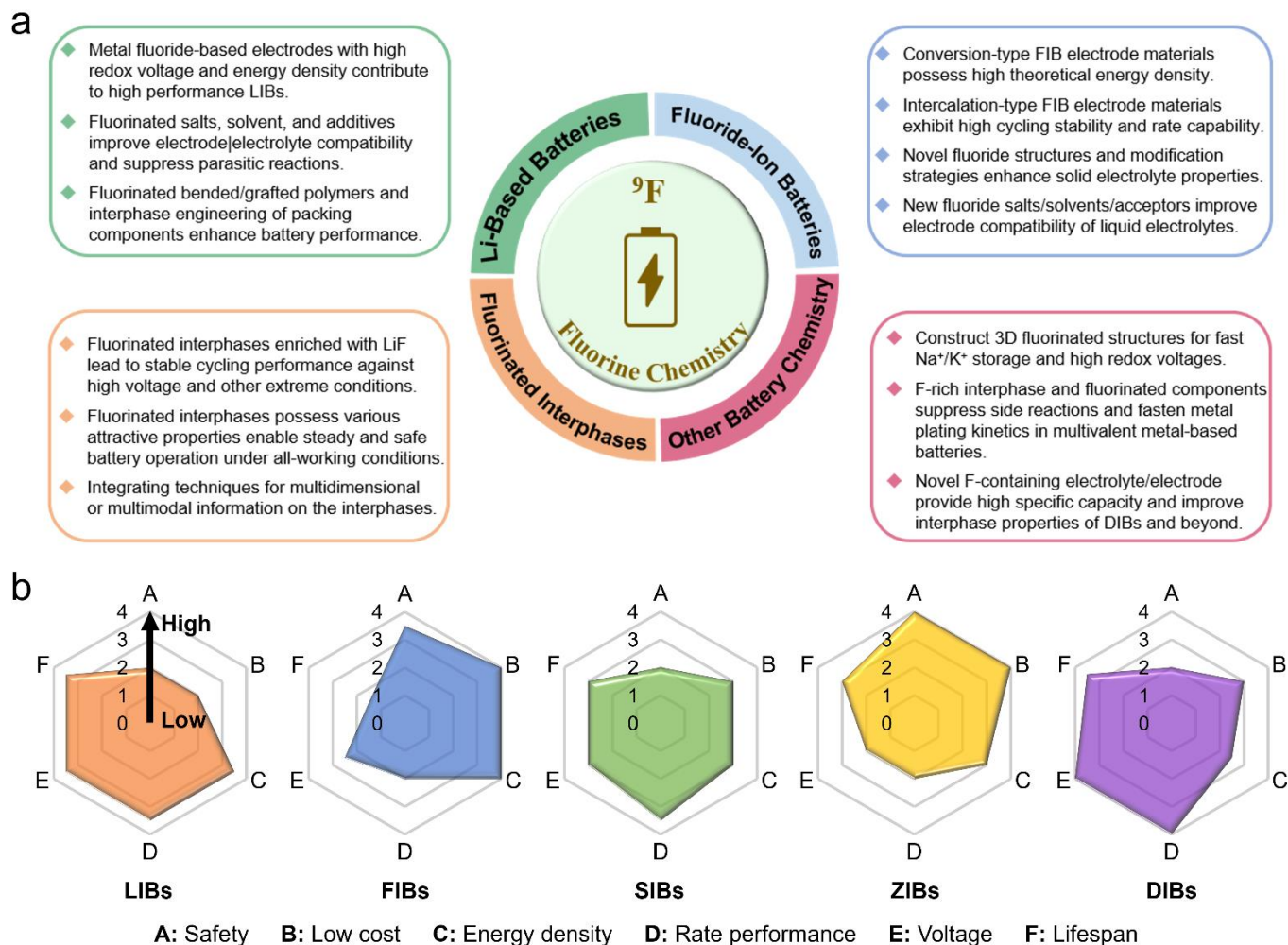


Figure 38. Fluorine chemistry in rechargeable batteries. (a) Strategies and prospects of fluorine chemistry in rechargeable batteries. (b) Radar diagrams of various batteries based on six parameters. (A, safety; B, low cost; C, energy density; D, rate performance; E, voltage; F, lifespan).

(1) Addressing the instinct low electrochemical kinetic of conversion-type metal fluoride-based cathodes. First, systematic studies on redox mechanisms and structural evolution are essential for a deeper understanding of these cathodes. Theoretical studies on these materials are limited to simple metal fluorides such as FeF_2 and CuF_2 . The expanding research of metal fluoride-based cathodes via theoretical simulation and heterometal modification will achieve structurally stable metal fluoride-based cathodes with rapid ion diffusion, which is promising for practical applications. Moreover, the low mass loadings and areal capacities of reported metal fluoride-based cathodes hinder a comprehensive evaluation of their energy density and cycling performance compared to conventional LIB cathodes. Therefore, developing high-loading metal fluoride-based cathodes with increased areal capacities is a priority. In parallel, fluorine chemistry can enhance conventional LIB cathodes such as layered oxides, through F substitution, F doping, and surficial fluoridation, improving the cycling stability and energy density of cathodes and providing insights for the development of high-performance LIBs.

Striking a balance between electrochemical performance, stability and environmentally considerations for optimizing F substitution/modification in battery components. The electrolytes for high-performance Li-based batteries can be tailored by combining the benefits of different partially fluorinated/per-fluorinated electrolytes. Future design for Li salts should focus on integrating functional groups with complementary roles for enhanced overall performance. Fluorinated solvents and co-solvents display unique physicochemical properties due to the high electronegativity, high ionic potential, and low polarizability of fluorine. Partial fluorination or optimization of fluorination positions can be applied to develop single-solvent electrolytes. In parallel, introducing per-fluorinated co-solvent into non-fluorinated solvents for multi-solvent electrolytes is also viable.

Fluorine can also be utilized to modify and functionalize battery separators, enhancing fire retardancy, preventing potential mechanical abuse, and also promoting the formation of a LiF-enriched SEI. Regarding battery binders, fluorine groups can be incorporated into polymer backbones, while fluorinated anions can be combined with ionic conductive polymers, enabling higher ion transfer, greater resistance to electrochemical oxidation, and enhanced thermal stability. Especially, fluorinated cross-linked network binder should be designed for alloy-type anodes, where massive fluorine groups improve mechanical features while chemical/physical cross-linking maintains electrode structures against volume changes. However, excessive fluorine content may lead to decay in electrode performance. Furthermore, current collectors can be modified by fluorinated carbon materials, lithiophilic metal fluoride coatings, F-containing interlayers, *etc.*, which regulates Li deposition and enhances interphasial stability. However, the environmental issues brought by F-substitution/modification must be taken seriously. Fluorinated compounds in prevalent battery components (*e.g.*, LiTFSI, PVDF and PTFE), which contain $-\text{CF}_3$ or $-\text{CF}_2-$ groups, are under consideration for prohibition under European Union regulations. Therefore, the optimization of F substitution/modification in battery components should be scrutinized to strike a balance between electrochemical performance, stability and environmentally considerations.¹²⁸

(2) Tailoring fluorinated interphases for Li-based batteries at all working conditions. The efficient operation of Li-based batteries especially under extreme conditions rely highly on the stability of interphases, including chemical stability, electrochemical stability, mechanical stability, and thermal stability. Interdisciplinary research should be encouraged to reveal the chemical nature of SEI/CEI. Considering the low Li^+ conductivity of LiF ($\sim 10^{-12} \text{ S cm}^{-1}$) restricts the high-rate performance, other fluorinated conducting components (*e.g.*, $\text{Li}_x\text{PO}_y\text{F}_z$) should be incorporated into LiF-rich interphases. Polymer-based organic SEI matrix can also be combined with fluorinated components to accommodate the large volume change of Li anodes. Besides, the LiF-rich CEI possessing excellent electrochemical stability can effectively protect high-voltage cathodes. Although the LiF-enriched SEI displays low interphase impedance/charge transfer resistance and high stability for facilitating low-temperature operation, the LiF

effects on the CEI at low temperatures remains a subject of debate. Further investigation is needed to deeply understand the macroscopic and microscopic properties of LiF, especially their roles and factors (*e.g.*, the distribution, particle size, and formation approach) affecting the performance of Li-based batteries under extreme conditions.

Unlocking fundamental issues regarding chemical compositions, spatial distributions, and realistic structure of interphases. Non-destructive and/or *in situ/operando* techniques (*e.g.*, cryo-TEM, *operando* EQCM, *in situ* XPS, liquid TOF-SIMs, *in situ* NMR, synchrotron-based XRD) are imperative for real-time, dynamic, and intuitive investigations of the structural, morphological, and chemical characteristics of interphases, and their correlations with the battery performance. Therefore, suitable electrochemical cells for *in situ* operations should be carefully designed, as different cell configurations can cause inconsistent and even misleading results. An integrated approach with complementary techniques is highly desirable for obtaining multidimensional and/or multimodal insights into interphases, facilitating the elucidation of structure-property relationships and guiding the design of stable interphases.

(3) Revolution of electrode and electrolyte materials for high energy density and cycling stability FIBs. The volume change and polarization issues of conversion-type electrode materials should be solved by reducing the particle size and constructing the conductive network, seeking for high-capacity intercalation-type electrode materials *via* theoretical screening and experimental verification, and preventing the fluorination of conductive additive through carbon stabilization process. In parallel, to advance the development of F⁻-conducting solid-state electrolytes, novel fluoride structures and modification strategies, such as creating point defects, introducing F vacancies, and optimizing synthesis methods, are highly required. For liquid electrolytes, it is essential to explore novel fluoride salts, solvents, and suitable anion/cation acceptors to facilitate the dissociation of fluoride salts. Furthermore, the “water-in-salt” strategy exhibits great prospect in expanding the ESW, suppressing the active material dissolutions, and addressing the HF formation in aqueous electrolytes.

(4) Establishing fluorinated material-function relationships to boost SIB/PIB performance. In SIBs, the development of F-based electrodes is shifted toward 3D fluorinated phases. An in-depth investigation is necessary to regulate the structure and phase transitions to mitigate volume changes, and to elucidate the structural-performance correlations, thereby reducing the activation energy barrier and band-gap energy for efficient Na⁺ diffusion. As for PIBs, surface modifications of potassium fluorophosphate compounds is necessary to improve both the electron and K⁺ transport. Besides, the fluorine to oxygen ratio should be carefully controlled to prevent disordered structures of fluorosulfates that suppresses the K⁺/vacancy formation and decreases the reversible K⁺ storage capacity. Moreover, F-doping can improve the surface disorder of carbonaceous anode materials, creating large amounts of surface defects to facilitate Na⁺/K⁺ adsorption. As for electrolyte developments in SIBs/PIBs, strategies from Li-based batteries are not

directly applicable due to potential adverse effects (*e.g.*, FEC). Notably, fluorine chemistry facilitates the discovery of novel conducting salts with wide ESW, film-forming ability, and fast ionic transport. However, the molecular structure-function relationships of fluorinated components remain unclear, necessitating targeted molecular selection. Further efforts should be focused on the challenging aspects of fluorinated interphases to optimize their properties.

(5) Exploring the potential of F-containing materials for other battery chemistries. Challenges including insufficient energy density of existing electrodes, sluggish plating/stripping dynamics kinetics of metallic anode and poor stability of electrolyte/electrode interphase hinder the utilization of the multivalent metal-based batteries with attractive advantages (*e.g.*, low cost and high energy density). Fluorine chemistry is important for seeking suitable F-containing electrode materials as well as providing a deep understanding of the construction of F-involved SEI film, which could positively or negatively affect the battery performance. As for DIBs/RDIBs, novel anions with smaller sizes and higher anti-oxidative stability, as well as multivalent anions with more charge numbers can potentially provide high theoretical specific capacity and energy density. Though fluorination treatment of electrolyte components can endow DIBs with enhanced performance, the fundamental role of these fluorinated components in the anion solvation, the relationship between fluorinated CEI features (*e.g.*, chemical components, micro/nanostructures, mechanical properties) and battery performances remain unclear. Furthermore, other battery chemistries necessitate the exploration of F-containing salts and novel electrolytes to construct protective and robust interphases.

The high-temperature sintering of inorganic materials containing fluorine element potentially detrimental to the furnace, impeding its scalability for large-scale synthesis. Thus, alternative soft chemical synthesis methods such as low-temperature solid-phase synthesis, chemical transfer synthesis and solvent thermal synthesis should be developed for preparing F-containing cathode and solid-state electrolyte materials in the future. Overall, significant breakthrough progress has been achieved by utilizing fluorine chemistry in rechargeable batteries. Although traditional lithium-ion batteries maintain a leading position in overall performance due to decades of research, other alternative battery systems also demonstrate significant advantages in specific aspects (**Figure 38b**). Thus, expanding fluorine chemistry research into these areas is expected to accelerate the application of these rising battery systems. Nonetheless, the ongoing development of fluorine chemistry is bringing many scientific and technical challenges, leaving substantial investigation room for its future applications. Thus, researchers are highly encouraged to unlock the fundamental role of fluorine chemistry in addressing the obstacles for various types of battery materials, thus promoting the widespread effectuation of fluorine chemistry in rechargeable batteries. More significantly, we hope this review can raise interest and provide key insights into the further development of fluorine chemistry for high-performance rechargeable batteries.

Author Information

Corresponding Author

Baohua Li - *Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, P. R. China.*

<https://orcid.org/0000-0002-4876-2659>; Email: libh@sz.tsinghua.edu.cn

Dong Zhou - *Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, P. R. China.*

<https://orcid.org/0000-0002-2578-7124>; Email: zhou.d@sz.tsinghua.edu.cn

Chunsheng Wang - *Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, MD 20742, USA.*

<https://orcid.org/0000-0002-8626-6381>; Email: cswang@umd.edu

Guoxiu Wang - *Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, New South Wales 2007, Australia.*

<https://orcid.org/0000-0003-4295-8578>; Email: Guoxiu.Wang@uts.edu.au

Authors

Yao Wang - *Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, P. R. China.*

Xu Yang - *Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, New South Wales 2007, Australia.*

Yuefeng Meng - *Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, P. R. China.*

Zuxin Wen - *Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, P. R. China.*

Ran Han - *Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, P. R. China.*

Xia Hu - *Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, P. R. China.*

Bing Sun - *Centre for Clean Energy Technology, School of Mathematical and Physical Sciences, Faculty of Science, University of Technology Sydney, Sydney, New South Wales 2007, Australia.*

Feiyu Kang - *Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, P. R. China.*

Author Contributions

[†] These authors contributed equally: Yao Wang, Xu Yang, Yuefeng Meng. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: Yao Wang, Xu Yang and Yuefeng Meng: investigation, mechanisms, writing-original draft; Zuxin Wen, Ran Han, Xia Hu and Bing Sun: methodology, validation, editing; Baohua Li, Dong Zhou, Chunsheng Wang, Guoxiu Wang: conceptualization, project administration, supervision, writing-original draft, writing-review & editing.

Notes

The authors declare no competing financial interest.

Biographies

Yao Wang is currently a post-doctoral researcher at Tsinghua Shenzhen International Graduate School, Tsinghua University (China). She received her PhD degree from City University of Hong Kong (CityU) in 2021. Her research mainly focuses on designing electrolyte systems and investigating electrode|electrolyte interphases for high-voltage and low-cost rechargeable batteries.

Xu Yang is currently a PhD student in the Centre for Clean Energy Technology at University of Technology Sydney (UTS). He received his BSc (2017) and MSc (2019) at Harbin Institute of Technology. His research interests focus on the development of low-cost rechargeable batteries and all-solid-state lithium-ion batteries.

Yuefeng Meng received her BSc (2018) and MSc (2023) majoring in Materials Science and Engineering at Tsinghua University (China). Her current research interests include safe electrolyte design and interphase chemistry for high-voltage lithium metal batteries.

Zuxin Wen is currently a PhD student at Tsinghua Shenzhen International Graduate School, Tsinghua University (China). He received his BSc (2020) and MSc (2023) at Central South University. His research interests focus on the development of low-cost rechargeable batteries and all-solid-state lithium-ion batteries.

Ran Han received his BSc (2020) at Hefei University of Technology and MSc (2023) at Shanghai University. His research interests focus on the development of low-temperature rechargeable batteries and aqueous batteries.

Xia Hu is currently a PhD student at Tsinghua Shenzhen International Graduate School, Tsinghua University (China). She obtained her BSc (2015) and MSc (2018) from Central South University. Her research is currently centered on the development of solid-state lithium-based batteries and the associated critical materials.

Bing Sun received his PhD in 2012 at University of Technology Sydney (UTS), Australia. Currently, he is a senior lecturer in the Centre for Clean Energy Technology at UTS. His research interests focus on the development of next-generation battery materials and technology for lithium-based batteries and sodium-based batteries. He is the recipient of Australian Research Council (ARC) Discovery Early Career Researcher Award and ARC Future Fellowship.

Feiyu Kang is a full professor in Department of Materials Science and Engineering, and also a dean in Graduate School at Shenzhen, Tsinghua University (China). He received his PhD degree from Hong Kong University of Science and Technology (HKUST). His research is focusing on nanocarbon materials, graphite, thermal conductive materials, lithium-ion battery, super-capacitors, electric vehicles, porous carbon and adsorption, indoor air clearing and water purification. Prof. Kang has published more than 630 refereed journal papers. His publications have attracted over 77,000 citations with an h-index of 143 (Google Scholar). He was ranked as the Global Highly Cited Researchers (top 1% by citation) by Clarivate Analytics in 2018–2023.

Baohua Li is currently a full professor and director of the Division of Energy and Environment at Tsinghua Shenzhen International Graduate School, Tsinghua University (China). He received his PhD degree from the Institute of Coal Chemistry (ICC), Chinese Academy of Sciences (CAS) in 2003. His research interests focus on carbon materials for energy storage, such as electrode materials for supercapacitors and lithium-ion batteries. Prof. Li has published more than 290 refereed journal papers. His publications have attracted over 38,000 citations with an h-index of 104 (Google Scholar). He was ranked as the World's Top 2%

Scientist by Stanford University in 2021. Prof. Li is also the director of Advanced Battery and Material Engineering Research Center of Guangdong, and a member of Academic Committee of Guangdong Key Laboratory of Thermal Management Engineering and Materials.

Dong Zhou is currently an assistant professor and PhD supervisor at Tsinghua Shenzhen International Graduate School, Tsinghua University (China). He received his PhD degree from Tsinghua University in 2017, and then worked as a postdoctoral research associate in University of Technology Sydney, Australia and the University of Tokyo, Japan. His research topic mainly focuses on the design and synthesis of specialized solid polymer electrolytes and nano electrode materials for various advanced energy storage devices, and investigation of the interfacial mechanisms. As first/corresponding author, his research has resulted in more than 30 refereed journal articles with a total citation of over 7,200 (Google scholar). He is the recipient of First Prize of Guangdong Natural Science in 2020, the Discovery Early Career Researcher Award (DECRA) and the Japan Society for the Promotion of Science (JSPS) Fellowship.

Chunsheng Wang is a Robert Franklin and Frances Riggs Wright Distinguished Chair Professor in the Chemical & Biomolecular Engineering, Department of Chemistry and Biochemistry, at the University of Maryland. He is an associate editor of ACS Applied Energy Materials and UMD Director of the UMD-ARL Center for Research in Extreme Battery. His research focuses on reachable batteries and fuel cells. Professor Wang has published more than 340 refereed journal papers. His publications have attracted over 70,000 citations with an h-index of 138 (Google Scholar). He was ranked as the Global Highly Cited Researchers (top 1% by citation) by Clarivate Analytics in 2018–2023.

Guoxiu Wang is the Director of the Centre for Clean Energy Technology and a Distinguished Professor at University of Technology Sydney (UTS), Australia. Currently, he serves as an Associate Editor for Electrochemical Energy Reviews (Springer-Nature) and Energy Storage Materials (Elsevier). His research interests include lithium-ion batteries, lithium-air batteries, sodium-ion batteries, lithium-sulfur batteries, supercapacitors, fuel-cells, 2D materials such as graphene and MXenes, and electrocatalysis for hydrogen production. Professor Wang has published more than 680 refereed journal papers. His publications have attracted over 75,000 citations with an h-index of 150 (Google Scholar). He has been recognized as a highly cited researcher in Chemistry and Materials Science by Web of Science/Clarivate Analytics. Professor Wang is an elected Fellow of the European Academy of Sciences (EurASc), a Fellow of the International Society of Electrochemistry (ISE), and a Fellow of the Royal Society of Chemistry (RSC).

Acknowledgement

B. Li would like to acknowledge the support by National Natural Science Foundation of China (NO. 52072208 and NO. 52261160384), Shenzhen Science and Technology Program (KCXFZ20211020163810015), the Fundamental Research Project of Shenzhen (NO. JCYJ20220818101004009), Local Innovative and Research Teams Project of Guangdong Pearl River Talents Program (2017BT01N111). G. Wang would like to acknowledge the support from the Australian Research Council (ARC) through the Discovery Projects (DP210101389 and DP230101579), ARC Linkage Project (LP200200926) and the ARC Research Hub for Integrated Energy Storage Solutions (IH180100020). Y. Wang would like to acknowledge the support by National Natural Science Foundation of China (NO. 22309102) and China Postdoctoral Science Foundation (Grant No. 2022M711788). B. Sun would like to thank the financial support from ARC through the ARC Future Fellowship (FT220100561).

References

This article references 751 other publications.

- (1) Whittingham, M. S. Lithium Batteries and Cathode Materials. *Chem. Rev.* **2004**, *104*, 4271-4301.
- (2) Dunn, B.; Kamath, H.; Tarascon, J. M. Electrical Energy Storage for the Grid: A Battery of Choices. *Science* **2011**, *334*, 928-935.
- (3) Schmich, R.; Wagner, R.; Höppl, G.; Placke, T.; Winter, M. Performance and Cost of Materials for Lithium-Based Rechargeable Automotive Batteries. *Nat. Energy* **2018**, *3*, 267-278.
- (4) Blomgren, G. E. The Development and Future of Lithium Ion Batteries. *J. Electrochem. Soc.* **2016**, *164*, A5019-A5025.
- (5) Bigelow, L. A. The Action of Elementary Fluorine upon Organic Compounds. *Chem. Rev.* **1947**, *40*, 51-115.
- (6) Groult, H.; Lantelme, F.; Salanne, M.; Simon, C.; Belhomme, C.; Morel, B.; Nicolas, F. Role of Elemental Fluorine in Nuclear Field. *J. Fluor. Chem.* **2007**, *128*, 285-295.
- (7) Dolbier, W. R. Fluorine Chemistry at the Millennium. *J. Fluor. Chem.* **2005**, *126*, 157-163.
- (8) Gardiner, J. Fluoropolymers: Origin, Production, and Industrial and Commercial Applications. *Aust. J. Chem.* **2015**, *68*.
- (9) Xiao, A. W.; Galatolo, G.; Pasta, M. The Case for Fluoride-Ion Batteries. *Joule* **2021**, *5*, 2823-2844.
- (10) Lide, D. R. CRC Handbook of Chemistry and Physics. *J. Am. Chem. Soc.* **2005**, *127*, 4542-4542.
- (11) U.S. Geological Survey. Mineral Commodity Summaries 2021. *Reston, VA* **2021**, <https://doi.org/10.3133/mcs2021>.
- (12) Goodenough, J. B.; Kim, Y. Challenges for Rechargeable Li Batteries. *Chem. Mater.* **2009**, *22*, 587-603.
- (13) Najib, S.; Erdem, E. Current Progress Achieved in Novel Materials for Supercapacitor Electrodes: Mini Review. *Nanoscale Adv.* **2019**, *1*, 2817-2827.
- (14) Ben Yahia, M.; Vergnet, J.; Saubanere, M.; Doublet, M. L. Unified Picture of Anionic Redox in Li/Na-Ion Batteries. *Nat. Mater.* **2019**, *18*, 496-502.
- (15) Hu, E.; Yu, X.; Lin, R.; Bi, X.; Lu, J.; Bak, S.; Nam, K.-W.; Xin, H. L.; Jaye, C.; Fischer, D. A.; et al. Evolution of Redox Couples in Li- and Mn-Rich Cathode Materials and Mitigation of Voltage Fade by Reducing Oxygen Release. *Nat. Energy* **2018**, *3*, 690-698.
- (16) Yan, P.; Zheng, J.; Liu, J.; Wang, B.; Cheng, X.; Zhang, Y.; Sun, X.; Wang, C.; Zhang, J.-G. Tailoring Grain Boundary Structures and Chemistry of Ni-Rich Layered Cathodes for Enhanced Cycle Stability of Lithium-Ion Batteries. *Nat. Energy* **2018**, *3*, 600-605.
- (17) Akhilash, M.; Salini, P. S.; John, B.; Mercy, T. D. A Journey through Layered Cathode Materials for Lithium Ion Cells – from Lithium Cobalt Oxide to Lithium-Rich Transition Metal Oxides. *J. Alloys Compd.* **2021**, *869*, 159239.
- (18) Akhilash, M.; Salini, P. S.; Jalaja, K.; John, B.; Mercy, T. D. Synthesis of $\text{Li}_{1.5}\text{Ni}_{0.25}\text{Mn}_{0.75}\text{O}_{2.5}$ Cathode Material via Carbonate Co-precipitation Method and Its Electrochemical Properties. *Inorg. Chem. Commun.* **2021**, *126*, 108434.
- (19) Kim, T.; Song, W.; Son, D.-Y.; Ono, L. K.; Qi, Y. Lithium-Ion Batteries: Outlook on Present, Future, and Hybridized Technologies. *J. Mater. Chem. A* **2019**, *7*, 2942-2964.

- (20) Cheng, X.-B.; Zhao, C.-Z.; Yao, Y.-X.; Liu, H.; Zhang, Q. Recent Advances in Energy Chemistry between Solid-State Electrolyte and Safe Lithium-Metal Anodes. *Chem* **2019**, *5*, 74-96.
- (21) Wang, H.; Yu, D.; Kuang, C.; Cheng, L.; Li, W.; Feng, X.; Zhang, Z.; Zhang, X.; Zhang, Y. Alkali Metal Anodes for Rechargeable Batteries. *Chem* **2019**, *5*, 313-338.
- (22) Zhang, J. G.; Xu, W.; Xiao, J.; Cao, X.; Liu, J. Lithium Metal Anodes with Nonaqueous Electrolytes. *Chem. Rev.* **2020**, *120*, 13312-13348.
- (23) Wei, C.; Tan, L.; Tao, Y.; An, Y.; Tian, Y.; Jiang, H.; Feng, J.; Qian, Y. Interfacial Passivation by Room-Temperature Liquid Metal Enabling Stable 5 V-class Lithium-Metal Batteries in Commercial Carbonate-Based Electrolyte. *Energy Storage Mater.* **2021**, *34*, 12-21.
- (24) Hobold, G. M.; Lopez, J.; Guo, R.; Minafra, N.; Banerjee, A.; Shirley Meng, Y.; Shao-Horn, Y.; Gallant, B. M. Moving beyond 99.9% Coulombic Efficiency for Lithium Anodes in Liquid Electrolytes. *Nat. Energy* **2021**, *6*, 951-960.
- (25) Zou, P.; Sui, Y.; Zhan, H.; Wang, C.; Xin, H. L.; Cheng, H. M.; Kang, F.; Yang, C. Polymorph Evolution Mechanisms and Regulation Strategies of Lithium Metal Anode under Multiphysical Fields. *Chem. Rev.* **2021**, *121*, 5986-6056.
- (26) Tan, S. J.; Wang, W. P.; Tian, Y. F.; Xin, S.; Guo, Y. G. Advanced Electrolytes Enabling Safe and Stable Rechargeable Li-Metal Batteries: Progress and Prospects. *Adv. Funct. Mater.* **2021**, *31*, 2105253.
- (27) Li, X.; Zhao, R.; Fu, Y.; Manthiram, A. Nitrate Additives for Lithium Batteries: Mechanisms, Applications, and Prospects. *eScience* **2021**, *1*, 108-123.
- (28) Ma, H.; Cheng, F.; Chen, J. Y.; Zhao, J. Z.; Li, C. S.; Tao, Z. L.; Liang, J. Nest-like Silicon Nanospheres for High-Capacity Lithium Storage. *Adv. Mater.* **2007**, *19*, 4067-4070.
- (29) Peng, B.; Cheng, F.; Tao, Z.; Chen, J. Lithium Transport at Silicon Thin Film: Barrier for High-Rate Capability Anode. *J. Chem. Phys.* **2010**, *133*, 034701.
- (30) Huang, A.; Ma, Y.; Peng, J.; Li, L.; Chou, S.-L.; Ramakrishna, S.; Peng, S. Tailoring the Structure of Silicon-Based Materials for Lithium-Ion Batteries via Electrospinning Technology. *eScience* **2021**, *1*, 141-162.
- (31) Nayak, P. K.; Yang, L.; Brehm, W.; Adelhelm, P. From Lithium-Ion to Sodium-Ion Batteries: Advantages, Challenges, and Surprises. *Angew. Chem. Int. Ed.* **2018**, *57*, 102-120.
- (32) Xu, J.; Dou, Y.; Wei, Z.; Ma, J.; Deng, Y.; Li, Y.; Liu, H.; Dou, S. Recent Progress in Graphite Intercalation Compounds for Rechargeable Metal (Li, Na, K, Al)-Ion Batteries. *Adv. Sci.* **2017**, *4*, 1700146.
- (33) Min, X.; Xiao, J.; Fang, M.; Wang, W.; Zhao, Y.; Liu, Y.; Abdelkader, A. M.; Xi, K.; Kumar, R. V.; Huang, Z. Potassium-Ion Batteries: Outlook on Present and Future Technologies. *Energy Environ. Sci.* **2021**, *14*, 2186-2243.
- (34) Vaalma, C.; Buchholz, D.; Weil, M.; Passerini, S. A Cost and Resource Analysis of Sodium-Ion Batteries. *Nat. Rev. Mater.* **2018**, *3*, 18013.
- (35) Rajagopalan, R.; Tang, Y.; Ji, X.; Jia, C.; Wang, H. Advancements and Challenges in Potassium Ion Batteries: A Comprehensive Review. *Adv. Funct. Mater.* **2020**, *30*, 1909486.
- (36) Liang, Y.; Dong, H.; Aurbach, D.; Yao, Y. Current Status and Future Directions of Multivalent Metal-Ion Batteries. *Nat. Energy* **2020**, *5*, 646-656.
- (37) Xie, J.; Zhang, Q. Recent Progress in Multivalent Metal (Mg, Zn, Ca, and Al) and Metal-Ion Rechargeable Batteries with Organic Materials as Promising Electrodes. *Small* **2019**, *15*, e1805061.
- (38) Liu, Q.; Wang, Y.; Yang, X.; Zhou, D.; Wang, X.; Jaumaux, P.; Kang, F.; Li, B.; Ji, X.; Wang, G. Rechargeable Anion-Shuttle Batteries for Low-Cost Energy Storage. *Chem* **2021**, *7*, 1993-2021.
- (39) Sandstrom, S. K.; Chen, X.; Ji, X. A Review of Halide Charge Carriers for Rocking-Chair and Dual-Ion Batteries. *Carbon Energy* **2021**, *3*, 627-653.
- (40) Gschwind, F.; Rodriguez-Garcia, G.; Sandbeck, D. J. S.; Gross, A.; Weil, M.; Fichtner, M.; Hörmann, N. Fluoride Ion Batteries: Theoretical Performance, Safety, Toxicity, and a Combinatorial Screening of New Electrodes. *J. Fluor. Chem.* **2016**, *182*, 76-90.
- (41) Nowroozi, M. A.; Mohammad, I.; Molaiyan, P.; Wissel, K.; Munnangi, A. R.; Clemens, O. Fluoride Ion Batteries – Past, Present, and Future. *J. Mater. Chem. A* **2021**, *9*, 5980-6012.
- (42) Gopinadh, S. V.; Phanendra, P. V. R. L.; John, B.; Mercy, T. D. Fluoride-Ion Batteries: State-of-the-Art and Future Perspectives. *SM&T* **2022**, *32*, e00436.
- (43) Anji Reddy, M.; Fichtner, M. Batteries Based on Fluoride Shuttle. *J. Mater. Chem.* **2011**, *21*, 17059.
- (44) Zhou, M.; Zhao, L.; Doi, T.; Okada, S.; Yamaki, J.-I. Thermal Stability of FeF₃ Cathode for Li-Ion Batteries. *J. Power Sources* **2010**, *195*, 4952-4956.
- (45) Zhou, M.; Zhao, L.; Okada, S.; Yamaki, J.-I. Thermal Characteristics of a FeF₃ Cathode via Conversion Reaction in Comparison with LiFePO₄. *J. Power Sources* **2011**, *196*, 8110-8115.

- (46) Zhang, L.; Wang, H.; Zhang, X.; Tang, Y. A Review of Emerging Dual-Ion Batteries: Fundamentals and Recent Advances. *Adv. Funct. Mater.* **2021**, *31*, 2010958.
- (47) Ou, X.; Gong, D.; Han, C.; Liu, Z.; Tang, Y. Advances and Prospects of Dual-Ion Batteries. *Adv. Energy Mater.* **2021**, *11*, 2102498.
- (48) Goodenough, J. B.; Park, K. S. The Li-Ion Rechargeable Battery: A Perspective. *J. Am. Chem. Soc.* **2013**, *135*, 1167-1176.
- (49) Tarascon, J. M.; Gozdz, A. S.; Schmutz, C.; Shokoohi, F.; Warren, P. C. Performance of Bellcore's Plastic Rechargeable Li-Ion Batteries. *Solid State Ion.* **1996**, *86-88*, 49-54.
- (50) Park, Y. U.; Seo, D. H.; Kim, B.; Hong, K. P.; Kim, H.; Lee, S.; Shakoob, R. A.; Miyasaka, K.; Tarascon, J. M.; Kang, K. Tailoring a Fluorophosphate as a Novel 4 V Cathode for Lithium-Ion Batteries. *Sci. Rep.* **2012**, *2*, 704.
- (51) Choi, N.-S.; Yew, K. H.; Lee, K. Y.; Sung, M.; Kim, H.; Kim, S.-S. Effect of Fluoroethylene Carbonate Additive on Interfacial Properties of Silicon Thin-Film Electrode. *J. Power Sources* **2006**, *161*, 1254-1259.
- (52) Davis, V. K.; Bates, C. M.; Omichi, K.; Savoie, B. M.; Momcilovic, N.; Xu, Q.; Wolf, W. J.; Webb, M. A.; Billings, K. J.; Chou, N. H.; et al. Room-Temperature Cycling of Metal Fluoride Electrodes: Liquid Electrolytes for High-Energy Fluoride Ion Cells. *Science* **2018**, *362*, 1144-1148.
- (53) Huang, Q.; Turcheniuk, K.; Ren, X.; Magasinski, A.; Song, A. Y.; Xiao, Y.; Kim, D.; Yushin, G. Cycle Stability of Conversion-Type Iron Fluoride Lithium Battery Cathode at Elevated Temperatures in Polymer Electrolyte Composites. *Nat. Mater.* **2019**, *18*, 1343-1349.
- (54) Park, H.; Lee, Y.; Cho, M.-K.; Kang, J.; Ko, W.; Jung, Y. H.; Jeon, T.-Y.; Hong, J.; Kim, H.; Myung, S.-T.; et al. $\text{Na}_2\text{Fe}_2\text{F}_7$: a fluoride-based cathode for high power and long life Na-ion batteries. *Energy Environ. Sci.* **2021**, *14*, 1469-1479.
- (55) Xu, J.; Zhang, J.; Pollard, T. P.; Li, Q.; Tan, S.; Hou, S.; Wan, H.; Chen, F.; He, H.; Hu, E.; et al. Electrolyte Design for Li-Ion Batteries under Extreme Operating Conditions. *Nature* **2023**, *614*, 694-700.
- (56) Shannon, R. D. Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides. *Acta Crystallogr. A* **1976**, *32*, 751-767.
- (57) Xu, K. Li-Ion Battery Electrolytes. *Nat. Energy* **2021**, *6*, 763-763.
- (58) Winter, M.; Barnett, B.; Xu, K. Before Li Ion Batteries. *Chem. Rev.* **2018**, *118*, 11433-11456.
- (59) Reddy, M. V.; Mauger, A.; Julien, C. M.; Paoletta, A.; Zaghib, K. Brief History of Early Lithium-Battery Development. *Materials* **2020**, *13*, 1884.
- (60) Aurbach, D.; Talyosef, Y.; Markovsky, B.; Markevich, E.; Zinigrad, E.; Asraf, L.; Gnanaraj, J. S.; Kim, H.-J. Design of Electrolyte Solutions for Li and Li-Ion Batteries: A Review. *Electrochim. Acta* **2004**, *50*, 247-254.
- (61) Kim, K.; Park, I.; Ha, S.-Y.; Kim, Y.; Woo, M.-H.; Jeong, M.-H.; Shin, W. C.; Ue, M.; Hong, S. Y.; Choi, N.-S. Understanding the Thermal Instability of Fluoroethylene Carbonate in LiPF_6 -Based Electrolytes for Lithium-Ion Batteries. *Electrochim. Acta* **2017**, *225*, 358-368.
- (62) Su, C.-C.; He, M.; Redfern, P. C.; Curtiss, L. A.; Shkrob, I. A.; Zhang, Z. Oxidatively Stable Fluorinated Sulfone Electrolytes for High Voltage High Energy Lithium-Ion Batteries. *Energy Environ. Sci.* **2017**, *10*, 900-904.
- (63) Nambu, N.; Sasaki, Y. Physical and Electrolytic Properties of Monofluorinated Ethyl Acetates and Their Application to Lithium Secondary Batteries. *Open J. Met.* **2015**, *05*, 1-9.
- (64) Bolloli, M.; Kalhoff, J.; Alloin, F.; Bresser, D.; Phung Le, M. L.; Langlois, B.; Passerini, S.; Sanchez, J.-Y. Fluorinated Carbamates as Suitable Solvents for LiTFSI-Based Lithium-Ion Electrolytes: Physicochemical Properties and Electrochemical Characterization. *J. Phys. Chem. C* **2015**, *119*, 22404-22414.
- (65) Meister, P.; Qi, X.; Klopsch, R.; Kramer, E.; Streipert, B.; Winter, M.; Placke, T. Anodic Behavior of the Aluminum Current Collector in Imide-Based Electrolytes: Influence of Solvent, Operating Temperature, and Native Oxide-Layer Thickness. *ChemSusChem* **2017**, *10*, 804-814.
- (66) He, M.; Hu, L.; Xue, Z.; Su, C. C.; Redfern, P.; Curtiss, L. A.; Polzin, B.; Von Cresce, A.; Xu, K.; Zhang, Z. Fluorinated Electrolytes for 5-V Li-Ion Chemistry: Probing Voltage Stability of Electrolytes with Electrochemical Floating Test. *J. Electrochem. Soc.* **2015**, *162*, A1725-A1729.
- (67) Oldiges, K.; Von Aspern, N.; Cekic-Laskovic, I.; Winter, M.; Brunklaus, G. Impact of Trifluoromethylation of Adiponitrile on Aluminum Dissolution Behavior in Dinitrile-Based Electrolytes. *J. Electrochem. Soc.* **2018**, *165*, A3773-A3781.
- (68) Tornheim, A.; He, M.; Su, C.-C.; Zhang, Z. The Role of Additives in Improving Performance in High Voltage Lithium-Ion Batteries with Potentiostatic Holds. *J. Electrochem. Soc.* **2017**, *164*, A6366-A6372.

- (69) Luo, Y.; Lu, T.; Zhang, Y.; Yan, L.; Xie, J.; Mao, S. S. Enhanced Electrochemical Performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode Using an Electrolyte with 3-(1,1, 2,2-Tetrafluoroethoxy)-1,1, 2,2-Tetrafluoropropane. *J. Power Sources* **2016**, *323*, 134-141.
- (70) Wang, C.; Tang, S.; Zuo, X.; Xiao, X.; Liu, J.; Nan, J. 3-(1,1,2,2-Tetrafluoroethoxy)-1,1,2,2-Tetrafluoropropane as a High Voltage Solvent for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ /Graphite Cells. *J. Electrochem. Soc.* **2015**, *162*, A1997-A2003.
- (71) Lu, J.; Wang, C.; Yu, H.; Gong, S.; Xia, G.; Jiang, P.; Xu, P.; Yang, K.; Chen, Q. Oxygen/Fluorine Dual-Doped Porous Carbon Nanopolyhedra Enabled Ultrafast and Highly Stable Potassium Storage. *Adv. Funct. Mater.* **2019**, *29*, 1906126.
- (72) Nowroozi, M. A.; Wissel, K.; Rohrer, J.; Munnangi, A. R.; Clemens, O. LaSrMnO_4 : Reversible Electrochemical Intercalation of Fluoride Ions in the Context of Fluoride Ion Batteries. *Chem. Mater.* **2017**, *29*, 3441-3453.
- (73) Bhatia, H.; Thieu, D. T.; Pohl, A. H.; Chakravadhanula, V. S. K.; Fawey, M. H.; Kubel, C.; Fichtner, M. Conductivity Optimization of Tysonite-type $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$ Solid Electrolytes for Advanced Fluoride Ion Battery. *ACS Appl. Mater. Interfaces* **2017**, *9*, 23707-23715.
- (74) Gschwind, F.; Bastien, J. Parametric Investigation of Room-Temperature Fluoride-Ion Batteries: Assessment of Electrolytes, Mg-Based Anodes, and BiF_3 -Cathodes. *J. Mater. Chem. A* **2015**, *3*, 5628-5634.
- (75) Zhang, L.; Reddy, M. A.; Gao, P.; Diemant, T.; Jürgen Behm, R.; Fichtner, M. Study of All Solid-State Rechargeable Fluoride Ion Batteries Based on Thin-Film Electrolyte. *J. Solid State Electrochem.* **2016**, *21*, 1243-1251.
- (76) Gong, C.; Pu, S. D.; Gao, X.; Yang, S.; Liu, J.; Ning, Z.; Rees, G. J.; Capone, I.; Pi, L.; Liu, B.; et al. Revealing the Role of Fluoride-Rich Battery Electrode Interphases by Operando Transmission Electron Microscopy. *Adv. Energy Mater.* **2021**, *11*, 2003118.
- (77) Seel, J. A.; Dahn, J. R. Electrochemical Intercalation of PF_6 into Graphite. *J. Electrochem. Soc.* **2000**, *147*, 892.
- (78) Shi, X.; Zhang, W.; Wang, J.; Zheng, W.; Huang, K.; Zhang, H.; Feng, S.; Chen, H. $(\text{EMI})^+(\text{PF}_6)^-$ Ionic Liquid Unlocks Optimum Energy/Power Density for Architecture of Nanocarbon-Based Dual-Ion Battery. *Adv. Energy Mater.* **2016**, *6*, 1601378.
- (79) Jiang, H.; Han, X.; Du, X.; Chen, Z.; Lu, C.; Li, X.; Zhang, H.; Zhao, J.; Han, P.; Cui, G. A PF_6^- -Permsselective Polymer Electrolyte with Anion Solvation Regulation Enabling Long-Cycle Dual-Ion Battery. *Adv. Mater.* **2022**, *34*, e2108665.
- (80) Yang, H.; Qin, T.; Zhou, X.; Feng, Y.; Wang, Z.; Ge, X.; Yue, N.; Li, D.; Zhang, W.; Zheng, W. Boosting the Kinetics of PF_6^- into Graphitic Layers for the Optimal Cathode of Dual-Ion Batteries: The Rehearsal of Pre-intercalating Li^+ . *J. Energy Chem.* **2022**, *71*, 392-399.
- (81) Placke, T.; Heckmann, A.; Schmuck, R.; Meister, P.; Beltrop, K.; Winter, M. Perspective on Performance, Cost, and Technical Challenges for Practical Dual-Ion Batteries. *Joule* **2018**, *2*, 2528-2550.
- (82) Qi, X.; Blizanac, B.; Dupasquier, A.; Meister, P.; Placke, T.; Oljaca, M.; Li, J.; Winter, M. Investigation of PF_6^- and TFSI $^-$ Anion Intercalation into Graphitized Carbon Blacks and Its Influence on High Voltage Lithium-Ion Batteries. *Phys. Chem. Chem. Phys.* **2014**, *16*, 25306-25313.
- (83) Aladinli, S.; Bordet, F.; Ahlbrecht, K.; Tübke, J.; Holzapfel, M. Anion Intercalation into a Graphite Cathode from Various Sodium-Based Electrolyte Mixtures for Dual-Ion Battery Applications. *Electrochim. Acta* **2017**, *231*, 468-478.
- (84) Tan, H.; Zhai, D.; Kang, F.; Zhang, B. Synergistic PF_6^- and FSI^- Intercalation Enables Stable Graphite Cathode for Potassium-Based Dual Ion Battery. *Carbon* **2021**, *178*, 363-370.
- (85) Kravchyk, K. V.; Bhauriyal, P.; Piveteau, L.; Guntlin, C. P.; Pathak, B.; Kovalenko, M. V. High-Energy-Density Dual-Ion Battery for Stationary Storage of Electricity Using Concentrated Potassium Fluorosulfonylimide. *Nat. Commun.* **2018**, *9*, 4469.
- (86) Tong, X.; Ou, X.; Wu, N.; Wang, H.; Li, J.; Tang, Y. High Oxidation Potential ≈ 6.0 V of Concentrated Electrolyte toward High-Performance Dual-Ion Battery. *Adv. Energy Mater.* **2021**, *11*, 2100151.
- (87) Beltrop, K.; Meister, P.; Klein, S.; Heckmann, A.; Grünebaum, M.; Wiemhöfer, H.-D.; Winter, M.; Placke, T. Does Size really Matter? New Insights into the Intercalation Behavior of Anions into a Graphite-Based Positive Electrode for Dual-Ion Batteries. *Electrochim. Acta* **2016**, *209*, 44-55.
- (88) Hao, J.; Li, X.; Song, X.; Guo, Z. Recent Progress and Perspectives on Dual-Ion Batteries. *EnergyChem* **2019**, *1*, 100004.

- (89) Zhang, Q.; Pan, J.; Lu, P.; Liu, Z.; Verbrugge, M. W.; Sheldon, B. W.; Cheng, Y. T.; Qi, Y.; Xiao, X. Synergetic Effects of Inorganic Components in Solid Electrolyte Interphase on High Cycle Efficiency of Lithium Ion Batteries. *Nano Lett.* **2016**, *16*, 2011-2016.
- (90) Huang, Y.; Wang, H. How Ethylene Carbonate/ γ -Butyrolactone Mixtures Affect BF_4^- Intercalation into Graphite Electrode. *J. Electrochem. Soc.* **2019**, *166*, A3838-A3843.
- (91) Li, C.; Lao, B.; Li, Z.; Yin, H.; Yang, Z.; Wang, H.; Chen, D.; Zhang, X.; Xu, Y.; Sun, C. Dual-Ion Battery with MoS_2 Cathode. *Energy Storage Mater.* **2020**, *32*, 159-166.
- (92) Carlin, R. T.; De Long, H. C.; Fuller, J.; Trulove, P. C. Dual Intercalating Molten Electrolyte Batteries. *J. Electrochem. Soc.* **2019**, *141*, L73-L76.
- (93) Wang, S.; Jiao, S.; Tian, D.; Chen, H. S.; Jiao, H.; Tu, J.; Liu, Y.; Fang, D. N. A Novel Ultrafast Rechargeable Multi-Ions Battery. *Adv. Mater.* **2017**, *29*, 1606349.
- (94) Liu, C.; Neale, Z. G.; Cao, G. Understanding Electrochemical Potentials of Cathode Materials in Rechargeable Batteries. *Mater. Today* **2016**, *19*, 109-123.
- (95) Hu, Q.; Yu, Z.; Tian, L.; Zhao, Y.; Liu, H.; Lai, C.; Yuan, Z. Porous Anhydrous CuF_2 with a Micro-Nano-Hierarchical Structure as High-Performance Cathode Material for Li-Ion Battery. *J. Mater. Sci.* **2023**, *58*, 10120-10130.
- (96) Xiao, A. W.; Lee, H. J.; Capone, I.; Robertson, A.; Wi, T. U.; Fawdon, J.; Wheeler, S.; Lee, H. W.; Grobert, N.; Pasta, M. Understanding the conversion mechanism and performance of monodisperse FeF_2 nanocrystal cathodes. *Nat. Mater.* **2020**, *19*, 644-654.
- (97) Lee, J.; Kang, B. Superior Electrochemical Performance of N-Doped Nanocrystalline FeF_3/C with a Single-Step Solid-State Process. *Chem. Commun.* **2016**, *52*, 12100-12103.
- (98) Villa, C.; Kim, S.; Lu, Y.; Dravid, V. P.; Wu, J. Cu-Substituted NiF_2 as a Cathode Material for Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 647-654.
- (99) Wang, X.; Gu, W.; Lee, J. T.; Nitta, N.; Benson, J.; Magasinski, A.; Schauer, M. W.; Yushin, G. Carbon Nanotube- CoF_2 Multifunctional Cathode for Lithium Ion Batteries: Effect of Electrolyte on Cycle Stability. *Small* **2015**, *11*, 5164-5173.
- (100) Groult, H.; Neveu, S.; Leclerc, S.; Porras-Gutierrez, A. G.; Julien, C. M.; Tressaud, A.; Durand, E.; Penin, N.; Labrugere, C. Nano- CoF_3 prepared by direct fluorination with F_2 gas: Application as electrode material in Li-ion battery. *J. Fluor. Chem.* **2017**, *196*, 117-127.
- (101) Rui, K.; Wen, Z.; Lu, Y.; Shen, C.; Jin, J. Anchoring Nanostructured Manganese Fluoride on Few-Layer Graphene Nanosheets as Anode for Enhanced Lithium Storage. *ACS Appl. Mater. Interfaces* **2016**, *8*, 1819-1826.
- (102) Wang, F.; Kim, S. W.; Seo, D. H.; Kang, K.; Wang, L.; Su, D.; Vajo, J. J.; Wang, J.; Graetz, J. Ternary Metal Fluorides as High-Energy Cathodes with Low Cycling Hysteresis. *Nat. Commun.* **2015**, *6*, 6668.
- (103) Cambaz, M. A.; Vinayan, B. P.; Clemens, O.; Munnangi, A. R.; Chakravadhanula, V. S.; Kubel, C.; Fichtner, M. Vanadium Oxyfluoride/Few-Layer Graphene Composite as a High-Performance Cathode Material for Lithium Batteries. *Inorg. Chem.* **2016**, *55*, 3789-3796.
- (104) Ni, D.; Sun, W.; Xie, L.; Fan, Q.; Wang, Z.; Sun, K. Bismuth Oxyfluoride @ CMK-3 Nanocomposite as Cathode for Lithium Ion Batteries. *J. Power Sources* **2018**, *374*, 166-174.
- (105) Kitajou, A.; Komatsu, H.; Nagano, R.; Okada, S. Synthesis of FeOF Using Roll-Quenching Method and the Cathode Properties for Lithium-Ion Battery. *J. Power Sources* **2013**, *243*, 494-498.
- (106) Louvain, N.; Karkar, Z.; El-Ghozzi, M.; Bonnet, P.; Guérin, K.; Willmann, P. Fluorination of Anatase TiO_2 Towards Titanium Oxyfluoride TiOF_2 : A Novel Synthesis Approach and Proof of the Li-Insertion Mechanism. *J. Mater. Chem. A* **2014**, *2*, 15308-15315.
- (107) Reddy, M. V.; Madhavi, S.; Subba Rao, G. V.; Chowdari, B. V. R. Metal Oxyfluorides TiOF_2 and NbO_2F as Anodes for Li-Ion Batteries. *J. Power Sources* **2006**, *162*, 1312-1321.
- (108) Hua, X.; Eggeman, A. S.; Castillo-Martinez, E.; Robert, R.; Geddes, H. S.; Lu, Z.; Pickard, C. J.; Meng, W.; Wiaderek, K. M.; Pereira, N.; et al. Revisiting Metal Fluorides as Lithium-Ion Battery Cathodes. *Nat. Mater.* **2021**, *20*, 841-850.
- (109) Liu, L.; Guo, H.; Zhou, M.; Wei, Q.; Yang, Z.; Shu, H.; Yang, X.; Tan, J.; Yan, Z.; Wang, X. A Comparison among $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$ and FeF_3 Cathode Materials for Lithium Ion Batteries: Structural, Electrochemical, and Mechanism Studies. *J. Power Sources* **2013**, *238*, 501-515.
- (110) Lemoine, K.; Zhang, L.; Dambournet, D.; Grenèche, J.-M.; Hémon-Ribaud, A.; Leblanc, M.; Borkiewicz, O. J.; Tarascon, J.-M.; Maisonneuve, V.; Lhoste, J. Synthesis by Thermal Decomposition of Two Iron Hydroxyfluorides: Structural Effects of Li Insertion. *Chem. Mater.* **2019**, *31*, 4246-4257.

- (111) Fan, X.; Hu, E.; Ji, X.; Zhu, Y.; Han, F.; Hwang, S.; Liu, J.; Bak, S.; Ma, Z.; Gao, T.; et al. High Energy-Density and Reversibility of Iron Fluoride Cathode Enabled via an Intercalation-Extrusion Reaction. *Nat. Commun.* **2018**, *9*, 2324.
- (112) Jung, S.-K.; Kim, H.; Cho, M. G.; Cho, S.-P.; Lee, B.; Kim, H.; Park, Y.-U.; Hong, J.; Park, K.-Y.; Yoon, G.; et al. Lithium-Free Transition Metal Monoxides for Positive Electrodes in Lithium-Ion Batteries. *Nat. Energy* **2017**, *2*, 16208.
- (113) Deng, D. Transition Metal Oxyfluorides for Next-Generation Rechargeable Batteries. *ChemNanoMat* **2017**, *3*, 146-159.
- (114) Sorensen, E. M.; Izumi, H. K.; Vaughey, J. T.; Stern, C. L.; Poeppelmeier, K. R. $\text{Ag}_4\text{V}_2\text{O}_6\text{F}_2$: An Electrochemically Active and High Silver Density Phase. *J. Am. Chem. Soc.* **2005**, *127*, 6347-6352.
- (115) Kim, M.; Lee, S.; Kang, B. Fast-Rate Capable Electrode Material with Higher Energy Density than LiFePO_4 : $4.2\text{V LiVPO}_4\text{F}$ Synthesized by Scalable Single-Step Solid-State Reaction. *Adv. Sci.* **2016**, *3*, 1500366.
- (116) Heo, J.; Jung, S.-K.; Hwang, I.; Cho, S.-P.; Eum, D.; Park, H.; Song, J.-H.; Yu, S.; Oh, K.; Kwon, G.; et al. Amorphous Iron Fluorosulfate as a High-Capacity Cathode Utilizing Combined Intercalation and Conversion Reactions with Unexpectedly High Reversibility. *Nat. Energy* **2022**, *8*, 30-39.
- (117) Jin, T.; Li, H.; Zhu, K.; Wang, P. F.; Liu, P.; Jiao, L. Polyanion-Type Cathode Materials for Sodium-Ion Batteries. *Chem. Soc. Rev.* **2020**, *49*, 2342-2377.
- (118) Recham, N.; Chotard, J. N.; Dupont, L.; Delacourt, C.; Walker, W.; Armand, M.; Tarascon, J. M. A 3.6 V Lithium-Based Fluorosulphate Insertion Positive Electrode for Lithium-Ion Batteries. *Nat. Mater.* **2010**, *9*, 68-74.
- (119) Barpanda, P.; Ati, M.; Melot, B. C.; Rousse, G.; Chotard, J. N.; Doublet, M. L.; Sougrati, M. T.; Corr, S. A.; Jumas, J. C.; Tarascon, J. M. A 3.90 V Iron-Based Fluorosulphate Material for Lithium-Ion Batteries Crystallizing in the Triplite Structure. *Nat. Mater.* **2011**, *10*, 772-779.
- (120) Andersson, A. M.; Abraham, D. P.; Haasch, R.; Maclaren, S.; Liu, J.; Amine, K. Surface Characterization of Electrodes from High Power Lithium-Ion Batteries. *J. Electrochem. Soc.* **2002**, *149*, A1358.
- (121) Rosina, K. J.; Jiang, M.; Zeng, D.; Salager, E.; Best, A. S.; Grey, C. P. Structure of Aluminum Fluoride Coated $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$ Cathodes for Secondary Lithium-Ion Batteries. *J. Mater. Chem.* **2012**, *22*, 20602.
- (122) Lu, C.; Wu, H.; Zhang, Y.; Liu, H.; Chen, B.; Wu, N.; Wang, S. Cerium Fluoride Coated Layered Oxide $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ as Cathode Materials with Improved Electrochemical Performance for Lithium-Ion Batteries. *J. Power Sources* **2014**, *267*, 682-691.
- (123) Lee, J.; Kitchaev, D. A.; Kwon, D. H.; Lee, C. W.; Papp, J. K.; Liu, Y. S.; Lun, Z.; Clement, R. J.; Shi, T.; McCloskey, B. D.; et al. Reversible $\text{Mn}^{2+}/\text{Mn}^{4+}$ Double Redox in Lithium-Excess Cathode Materials. *Nature* **2018**, *556*, 185-190.
- (124) Li, L.; Ahn, J.; Yue, Y.; Tong, W.; Chen, G.; Wang, C. Fluorination-Enhanced Surface Stability of Disordered Rocksalt Cathodes. *Adv. Mater.* **2022**, *34*, e2106256.
- (125) Bieker, P.; Winter, M. Lithium-Ionen-Technologie und Was Danach Kommen Könnte. *Chemie Unserer Zeit* **2016**, *50*, 172-186.
- (126) Barlowz, C. G. Reaction of Water with Hexafluorophosphates and with Li Bis(perfluoroethylsulfonyl)imide Salt. *Electrochem. Solid-State Lett.* **1999**, *2*, 362.
- (127) Matsumoto, K.; Inoue, K.; Nakahara, K.; Yuge, R.; Noguchi, T.; Utsugi, K. Suppression of Aluminum Corrosion by Using High Concentration LiTFSI Electrolyte. *J. Power Sources* **2013**, *231*, 234-238.
- (128) Lohmann, R.; Cousins, I. T.; Dewitt, J. C.; Gluge, J.; Goldenman, G.; Herzke, D.; Lindstrom, A. B.; Miller, M. F.; Ng, C. A.; Patton, S.; et al. Are Fluoropolymers Really of Low Concern for Human and Environmental Health a Separate from Other PFAS? *Environ. Sci. Technol.* **2020**, *54*, 12820-12828.
- (129) Xia, Y.; Zhou, P.; Kong, X.; Tian, J.; Zhang, W.; Yan, S.; Hou, W.-H.; Zhou, H.-Y.; Dong, H.; Chen, X.; et al. Designing an Asymmetric Ether-Like Lithium Salt to Enable Fast-Cycling High-Energy Lithium Metal Batteries. *Nat. Energy* **2023**, *8*, 934-945.
- (130) Von Aspern, N.; Roschenthaler, G. V.; Winter, M.; Cekic-Laskovic, I. Fluorine and Lithium: Ideal Partners for High-Performance Rechargeable Battery Electrolytes. *Angew. Chem. Int. Ed.* **2019**, *58*, 15978-16000.
- (131) Nakajima, T. Fluorine Compounds as Energy Conversion Materials. *J. Fluor. Chem.* **2013**, *149*, 104-111.
- (132) Suo, L.; Hu, Y. S.; Li, H.; Armand, M.; Chen, L. A New Class of Solvent-in-Salt Electrolyte for High-Energy Rechargeable Metallic Lithium Batteries. *Nat. Commun.* **2013**, *4*, 1481.
- (133) Kim, H.; Hong, J.; Park, K. Y.; Kim, H.; Kim, S. W.; Kang, K. Aqueous Rechargeable Li and Na Ion Batteries. *Chem. Rev.* **2014**, *114*, 11788-11827.
- (134) Wang, Y.; Yi, J.; Xia, Y. Recent Progress in Aqueous Lithium-Ion Batteries. *Adv. Energy Mater.* **2012**, *2*, 830-840.

- (135) Suo, L.; Borodin, O.; Gao, T.; Olguin, M.; Ho, J.; Fan, X.; Luo, C.; Wang, C.; Xu, K. "Water-in-Salt" Electrolyte Enables High-Voltage Aqueous Lithium-Ion Chemistries. *Science* **2015**, 350, 938-943.
- (136) Yamada, Y.; Chiang, C. H.; Sodeyama, K.; Wang, J.; Tateyama, Y.; Yamada, A. Corrosion Prevention Mechanism of Aluminum Metal in Superconcentrated Electrolytes. *ChemElectroChem* **2015**, 2, 1687-1694.
- (137) Zheng, J.; Fan, X.; Ji, G.; Wang, H.; Hou, S.; Demella, K. C.; Raghavan, S. R.; Wang, J.; Xu, K.; Wang, C. Manipulating Electrolyte and Solid Electrolyte Interphase to Enable Safe and Efficient Li-S Batteries. *Nano Energy* **2018**, 50, 431-440.
- (138) Diederichsen, K. M.; Mcshane, E. J.; McCloskey, B. D. Promising Routes to a High Li^+ Transference Number Electrolyte for Lithium Ion Batteries. *ACS Energy Lett.* **2017**, 2, 2563-2575.
- (139) Yamada, Y.; Wang, J.; Ko, S.; Watanabe, E.; Yamada, A. Advances and Issues in Developing Salt-Concentrated Battery Electrolytes. *Nat. Energy* **2019**, 4, 269-280.
- (140) Pei, Z.; Gu, J.; Wang, Y.; Tang, Z.; Liu, Z.; Huang, Y.; Huang, Y.; Zhao, J.; Chen, Z.; Zhi, C. Component Matters: Paving the Roadmap toward Enhanced Electrocatalytic Performance of Graphitic C_3N_4 -Based Catalysts via Atomic Tuning. *ACS Nano* **2017**, 11, 6004-6014.
- (141) Jeong, S.-K.; Inaba, M.; Iriyama, Y.; Abe, T.; Ogumi, Z. Interfacial Reactions between Graphite Electrodes and Propylene Carbonate-Based Solutions: Electrolyte-Concentration Dependence of Electrochemical Lithium Intercalation Reaction. *J. Power Sources* **2008**, 175, 540-546.
- (142) Jeong, S.-K.; Seo, H.-Y.; Kim, D.-H.; Han, H.-K.; Kim, J.-G.; Lee, Y. B.; Iriyama, Y.; Abe, T.; Ogumi, Z. Suppression of Dendritic Lithium Formation by Using Concentrated Electrolyte Solutions. *Electrochem. commun.* **2008**, 10, 635-638.
- (143) Yamada, Y.; Takazawa, Y.; Miyazaki, K.; Abe, T. Electrochemical Lithium Intercalation into Graphite in Dimethyl Sulfoxide-Based Electrolytes: Effect of Solvation Structure of Lithium Ion. *J. Phys. Chem. C* **2010**, 114, 11680-11685.
- (144) Yamada, Y.; Furukawa, K.; Sodeyama, K.; Kikuchi, K.; Yaegashi, M.; Tateyama, Y.; Yamada, A. Unusual Stability of Acetonitrile-Based Superconcentrated Electrolytes for Fast-Charging Lithium-Ion Batteries. *J. Am. Chem. Soc.* **2014**, 136, 5039-5046.
- (145) Yamada, Y.; Usui, K.; Chiang, C. H.; Kikuchi, K.; Furukawa, K.; Yamada, A. General Observation of Lithium Intercalation into Graphite in Ethylene-Carbonate-Free Superconcentrated Electrolytes. *ACS Appl. Mater. Interfaces* **2014**, 6, 10892-10899.
- (146) Qian, J.; Henderson, W. A.; Xu, W.; Bhattacharya, P.; Engelhard, M.; Borodin, O.; Zhang, J. G. High Rate and Stable Cycling of Lithium Metal Anode. *Nat. Commun.* **2015**, 6, 6362.
- (147) Mcowen, D. W.; Seo, D. M.; Borodin, O.; Vatamanu, J.; Boyle, P. D.; Henderson, W. A. Concentrated Electrolytes: Decrypting Electrolyte Properties and Reassessing Al Corrosion Mechanisms. *Energy Environ. Sci.* **2014**, 7, 416-426.
- (148) Möller, K. C.; Hodal, T.; Appel, W. K.; Winter, M.; Besenhard, J. O. Fluorinated Organic Solvents in Electrolytes for Lithium Ion Cells. *J. Power Sources* **2001**, 97-98, 595-597.
- (149) Qin, M.; Zeng, Z.; Wu, Q.; Yan, H.; Liu, M.; Wu, Y.; Zhang, H.; Lei, S.; Cheng, S.; Xie, J. Dipole-Dipole Interactions for Inhibiting Solvent Co-intercalation into a Graphite Anode to Extend the Horizon of Electrolyte Design. *Energy Environ. Sci.* **2023**, 16, 546-556.
- (150) Yu, Z.; Rudnicki, P. E.; Zhang, Z.; Huang, Z.; Celik, H.; Oyakhire, S. T.; Chen, Y.; Kong, X.; Kim, S. C.; Xiao, X.; et al. Rational Solvent Molecule Tuning for High-Performance Lithium Metal Battery Electrolytes. *Nat. Energy* **2022**, 7, 94-106.
- (151) Lee, S.; Park, K.; Koo, B.; Park, C.; Jang, M.; Lee, H.; Lee, H. Safe, Stable Cycling of Lithium Metal Batteries with Low-Viscosity, Fire-Retardant Locally Concentrated Ionic Liquid Electrolytes. *Adv. Funct. Mater.* **2020**, 30, 2003132.
- (152) Yang, Y.; Davies, D. M.; Yin, Y.; Borodin, O.; Lee, J. Z.; Fang, C.; Olguin, M.; Zhang, Y.; Sablina, E. S.; Wang, X.; et al. High-Efficiency Lithium-Metal Anode Enabled by Liquefied Gas Electrolytes. *Joule* **2019**, 3, 1986-2000.
- (153) Smart, M. C.; Ratnakumar, B. V.; Surampudi, S. Use of Organic Esters as Cosolvents in Electrolytes for Lithium-Ion Batteries with Improved Low Temperature Performance. *J. Electrochem. Soc.* **2002**, 149, A361.
- (154) Dong, X.; Guo, Z.; Guo, Z.; Wang, Y.; Xia, Y. Organic Batteries Operated at -70°C . *Joule* **2018**, 2, 902-913.
- (155) Liang, H. J.; Gu, Z. Y.; Zhao, X. X.; Guo, J. Z.; Yang, J. L.; Li, W. H.; Li, B.; Liu, Z. M.; Sun, Z. H.; Zhang, J. P.; et al. Advanced Flame-Retardant Electrolyte for Highly Stabilized K-ion Storage in Graphite Anode. *Sci. Bull.* **2022**, 67, 1581-1588.

- (156) Dokko, K.; Tachikawa, N.; Yamauchi, K.; Tsuchiya, M.; Yamazaki, A.; Takashima, E.; Park, J.-W.; Ueno, K.; Seki, S.; Serizawa, N.; et al. Solvate Ionic Liquid Electrolyte for Li-S Batteries. *J. Electrochem. Soc.* **2013**, *160*, A1304-A1310.
- (157) Chen, S.; Zheng, J.; Mei, D.; Han, K. S.; Engelhard, M. H.; Zhao, W.; Xu, W.; Liu, J.; Zhang, J. G. High-Voltage Lithium-Metal Batteries Enabled by Localized High-Concentration Electrolytes. *Adv. Mater.* **2018**, *30*, e1706102.
- (158) Lin, S.; Hua, H.; Lai, P.; Zhao, J. A Multifunctional Dual-Salt Localized High-Concentration Electrolyte for Fast Dynamic High-Voltage Lithium Battery in Wide Temperature Range. *Adv. Energy Mater.* **2021**, *11*, 2101775.
- (159) Chen, X.; Qin, L.; Sun, J.; Zhang, S.; Xiao, D.; Wu, Y. Phase Transfer-Mediated Degradation of Ether-Based Localized High-Concentration Electrolytes in Alkali Metal Batteries. *Angew. Chem. Int. Ed.* **2022**, *61*, e202207018.
- (160) Zhu, C.; Sun, C.; Li, R.; Weng, S.; Fan, L.; Wang, X.; Chen, L.; Noked, M.; Fan, X. Anion-Diluent Pairing for Stable High-Energy Li Metal Batteries. *ACS Energy Lett.* **2022**, *7*, 1338-1347.
- (161) Wu, Y.; Wang, A.; Hu, Q.; Liang, H.; Xu, H.; Wang, L.; He, X. Significance of Antisolvents on Solvation Structures Enhancing Interfacial Chemistry in Localized High-Concentration Electrolytes. *ACS Cent. Sci.* **2022**, *8*, 1290-1298.
- (162) Ding, J. F.; Xu, R.; Yao, N.; Chen, X.; Xiao, Y.; Yao, Y. X.; Yan, C.; Xie, J.; Huang, J. Q. Non-Solvating and Low-Dielectricity Cosolvent for Anion-Derived Solid Electrolyte Interphases in Lithium Metal Batteries. *Angew. Chem. Int. Ed.* **2021**, *60*, 11442-11447.
- (163) Kim, S. C.; Kong, X.; Vila, R. A.; Huang, W.; Chen, Y.; Boyle, D. T.; Yu, Z.; Wang, H.; Bao, Z.; Qin, J.; et al. Potentiometric Measurement to Probe Solvation Energy and Its Correlation to Lithium Battery Cyclability. *J. Am. Chem. Soc.* **2021**, *143*, 10301-10308.
- (164) Piao, N.; Ji, X.; Xu, H.; Fan, X.; Chen, L.; Liu, S.; Garaga, M. N.; Greenbaum, S. G.; Wang, L.; Wang, C.; et al. Countersolvent Electrolytes for Lithium-Metal Batteries. *Adv. Energy Mater.* **2020**, *10*, 1903568.
- (165) Zhang, Q. K.; Zhang, X. Q.; Hou, L. P.; Sun, S. Y.; Zhan, Y. X.; Liang, J. L.; Zhang, F. S.; Feng, X. N.; Li, B. Q.; Huang, J. Q. Regulating Solvation Structure in Nonflammable Amide-Based Electrolytes for Long-Cycling and Safe Lithium Metal Batteries. *Adv. Energy Mater.* **2022**, *12*, 2200139.
- (166) Meng, Y.; Zhou, D.; Liu, R.; Tian, Y.; Gao, Y.; Wang, Y.; Sun, B.; Kang, F.; Armand, M.; Li, B.; et al. Designing Phosphazene-Derivative Electrolyte Matrices to Enable High-Voltage Lithium Metal Batteries for Extreme Working Conditions. *Nat. Energy* **2023**, *8*, 1023-1033.
- (167) Xu, K. Nonaqueous Liquid Electrolytes for Lithium-Based Rechargeable Batteries. *Chem. Rev.* **2004**, *104*, 4303-4417.
- (168) Zhang, X.-Q.; Cheng, X.-B.; Chen, X.; Yan, C.; Zhang, Q. Fluoroethylene Carbonate Additives to Render Uniform Li Deposits in Lithium Metal Batteries. *Adv. Funct. Mater.* **2017**, *27*, 1605989.
- (169) Okuno, Y.; Ushirogata, K.; Sodeyama, K.; Tateyama, Y. Decomposition of the Fluoroethylene Carbonate Additive and the Glue Effect of Lithium Fluoride Products for the Solid Electrolyte Interphase: An Ab Initio Study. *Phys. Chem. Chem. Phys.* **2016**, *18*, 8643-8653.
- (170) Choudhury, S.; Archer, L. A. Lithium Fluoride Additives for Stable Cycling of Lithium Batteries at High Current Densities. *Adv. Electron. Mater.* **2016**, *2*, 1500246.
- (171) Ma, Y.; Zhou, Z.; Li, C.; Wang, L.; Wang, Y.; Cheng, X.; Zuo, P.; Du, C.; Huo, H.; Gao, Y.; et al. Enabling Reliable Lithium Metal Batteries by a Bifunctional Anionic Electrolyte Additive. *Energy Storage Mater.* **2018**, *11*, 197-204.
- (172) Lee, Y.-M.; Nam, K.-M.; Hwang, E.-H.; Kwon, Y.-G.; Kang, D.-H.; Kim, S.-S.; Song, S.-W. Interfacial Origin of Performance Improvement and Fade for 4.6 V $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ Battery Cathodes. *J. Phys. Chem. C.* **2014**, *118*, 10631-10639.
- (173) Wang, X.; Liao, X.; Huang, W.; Xing, L.; Liao, Y.; Huang, Q.; Xu, M.; Li, W. Improved Cyclic Stability of Layered Lithium Cobalt Oxide at High Potential via Cathode Electrolyte Interphase Formed by 4-(Trifluoromethyl) Benzonitrile. *Electrochim. Acta* **2015**, *184*, 94-101.
- (174) Doughty, D. H.; Roth, E. P.; Crafts, C. C.; Nagasubramanian, G.; Henriksen, G.; Amine, K. Effects of Additives on Thermal Stability of Li Ion Cells. *J. Power Sources* **2005**, *146*, 116-120.
- (175) Zhang, S. S.; Xu, K.; Jow, T. R. Tris(2,2, 2-Trifluoroethyl) Phosphite as a Co-solvent for Nonflammable Electrolytes in Li-Ion Batteries. *J. Power Sources* **2003**, *113*, 166-172.
- (176) Li, Y.; An, Y.; Tian, Y.; Fei, H.; Xiong, S.; Qian, Y.; Feng, J. Stable and Safe Lithium Metal Batteries with Ni-Rich Cathodes Enabled by a High Efficiency Flame Retardant Additive. *J. Electrochem. Soc.* **2019**, *166*, A2736-A2740.

- (177) Liu, J.; Song, X.; Zhou, L.; Wang, S.; Song, W.; Liu, W.; Long, H.; Zhou, L.; Wu, H.; Feng, C.; et al. Fluorinated Phosphazene Derivative – a Promising Electrolyte Additive for High Voltage Lithium Ion Batteries: From Electrochemical Performance to Corrosion Mechanism. *Nano Energy* **2018**, *46*, 404-414.
- (178) Ji, Y.; Zhang, P.; Lin, M.; Zhao, W.; Zhang, Z.; Zhao, Y.; Yang, Y. Toward a Stable Electrochemical Interphase with Enhanced Safety on High-Voltage LiCoO₂ Cathode: A Case of Phosphazene Additives. *J. Power Sources* **2017**, *359*, 391-399.
- (179) Casselman, M. D.; Kaur, A. P.; Narayana, K. A.; Elliott, C. F.; Risko, C.; Odom, S. A. The Fate of Phenothiazine-Based Redox Shuttles in Lithium-Ion Batteries. *Phys. Chem. Chem. Phys.* **2015**, *17*, 6905-6912.
- (180) Kaur, A. P.; Casselman, M. D.; Elliott, C. F.; Parkin, S. R.; Risko, C.; Odom, S. A. Overcharge Protection of Lithium-Ion Batteries above 4 V with a Perfluorinated Phenothiazine Derivative. *J. Mater. Chem. A* **2016**, *4*, 5410-5414.
- (181) Beichel, W.; Klose, P.; Blattmann, H.; Hoecker, J.; Kratzert, D.; Krossing, I. Simple Green Synthesis and Electrochemical Performance of a New Fluorinated Carbonate as Additive for Lithium-Ion Batteries. *ChemElectroChem* **2018**, *5*, 1415-1420.
- (182) Hu, J.; Chen, K.; Li, C. Nanostructured Li-Rich Fluoride Coated by Ionic Liquid as High Ion-Conductivity Solid Electrolyte Additive to Suppress Dendrite Growth at Li Metal Anode. *ACS Appl. Mater. Interfaces* **2018**, *10*, 34322-34331.
- (183) Li, Q.; Xue, W.; Sun, X.; Yu, X.; Li, H.; Chen, L. Gaseous Electrolyte Additive BF₃ for High-Power Li/CF_x Primary Batteries. *Energy Storage Mater.* **2021**, *38*, 482-488.
- (184) Xue, W.; Huang, M.; Li, Y.; Zhu, Y. G.; Gao, R.; Xiao, X.; Zhang, W.; Li, S.; Xu, G.; Yu, Y.; et al. Ultra-High-Voltage Ni-Rich Layered Cathodes in Practical Li Metal Batteries Enabled by a Sulfonamide-Based Electrolyte. *Nat. Energy* **2021**, *6*, 495-505.
- (185) Zhao, Q.; Stalin, S.; Archer, L. A. Stabilizing Metal Battery Anodes through the Design of Solid Electrolyte Interphases. *Joule* **2021**, *5*, 1119-1142.
- (186) Jiang, F. N.; Cheng, X. B.; Yang, S. J.; Xie, J.; Yuan, H.; Liu, L.; Huang, J. Q.; Zhang, Q. Thermoresponsive Electrolytes for Safe Lithium-Metal Batteries. *Adv. Mater.* **2023**, *35*, e2209114.
- (187) Xia, L.; Xia, Y.; Liu, Z. A Novel Fluorocyclophosphazene as Bifunctional Additive for Safer Lithium-Ion Batteries. *J. Power Sources* **2015**, *278*, 190-196.
- (188) Zhang, S. S.; Xu, K.; Jow, T. R. A Thermal Stabilizer for LiPF₆-Based Electrolytes of Li-Ion Cells. *Electrochem. Solid-State Lett.* **2002**, *5*, A206-A208.
- (189) Buhrmester, C.; Chen, J.; Moshurchak, L.; Jiang, J.; Wang, R. L.; Dahn, J. R. Studies of Aromatic Redox Shuttle Additives for LiFePO₄-Based Li-Ion Cells. *J. Electrochem. Soc.* **2005**, *152*, A2390.
- (190) Chen, J.; Buhrmester, C.; Dahn, J. R. Chemical Overcharge and Overdischarge Protection for Lithium-Ion Batteries. *Electrochem. Solid-State Lett.* **2005**, *8*, A59-A62.
- (191) Wang, Y.; Li, Z.; Hou, Y.; Hao, Z.; Zhang, Q.; Ni, Y.; Lu, Y.; Yan, Z.; Zhang, K.; Zhao, Q.; et al. Emerging Electrolytes with Fluorinated Solvents for Rechargeable Lithium-Based Batteries. *Chem. Soc. Rev.* **2023**, *52*, 2713-2763.
- (192) Hall, D. S.; Self, J.; Dahn, J. R. Dielectric Constants for Quantum Chemistry and Li-Ion Batteries: Solvent Blends of Ethylene Carbonate and Ethyl Methyl Carbonate. *J. Phys. Chem. C* **2015**, *119*, 22322-22330.
- (193) Meyer, W. H. Polymer Electrolytes for Lithium-Ion Batteries. *Adv. Mater.* **1998**, *10*, 439-448.
- (194) Young, W.-S.; Albert, J. N. L.; Schantz, A. B.; Epps, T. H. Mixed-Salt Effects on the Ionic Conductivity of Lithium-Doped PEO-Containing Block Copolymers. *Macromolecules* **2011**, *44*, 8116-8123.
- (195) Su, Y.; Rong, X.; Gao, A.; Liu, Y.; Li, J.; Mao, M.; Qi, X.; Chai, G.; Zhang, Q.; Suo, L.; et al. Rational Design of a Topological Polymeric Solid Electrolyte for High-Performance All-Solid-State Alkali Metal Batteries. *Nat. Commun.* **2022**, *13*, 4181.
- (196) Sun, Y.; Zhang, X.; Ma, C.; Guo, N.; Liu, Y.; Liu, J.; Xie, H. Fluorine-Containing Triblock Copolymers as Solid-State Polymer Electrolytes for Lithium Metal Batteries. *J. Power Sources* **2021**, *516*, 230686.
- (197) Jia, M.; Wen, P.; Wang, Z.; Zhao, Y.; Liu, Y.; Lin, J.; Chen, M.; Lin, X. Fluorinated Bifunctional Solid Polymer Electrolyte Synthesized under Visible Light for Stable Lithium Deposition and Dendrite-Free All-Solid-State Batteries. *Adv. Funct. Mater.* **2021**, *31*, 2101736.
- (198) Sun, H.; Xie, X.; Huang, Q.; Wang, Z.; Chen, K.; Li, X.; Gao, J.; Li, Y.; Li, H.; Qiu, J.; et al. Fluorinated Poly-oxalate Electrolytes Stabilizing both Anode and Cathode Interfaces for All-Solid-State Li/NMC811 Batteries. *Angew. Chem. Int. Ed.* **2021**, *60*, 18335-18343.

- (199) Shi, P.; Ma, J.; Liu, M.; Guo, S.; Huang, Y.; Wang, S.; Zhang, L.; Chen, L.; Yang, K.; Liu, X.; et al. A Dielectric Electrolyte Composite with High Lithium-Ion Conductivity for High-Voltage Solid-State Lithium Metal Batteries. *Nat. Nanotechnol.* **2023**, *18*, 602-610.
- (200) Tsuchida, E.; Ohno, H.; Tsunemi, K. Conduction of Lithium Ions in Polyvinylidene Fluoride and Its Derivatives—I. *Electrochim. Acta* **1983**, *28*, 591-595.
- (201) Jiang, Z.; Carroll, B.; Abraham, K. M. Studies of Some Poly(vinylidene fluoride) Electrolytes. *Electrochim. Acta* **1997**, *42*, 2667-2677.
- (202) Feinauer, M.; Euchner, H.; Fichtner, M.; Reddy, M. A. Unlocking the Potential of Fluoride-Based Solid Electrolytes for Solid-State Lithium Batteries. *ACS Appl. Energy Mater.* **2019**, *2*, 7196-7203.
- (203) Hu, J.; Yao, Z.; Chen, K.; Li, C. High-Conductivity Open Framework Fluorinated Electrolyte Bonded by Solidified Ionic Liquid Wires for Solid-State Li Metal Batteries. *Energy Storage Mater.* **2020**, *28*, 37-46.
- (204) Zhang, B.; Zhong, J.; Zhang, Y.; Yang, L.; Yang, J.; Li, S.; Wang, L.-W.; Pan, F.; Lin, Z. Discovering a New Class of Fluoride Solid-Electrolyte Materials via Screening the Structural Property of Li-Ion Sublattice. *Nano Energy* **2021**, *79*, 105407.
- (205) Arnold, W.; Shreyas, V.; Li, Y.; Koralalage, M. K.; Jasinski, J. B.; Thapa, A.; Sumanasekera, G.; Ngo, A. T.; Narayanan, B.; Wang, H. Synthesis of Fluorine-Doped Lithium Argyrodite Solid Electrolytes for Solid-State Lithium Metal Batteries. *ACS Appl. Mater. Interfaces* **2022**, *14*, 11483-11492.
- (206) Li, X.; Ren, Z.; Norouzi Banis, M.; Deng, S.; Zhao, Y.; Sun, Q.; Wang, C.; Yang, X.; Li, W.; Liang, J.; et al. Unravelling the Chemistry and Microstructure Evolution of a Cathodic Interface in Sulfide-Based All-Solid-State Li-Ion Batteries. *ACS Energy Lett.* **2019**, *4*, 2480-2488.
- (207) Ryu, H.-H.; Namkoong, B.; Kim, J.-H.; Belharouak, I.; Yoon, C. S.; Sun, Y.-K. Capacity Fading Mechanisms in Ni-Rich Single-Crystal NCM Cathodes. *ACS Energy Lett.* **2021**, *6*, 2726-2734.
- (208) Wan, H.; Zhang, J.; Xia, J.; Ji, X.; He, X.; Liu, S.; Wang, C. F and N Rich Solid Electrolyte for Stable All-Solid-State Battery. *Adv. Funct. Mater.* **2021**, *32*, 2110876.
- (209) Zhao, F.; Sun, Q.; Yu, C.; Zhang, S.; Adair, K.; Wang, S.; Liu, Y.; Zhao, Y.; Liang, J.; Wang, C.; et al. Ultrastable Anode Interface Achieved by Fluorinating Electrolytes for All-Solid-State Li Metal Batteries. *ACS Energy Lett.* **2020**, *5*, 1035-1043.
- (210) Liu, J.; Wang, J.; Zhu, L.; Chen, X.; Ma, Q.; Wang, L.; Wang, X.; Yan, W. A High-Safety and Multifunctional MOFs Modified Aramid Nanofiber Separator for Lithium-Sulfur Batteries. *Chem. Eng. J.* **2021**, *411*, 128540.
- (211) Feng, X.; Ren, D.; He, X.; Ouyang, M. Mitigating Thermal Runaway of Lithium-Ion Batteries. *Joule* **2020**, *4*, 743-770.
- (212) Choi, S.-S.; Lee, Y. S.; Joo, C. W.; Lee, S. G.; Park, J. K.; Han, K.-S. Electrospun PVDF Nanofiber Web as Polymer Electrolyte or Separator. *Electrochim. Acta* **2004**, *50*, 339-343.
- (213) Liang, Y.; Lin, Z.; Qiu, Y.; Zhang, X. Fabrication and Characterization of LATP/PAN Composite Fiber-Based Lithium-Ion Battery Separators. *Electrochim. Acta* **2011**, *56*, 6474-6480.
- (214) Lee, P.-C.; Han, T.-H.; Hwang, T.; Oh, J.-S.; Kim, S.-J.; Kim, B.-W.; Lee, Y.; Choi, H. R.; Jeoung, S. K.; Yoo, S. E.; et al. Electrochemical Double Layer Capacitor Performance of Electrospun Polymer Fiber-Electrolyte Membrane Fabricated by Solvent-Assisted and Thermally Induced Compression Molding Processes. *J. Membr. Sci.* **2012**, *409-410*, 365-370.
- (215) Kim, Y.-J.; Kim, H.-S.; Doh, C.-H.; Kim, S. H.; Lee, S.-M. Technological Potential and Issues of Polyacrylonitrile Based Nanofiber Non-woven Separator for Li-Ion Rechargeable Batteries. *J. Power Sources* **2013**, *244*, 196-206.
- (216) Cai, M.; Yuan, D.; Zhang, X.; Pu, Y.; Liu, X.; He, H.; Zhang, L.; Ning, X. Lithium Ion Battery Separator with Improved Performance via Side-by-Side Bicomponent Electrospinning of PVDF-HFP/PI Followed by 3D Thermal Crosslinking. *J. Power Sources* **2020**, *461*, 228123.
- (217) Hwang, K.; Kwon, B.; Byun, H. Preparation of PVdF Nanofiber Membranes by Electrospinning and Their Use as Secondary Battery Separators. *J. Membr. Sci.* **2011**, *378*, 111-116.
- (218) Orendorff, C. J.; Lambert, T. N.; Chavez, C. A.; Bencomo, M.; Fenton, K. R. Polyester Separators for Lithium-Ion Cells: Improving Thermal Stability and Abuse Tolerance. *Adv. Energy Mater.* **2013**, *3*, 314-320.
- (219) Croce, F.; Focarete, M. L.; Hassoun, J.; Meschini, I.; Scrosati, B. A Safe, High-Rate and High-Energy Polymer Lithium-Ion Battery Based on Gelled Membranes Prepared by Electrospinning. *Energy Environ. Sci.* **2011**, *4*, 921-927.
- (220) Raghavan, P.; Zhao, X.; Shin, C.; Baek, D.-H.; Choi, J.-W.; Manuel, J.; Heo, M.-Y.; Ahn, J.-H.; Nah, C. Preparation and Electrochemical Characterization of Polymer Electrolytes Based on Electrospun Poly(vinylidene

- Fluoride-Co-Hexafluoropropylene)/Polyacrylonitrile Blend/Composite Membranes for Lithium Batteries. *J. Power Sources* **2010**, *195*, 6088-6094.
- (221) Zhou, X.; Yue, L.; Zhang, J.; Kong, Q.; Liu, Z.; Yao, J.; Cui, G. A Core-Shell Structured Polysulfonamide-Based Composite Nonwoven towards High Power Lithium Ion Battery Separator. *J. Electrochem. Soc.* **2013**, *160*, A1341-A1347.
- (222) Zhang, F.; Ma, X.; Cao, C.; Li, J.; Zhu, Y. Poly(vinylidene fluoride)/SiO₂ Composite Membranes Prepared by Electrospinning and Their Excellent Properties for Nonwoven Separators for Lithium-Ion Batteries. *J. Power Sources* **2014**, *251*, 423-431.
- (223) Hao, J.; Lei, G.; Li, Z.; Wu, L.; Xiao, Q.; Wang, L. A Novel Polyethylene Terephthalate Nonwoven Separator Based on Electrospinning Technique for Lithium Ion Battery. *J. Membr. Sci.* **2013**, *428*, 11-16.
- (224) Zhang, C.; Bai, Y.; Sun, Y.; Gu, J.; Xu, Y. Preparation of Hydrophilic HDPE Porous Membranes via Thermally Induced Phase Separation by Blending of Amphiphilic PE-b-PEG Copolymer. *J. Membr. Sci.* **2010**, *365*, 216-224.
- (225) Zhai, Y.; Wang, N.; Mao, X.; Si, Y.; Yu, J.; Al-Deyab, S. S.; El-Newehy, M.; Ding, B. Sandwich-Structured PVdF/PMIA/PVdF Nanofibrous Separators with Robust Mechanical Strength and Thermal Stability for Lithium-Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 14511-14518.
- (226) Lee, Y. M.; Kim, J.-W.; Choi, N.-S.; Lee, J. A.; Seol, W.-H.; Park, J.-K. Novel Porous Separator Based on PVdF and PE Non-woven Matrix for Rechargeable Lithium Batteries. *J. Power Sources* **2005**, *139*, 235-241.
- (227) Song, K. W.; Kim, C. K. Coating with Macroporous Polyarylate via a Nonsolvent Induced Phase Separation Process for Enhancement of Polyethylene Separator Thermal Stability. *J. Membr. Sci.* **2010**, *352*, 239-246.
- (228) Ryou, M. H.; Lee, Y. M.; Park, J. K.; Choi, J. W. Mussel-Inspired Polydopamine-Treated Polyethylene Separators for High-Power Li-Ion Batteries. *Adv. Mater.* **2011**, *23*, 3066-3070.
- (229) Dai, J.; Shi, C.; Li, C.; Shen, X.; Peng, L.; Wu, D.; Sun, D.; Zhang, P.; Zhao, J. A Rational Design of Separator with Substantially Enhanced Thermal Features for Lithium-Ion Batteries by the Polydopamine–Ceramic Composite Modification of Polyolefin Membranes. *Energy Environ. Sci.* **2016**, *9*, 3252-3261.
- (230) Yang, C. L.; Li, Z. H.; Li, W. J.; Liu, H. Y.; Xiao, Q. Z.; Lei, G. T.; Ding, Y. H. Batwing-Like Polymer Membrane Consisting of PMMA-Grafted Electrospun PVdF–SiO₂ Nanocomposite Fibers for Lithium-Ion Batteries. *J. Membr. Sci.* **2015**, *495*, 341-350.
- (231) Li, S.; Gao, K. The Study on Methyl Methacrylate Graft-Copolymerized Composite Separator Prepared by Pre-irradiation Method for Li-Ion Batteries. *Surf. Coat. Technol.* **2010**, *204*, 2822-2828.
- (232) Jin, S. Y.; Manuel, J.; Zhao, X.; Park, W. H.; Ahn, J.-H. Surface-Modified Polyethylene Separator via Oxygen Plasma Treatment for Lithium Ion Battery. *J. Ind. Eng. Chem.* **2017**, *45*, 15-21.
- (233) Li, X.; He, J.; Wu, D.; Zhang, M.; Meng, J.; Ni, P. Development of Plasma-Treated Polypropylene Nonwoven-Based Composites for High-Performance Lithium-Ion Battery Separators. *Electrochim. Acta* **2015**, *167*, 396-403.
- (234) Bicy, K.; Gueye, A. B.; Rouxel, D.; Kalarikkal, N.; Thomas, S. Lithium-Ion Battery Separators Based on Electrospun PVDF: A Review. *Surf. Interfaces* **2022**, *31*, 101977.
- (235) Costa, C. M.; Silva, M. M.; Lanceros-Méndez, S. Battery Separators Based on Vinylidene Fluoride (VDF) Polymers and Copolymers for Lithium Ion Battery Applications. *RSC Adv.* **2013**, *3*, 11404.
- (236) Abbrent, S.; Plestil, J.; Hlavata, D.; Lindgren, J.; Tegenfeldt, J.; Wendsjö, Å. Crystallinity and Morphology of PVdF–HFP-Based Gel Electrolytes. *Polymer* **2001**, *42*, 1407-1416.
- (237) Wu, Q.-Y.; Liang, H.-Q.; Gu, L.; Yu, Y.; Huang, Y.-Q.; Xu, Z.-K. PVDF/PAN Blend Separators via Thermally Induced Phase Separation for Lithium Ion Batteries. *Polymer* **2016**, *107*, 54-60.
- (238) Chen, W.; Liu, Y.; Ma, Y.; Liu, J.; Liu, X. Improved Performance of PVdF-HFP/PI Nanofiber Membrane for Lithium-Ion Battery Separator Prepared by a Bicomponent Cross-Electrospinning Method. *Mater. Lett.* **2014**, *133*, 67-70.
- (239) Bicy, K.; Mathew, D. E.; Stephen, A. M.; Royaud, I.; Poncot, M.; Godard, O.; Aranda, L.; Rouxel, D.; Kalarikkal, N.; Thomas, S. Sustainable Lithium-Ion Battery Separators Derived from Polyethylene Oxide/Lignocellulose Coated Electrospun P(VDF-TrFE) Nanofibrous Membranes. *Surf. Interfaces* **2022**, *29*, 101716.
- (240) K, B.; Paul P, A.; Kalarikkal, N.; Stephen, A. M.; G, G. V.; Rouxel, D.; Thomas, S. Effects of Nanofillers on Morphology and Surface Wetting of Microporous Polypropylene Composite Membranes. *Mater. Chem. Phys.* **2021**, *257*, 123742.

- (241) Xiao, J.; Zhai, P.; Wei, Y.; Zhang, X.; Yang, W.; Cui, S.; Jin, C.; Liu, W.; Wang, X.; Jiang, H.; et al. In-Situ Formed Protecting Layer from Organic/Inorganic Concrete for Dendrite-Free Lithium Metal Anodes. *Nano Lett.* **2020**, *20*, 3911-3917.
- (242) Jeon, I.-Y.; Ju, M. J.; Xu, J.; Choi, H.-J.; Seo, J.-M.; Kim, M.-J.; Choi, I. T.; Kim, H. M.; Kim, J. C.; Lee, J.-J.; et al. Edge-Fluorinated Graphene Nanoplatelets as High Performance Electrodes for Dye-Sensitized Solar Cells and Lithium Ion Batteries. *Adv. Funct. Mater.* **2015**, *25*, 1170-1179.
- (243) Sun, S.; Wang, J.; Chen, X.; Ma, Q.; Wang, Y.; Yang, K.; Yao, X.; Yang, Z.; Liu, J.; Xu, H.; et al. Thermally Stable and Dendrite-Resistant Separators toward Highly Robust Lithium Metal Batteries. *Adv. Energy Mater.* **2022**, *12*, 2202206.
- (244) Qian, Y.; Chen, K.; Feng, Z.; Ouyang, Y.; Lan, Q.; Zhang, C.; Feng, W.; Miao, Y.-E.; Liu, T. A Fluorinated-Polyimide-Based Composite Nanofibrous Separator with Homogenized Pore Size for Wide-Temperature Lithium Metal Batteries. *Small Struct.* **2023**, *4*, 2200383.
- (245) Zhang, K.; Li, X.; Ma, L.; Chen, F.; Chen, Z.; Yuan, Y.; Zhao, Y.; Yang, J.; Liu, J.; Xie, K.; et al. Fluorinated Covalent Organic Framework-Based Nanofluidic Interface for Robust Lithium-Sulfur Batteries. *ACS Nano* **2023**, *17*, 2901-2911.
- (246) Wang, Z.; Zhang, J.; Yang, Y.; Yue, X.; Hao, X.; Sun, W.; Rooney, D.; Sun, K. Flexible Carbon Nanofiber/Polyvinylidene Fluoride Composite Membranes as Interlayers in High-Performance Lithium Sulfur Batteries. *J. Power Sources* **2016**, *329*, 305-313.
- (247) Wei, H.; Ma, J.; Li, B.; Zuo, Y.; Xia, D. Enhanced Cycle Performance of Lithium-Sulfur Batteries Using a Separator Modified with a PVDF-C Layer. *ACS Appl. Mater. Interfaces* **2014**, *6*, 20276-20281.
- (248) Vizintin, A.; Lozinšek, M.; Chellappan, R. K.; Foix, D.; Krajnc, A.; Mali, G.; Drazic, G.; Genorio, B.; Dedryvère, R.; Dominko, R. Fluorinated Reduced Graphene Oxide as an Interlayer in Li-S Batteries. *Chem. Mater.* **2015**, *27*, 7070-7081.
- (249) Xia, S.; Zhang, X.; Yang, G.; Shi, L.; Cai, L.; Xia, Y.; Yang, J.; Zheng, S. Bifunctional Fluorinated Separator Enabling Polysulfide Trapping and Li Deposition for Lithium-Sulfur Batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 11920-11929.
- (250) Xiong, P.; Zhang, F.; Zhang, X.; Liu, Y.; Wu, Y.; Wang, S.; Safaei, J.; Sun, B.; Ma, R.; Liu, Z.; et al. Atomic-Scale Regulation of Anionic and Cationic Migration in Alkali Metal Batteries. *Nat. Commun.* **2021**, *12*, 4184.
- (251) Liu, W.; Zhang, K.; Ma, L.; Ning, R.; Chen, Z.; Li, J.; Yan, Y.; Shang, T.; Lyu, Z.; Li, Z.; et al. An Ion Sieving Conjugated Microporous Thermoset Ultrathin Membrane for High-Performance Li-S Battery. *Energy Storage Mater.* **2022**, *49*, 1-10.
- (252) Zou, F.; Manthiram, A. A Review of the Design of Advanced Binders for High-Performance Batteries. *Adv. Energy Mater.* **2020**, *10*, 2002508.
- (253) Huang, S.; Ren, J.; Liu, R.; Yue, M.; Huang, Y.; Yuan, G. The Progress of Novel Binder as a Non-ignorable Part to Improve the Performance of Si-Based Anodes for Li-Ion Batteries. *Int. J. Energy Res.* **2018**, *42*, 919-935.
- (254) Ai, G.; Dai, Y.; Ye, Y.; Mao, W.; Wang, Z.; Zhao, H.; Chen, Y.; Zhu, J.; Fu, Y.; Battaglia, V.; et al. Investigation of Surface Effects Through the Application of Functional Binders in Lithium-Sulfur Batteries. *Nano Energy* **2015**, *16*, 28-37.
- (255) Kwon, T. W.; Choi, J. W.; Coskun, A. The Emerging Era of Supramolecular Polymeric Binders in Silicon Anodes. *Chem. Soc. Rev.* **2018**, *47*, 2145-2164.
- (256) Chen, H.; Ling, M.; Hencz, L.; Ling, H. Y.; Li, G.; Lin, Z.; Liu, G.; Zhang, S. Exploring Chemical, Mechanical, and Electrical Functionalities of Binders for Advanced Energy-Storage Devices. *Chem. Rev.* **2018**, *118*, 8936-8982.
- (257) Fu, Z.; Feng, H. L.; Xiang, X. D.; Rao, M. M.; Wu, W.; Luo, J. C.; Chen, T. T.; Hu, Q. P.; Feng, A. B.; Li, W. S. A Novel Polymer Composite as Cathode Binder of Lithium-Ion Batteries with Improved Rate Capability and Cyclic Stability. *J. Power Sources* **2014**, *261*, 170-174.
- (258) Byun, S.; Choi, J.; Roh, Y.; Song, D.; Ryou, M.-H.; Lee, Y. M. Mechanical Robustness of Composite Electrode for Lithium-Ion Battery: Insight into Entanglement & Crystallinity of Polymeric Binder. *Electrochim. Acta* **2020**, *332*, 135471.
- (259) Huang, H.; Li, Z.; Gu, S.; Bian, J.; Li, Y.; Chen, J.; Liao, K.; Gan, Q.; Wang, Y.; Wu, S.; et al. Dextran Sulfate Lithium as Versatile Binder to Stabilize High-Voltage LiCoO₂ to 4.6 V. *Adv. Energy Mater.* **2021**, *11*, 2101864.

- (260) Pieczonka, N. P. W.; Borgel, V.; Ziv, B.; Leifer, N.; Dargel, V.; Aurbach, D.; Kim, J.-H.; Liu, Z.; Huang, X.; Krachkovskiy, S. A.; et al. Lithium Polyacrylate (LiPAA) as an Advanced Binder and a Passivating Agent for High-Voltage Li-Ion Batteries. *Adv. Energy Mater.* **2015**, *5*, 1501008.
- (261) Liang, J.; Chen, D.; Adair, K.; Sun, Q.; Holmes, N. G.; Zhao, Y.; Sun, Y.; Luo, J.; Li, R.; Zhang, L.; et al. Insight into Prolonged Cycling Life of 4 V All-Solid-State Polymer Batteries by a High-Voltage Stable Binder. *Adv. Energy Mater.* **2020**, *11*, 2002455.
- (262) Pham, H. Q.; Kim, G.; Jung, H. M.; Song, S.-W. Fluorinated Polyimide as a Novel High-Voltage Binder for High-Capacity Cathode of Lithium-Ion Batteries. *Adv. Funct. Mater.* **2018**, *28*, 1704690.
- (263) Li, J.; Le, D.-B.; Ferguson, P. P.; Dahn, J. R. Lithium Polyacrylate as a Binder for Tin–Cobalt–Carbon Negative Electrodes in Lithium-Ion Batteries. *Electrochim. Acta* **2010**, *55*, 2991-2995.
- (264) Tsao, C.-H.; Hsu, C.-H.; Kuo, P.-L. Ionic Conducting and Surface Active Binder of Poly(ethylene oxide)-Block-Poly(acrylonitrile) for High Power Lithium-Ion Battery. *Electrochim. Acta* **2016**, *196*, 41-47.
- (265) Wei, Z.; Xue, L.; Nie, F.; Sheng, J.; Shi, Q.; Zhao, X. Study of Sulfonated Polyether Ether Ketone with Pendant Lithiated Fluorinated Sulfonic Groups as Ion-Conductive Binder in Lithium-Ion Batteries. *J. Power Sources* **2014**, *256*, 28-31.
- (266) Shi, Q.; Xue, L.; Wei, Z.; Liu, F.; Du, X.; Desmarteau, D. D. Improvement in LiFePO₄-Li Battery Performance via Poly(perfluoroalkylsulfonyl)imide (PFSI) Based Ionene Composite Binder. *J. Mater. Chem. A* **2013**, *1*, 15016.
- (267) Chiu, K.-F.; Su, S. H.; Leu, H.-J.; Chen, Y. S. Application of Lithiated Perfluorosulfonate Ionomer Binders to Enhance High Rate Capability in LiMn₂O₄ Cathodes for Lithium-Ion Batteries. *Electrochim. Acta* **2014**, *117*, 134-138.
- (268) Vauthier, S.; Alvarez-Tirado, M.; Guzmán-González, G.; Tomé, L. C.; Cotte, S.; Castro, L.; Guéguen, A.; Mecerreyes, D.; Casado, N. High-Performance Pyrrolidinium-Based Poly(ionic Liquid) Binders for Li-Ion and Li-Air Batteries. *Mater. Today Chem.* **2023**, *27*, 101293.
- (269) Tsao, C.-H.; Wu, E. T.; Lee, W.-H.; Chiu, C.-C.; Kuo, P.-L. Fluorinated Copolymer Functionalized with Ethylene Oxide as Novel Water-Borne Binder for a High-Power Lithium Ion Battery: Synthesis, Mechanism, and Application. *ACS Appl. Energy Mater.* **2018**, *1*, 3999-4008.
- (270) Lee, J. I.; Kang, H.; Park, K. H.; Shin, M.; Hong, D.; Cho, H. J.; Kang, N. R.; Lee, J.; Lee, S. M.; Kim, J. Y.; et al. Amphiphilic Graft Copolymers as a Versatile Binder for Various Electrodes of High-Performance Lithium-Ion Batteries. *Small* **2016**, *12*, 3119-3127.
- (271) Cai, Y.; Li, Y.; Jin, B.; Ali, A.; Ling, M.; Cheng, D.; Lu, J.; Hou, Y.; He, Q.; Zhan, X.; et al. Dual Cross-Linked Fluorinated Binder Network for High-Performance Silicon and Silicon Oxide Based Anodes in Lithium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2019**, *11*, 46800-46807.
- (272) Preman, A. N.; Lee, H.; Yoo, J.; Kim, I. T.; Saito, T.; Ahn, S.-K. Progress of 3D Network Binders in Silicon Anodes for Lithium Ion Batteries. *J. Mater. Chem. A* **2020**, *8*, 25548-25570.
- (273) Li, S.; Liu, Y.-M.; Zhang, Y.-C.; Song, Y.; Wang, G.-K.; Liu, Y.-X.; Wu, Z.-G.; Zhong, B.-H.; Zhong, Y.-J.; Guo, X.-D. A Review of Rational Design and Investigation of Binders Applied in Silicon-Based Anodes for Lithium-Ion Batteries. *J. Power Sources* **2021**, *485*, 229331.
- (274) Li, J.; Christensen, L.; Obrovac, M. N.; Hewitt, K. C.; Dahn, J. R. Effect of Heat Treatment on Si Electrodes Using Polyvinylidene Fluoride Binder. *J. Electrochem. Soc.* **2008**, *155*, A234.
- (275) Chen, Z.; Christensen, L.; Dahn, J. R. Large-Volume-Change Electrodes for Li-Ion Batteries of Amorphous Alloy Particles Held by Elastomeric Tethers. *Electrochem. commun.* **2003**, *5*, 919-923.
- (276) Rongeat, C.; Reddy, M. A.; Witter, R.; Fichtner, M. Solid Electrolytes for Fluoride Ion Batteries: Ionic Conductivity in Polycrystalline Tysonite-Type Fluorides. *ACS Appl. Mater. Interfaces* **2014**, *6*, 2103-2110.
- (277) Choi, S.; Kwon, T. W.; Coskun, A.; Choi, J. W. Highly Elastic Binders Integrating Polyrotaxanes for Silicon Microparticle Anodes in Lithium Ion Batteries. *Science* **2017**, *357*, 279-283.
- (278) Koo, B.; Kim, H.; Cho, Y.; Lee, K. T.; Choi, N. S.; Cho, J. A Highly Cross-Linked Polymeric Binder for High-Performance Silicon Negative Electrodes in Lithium-Ion Batteries. *Angew. Chem. Int. Ed.* **2012**, *51*, 8762-8767.
- (279) Li, C.; Shi, T.; Yoshitake, H.; Wang, H. Improved Performance in Micron-Sized Silicon Anodes by In Situ Polymerization of Acrylic Acid-Based Slurry. *J. Mater. Chem. A* **2016**, *4*, 16982-16991.
- (280) Song, J.; Zhou, M.; Yi, R.; Xu, T.; Gordin, M. L.; Tang, D.; Yu, Z.; Regula, M.; Wang, D. Interpenetrated Gel Polymer Binder for High-Performance Silicon Anodes in Lithium-ion Batteries. *Adv. Funct. Mater.* **2014**, *24*, 5904-5910.

- (281) Qin, D.; Xue, L.; Du, B.; Wang, J.; Nie, F.; Wen, L. Flexible Fluorine-Containing Ionic Binders to Mitigate the Negative Impact Caused by the Drastic Volume Fluctuation from Silicon Nanoparticles in High-Capacity Anodes of Lithium-Ion Batteries. *J. Mater. Chem. A* **2015**, *3*, 10928-10934.
- (282) Wang, L.; He, X.; Li, J.; Gao, J.; Fang, M.; Tian, G.; Wang, J.; Fan, S. Graphene-Coated Plastic Film as Current Collector for Lithium/Sulfur Batteries. *J. Power Sources* **2013**, *239*, 623-627.
- (283) Gabryelczyk, A.; Ivanov, S.; Bund, A.; Lota, G. Corrosion of aluminium current collector in lithium-ion batteries: A review. *J. Energy Storage* **2021**, *43*, 103226.
- (284) Zheng, J.; Engelhard, M. H.; Mei, D.; Jiao, S.; Polzin, B. J.; Zhang, J.-G.; Xu, W. Electrolyte Additive Enabled Fast Charging and Stable Cycling Lithium Metal Batteries. *Nat. Energy* **2017**, *2*, 17012.
- (285) Ding, F.; Xu, W.; Graff, G. L.; Zhang, J.; Sushko, M. L.; Chen, X.; Shao, Y.; Engelhard, M. H.; Nie, Z.; Xiao, J.; et al. Dendrite-Free Lithium Deposition via Self-Healing Electrostatic Shield Mechanism. *J. Am. Chem. Soc.* **2013**, *135*, 4450-4456.
- (286) Yan, C.; Cheng, X.-B.; Zhao, C.-Z.; Huang, J.-Q.; Yang, S.-T.; Zhang, Q. Lithium Metal Protection Through In-Situ Formed Solid Electrolyte Interphase in Lithium-Sulfur Batteries: The Role of Polysulfides on Lithium Anode. *J. Power Sources* **2016**, *327*, 212-220.
- (287) Cheng, X. B.; Zhao, M. Q.; Chen, C.; Pentecost, A.; Maleski, K.; Mathis, T.; Zhang, X. Q.; Zhang, Q.; Jiang, J.; Gogotsi, Y. Nanodiamonds Suppress the Growth of Lithium Dendrites. *Nat. Commun.* **2017**, *8*, 336.
- (288) Li, N. W.; Yin, Y. X.; Yang, C. P.; Guo, Y. G. An Artificial Solid Electrolyte Interphase Layer for Stable Lithium Metal Anodes. *Adv. Mater.* **2016**, *28*, 1853-1858.
- (289) Zhao, J.; Liao, L.; Shi, F.; Lei, T.; Chen, G.; Pei, A.; Sun, J.; Yan, K.; Zhou, G.; Xie, J.; et al. Surface Fluorination of Reactive Battery Anode Materials for Enhanced Stability. *J. Am. Chem. Soc.* **2017**, *139*, 11550-11558.
- (290) Fu, K.; Gong, Y.; Hitz, G. T.; Mcowen, D. W.; Li, Y.; Xu, S.; Wen, Y.; Zhang, L.; Wang, C.; Pastel, G.; et al. Three-Dimensional Bilayer Garnet Solid Electrolyte Based High Energy Density Lithium Metal-Sulfur Batteries. *Energy Environ. Sci.* **2017**, *10*, 1568-1575.
- (291) Liu, Y.; Lin, D.; Yuen, P. Y.; Liu, K.; Xie, J.; Dauskardt, R. H.; Cui, Y. An Artificial Solid Electrolyte Interphase with High Li-Ion Conductivity, Mechanical Strength, and Flexibility for Stable Lithium Metal Anodes. *Adv. Mater.* **2017**, *29*, 1605531.
- (292) Pang, Q.; Liang, X.; Shyamsunder, A.; Nazar, L. F. An In Vivo Formed Solid Electrolyte Surface Layer Enables Stable Plating of Li Metal. *Joule* **2017**, *1*, 871-886.
- (293) Liu, W.; Lin, D.; Pei, A.; Cui, Y. Stabilizing Lithium Metal Anodes by Uniform Li-Ion Flux Distribution in Nanochannel Confinement. *J. Am. Chem. Soc.* **2016**, *138*, 15443-15450.
- (294) Cheng, X. B.; Hou, T. Z.; Zhang, R.; Peng, H. J.; Zhao, C. Z.; Huang, J. Q.; Zhang, Q. Dendrite-Free Lithium Deposition Induced by Uniformly Distributed Lithium Ions for Efficient Lithium Metal Batteries. *Adv. Mater.* **2016**, *28*, 2888-2895.
- (295) Li, N.; Ye, Q.; Zhang, K.; Yan, H.; Shen, C.; Wei, B.; Xie, K. Normalized Lithium Growth from the Nucleation Stage for Dendrite-Free Lithium Metal Anodes. *Angew. Chem. Int. Ed.* **2019**, *58*, 18246-18251.
- (296) Chen, X.; Hou, T.-Z.; Li, B.; Yan, C.; Zhu, L.; Guan, C.; Cheng, X.-B.; Peng, H.-J.; Huang, J.-Q.; Zhang, Q. Towards Stable Lithium-Sulfur Batteries: Mechanistic Insights into Electrolyte Decomposition on Lithium Metal Anode. *Energy Storage Mater.* **2017**, *8*, 194-201.
- (297) Zuo, T. T.; Wu, X. W.; Yang, C. P.; Yin, Y. X.; Ye, H.; Li, N. W.; Guo, Y. G. Graphitized Carbon Fibers as Multifunctional 3D Current Collectors for High Areal Capacity Li Anodes. *Adv. Mater.* **2017**, *29*, 1700389.
- (298) Zhang, R.; Chen, X. R.; Chen, X.; Cheng, X. B.; Zhang, X. Q.; Yan, C.; Zhang, Q. Lithiophilic Sites in Doped Graphene Guide Uniform Lithium Nucleation for Dendrite-Free Lithium Metal Anodes. *Angew. Chem. Int. Ed.* **2017**, *56*, 7764-7768.
- (299) Sun, Y.; Zheng, G.; Seh, Z. W.; Liu, N.; Wang, S.; Sun, J.; Lee, H. Y.; Cui, Y. Graphite-Encapsulated Li-Metal Hybrid Anodes for High-Capacity Li Batteries. *Chem* **2016**, *1*, 287-297.
- (300) Liu, L.; Yin, Y.-X.; Li, J.-Y.; Li, N.-W.; Zeng, X.-X.; Ye, H.; Guo, Y.-G.; Wan, L.-J. Free-Standing Hollow Carbon Fibers as High-Capacity Containers for Stable Lithium Metal Anodes. *Joule* **2017**, *1*, 563-575.
- (301) Yang, Q.; Li, C. Li Metal Batteries and Solid State Batteries Benefiting from Halogen-Based Strategies. *Energy Storage Mater.* **2018**, *14*, 100-117.
- (302) Li, T.; Zhang, X.-Q.; Shi, P.; Zhang, Q. Fluorinated Solid-Electrolyte Interphase in High-Voltage Lithium Metal Batteries. *Joule* **2019**, *3*, 2647-2661.
- (303) Wang, Y.; Liang, J.; Song, X.; Jin, Z. Recent Progress in Constructing Halogenated Interfaces for Highly Stable Lithium Metal Anodes. *Energy Storage Mater.* **2023**, *54*, 732-775.

- (304) Zhang, X. Q.; Chen, X.; Xu, R.; Cheng, X. B.; Peng, H. J.; Zhang, R.; Huang, J. Q.; Zhang, Q. Columnar Lithium Metal Anodes. *Angew. Chem. Int. Ed.* **2017**, *56*, 14207-14211.
- (305) Luo, J.; Fang, C.-C.; Wu, N.-L. High Polarity Poly(vinylidene difluoride) Thin Coating for Dendrite-Free and High-Performance Lithium Metal Anodes. *Adv. Energy Mater.* **2018**, *8*, 1701482.
- (306) Cheng, H.; Mao, Y.; Lu, Y.; Zhang, P.; Xie, J.; Zhao, X. Trace Fluorinated-Carbon-Nanotube-Induced Lithium Dendrite Elimination for High-Performance Lithium-Oxygen Cells. *Nanoscale* **2020**, *12*, 3424-3434.
- (307) Cui, C.; Yang, C.; Eidson, N.; Chen, J.; Han, F.; Chen, L.; Luo, C.; Wang, P. F.; Fan, X.; Wang, C. A Highly Reversible, Dendrite-Free Lithium Metal Anode Enabled by a Lithium-Fluoride-Enriched Interphase. *Adv. Mater.* **2020**, *32*, e1906427.
- (308) Li, Z.; Li, X.; Zhou, L.; Xiao, Z.; Zhou, S.; Zhang, X.; Li, L.; Zhi, L. A Synergistic Strategy for Stable Lithium Metal Anodes Using 3D Fluorine-Doped Graphene Shuttle-Implanted Porous Carbon Networks. *Nano Energy* **2018**, *49*, 179-185.
- (309) Jamaluddin, A.; Sin, Y.-Y.; Adhitama, E.; Prayogi, A.; Wu, Y.-T.; Chang, J.-K.; Su, C.-Y. Fluorinated Graphene as a Dual-Functional Anode to Achieve Dendrite-Free and High-Performance Lithium Metal Batteries. *Carbon* **2022**, *197*, 141-151.
- (310) Gao, Y.; Rojas, T.; Wang, K.; Liu, S.; Wang, D.; Chen, T.; Wang, H.; Ngo, A. T.; Wang, D. Low-Temperature and High-Rate-Charging Lithium Metal Batteries Enabled by an Electrochemically Active Monolayer-Regulated Interface. *Nat. Energy* **2020**, *5*, 534-542.
- (311) Huang, G.; Chen, S.; Guo, P.; Tao, R.; Jie, K.; Liu, B.; Zhang, X.; Liang, J.; Cao, Y.-C. In Situ Constructing Lithiophilic NiF_x Nanosheets on Ni Foam Current Collector for Stable Lithium Metal Anode via a Succinct Fluorination Strategy. *Chem. Eng. J.* **2020**, *395*, 125122.
- (312) Cao, J.; Qian, G.; Lu, X.; Lu, X. Advanced Composite Lithium Metal Anodes with 3D Frameworks: Preloading Strategies, Interfacial Optimization, and Perspectives. *Small* **2023**, *19*, e2205653.
- (313) Hou, W.; Li, S.; Liang, J.; Yuan, B.; Hu, R. Lithiophilic NiF₂ Coating Inducing LiF-Rich Solid Electrolyte Interphase by a Novel NF₃ Plasma Treatment for Highly Stable Li Metal Anode. *Electrochim. Acta* **2022**, *402*, 139561.
- (314) Richards, W. D.; Miara, L. J.; Wang, Y.; Kim, J. C.; Ceder, G. Interface Stability in Solid-State Batteries. *Chem. Mater.* **2015**, *28*, 266-273.
- (315) Mason, W. P.; Mayer, W. G. Physical Acoustics, Principles and Methods. *Phys. Today* **1965**, *18*, 67-67.
- (316) Suo, L.; Xue, W.; Gobet, M.; Greenbaum, S. G.; Wang, C.; Chen, Y.; Yang, W.; Li, Y.; Li, J. Fluorine-Donating Electrolytes Enable Highly Reversible 5-V-Class Li Metal Batteries. *Proc. Natl. Acad. Sci. U.S.A.* **2018**, *115*, 1156-1161.
- (317) Xu, R.; Zhang, X.-Q.; Cheng, X.-B.; Peng, H.-J.; Zhao, C.-Z.; Yan, C.; Huang, J.-Q. Artificial Soft-Rigid Protective Layer for Dendrite-Free Lithium Metal Anode. *Adv. Funct. Mater.* **2018**, *28*, 1705838.
- (318) Chen, L.; Chen, K. S.; Chen, X.; Ramirez, G.; Huang, Z.; Geise, N. R.; Steinruck, H. G.; Fisher, B. L.; Shahbazian-Yassar, R.; Toney, M. F.; et al. Novel ALD Chemistry Enabled Low-Temperature Synthesis of Lithium Fluoride Coatings for Durable Lithium Anodes. *ACS Appl. Mater. Interfaces* **2018**, *10*, 26972-26981.
- (319) Lin, D.; Liu, Y.; Chen, W.; Zhou, G.; Liu, K.; Dunn, B.; Cui, Y. Conformal Lithium Fluoride Protection Layer on Three-Dimensional Lithium by Nonhazardous Gaseous Reagent Freon. *Nano Lett.* **2017**, *17*, 3731-3737.
- (320) Yan, C.; Cheng, X. B.; Yao, Y. X.; Shen, X.; Li, B. Q.; Li, W. J.; Zhang, R.; Huang, J. Q.; Li, H.; Zhang, Q. An Armored Mixed Conductor Interphase on a Dendrite-Free Lithium-Metal Anode. *Adv. Mater.* **2018**, *30*, e1804461.
- (321) Pathak, R.; Chen, K.; Gurung, A.; Reza, K. M.; Bahrami, B.; Pokharel, J.; Baniya, A.; He, W.; Wu, F.; Zhou, Y.; et al. Fluorinated Hybrid Solid-Electrolyte-Interphase for Dendrite-Free Lithium Deposition. *Nat. Commun.* **2020**, *11*, 93.
- (322) Yang, Q.; Hu, J.; Meng, J.; Li, C. C-F-rich Oil Drop as a Non-expendable Fluid Interface Modifier with Low Surface Energy to Stabilize a Li Metal Anode. *Energy Environ. Sci.* **2021**, *14*, 3621-3631.
- (323) Fan, X.; Ji, X.; Han, F.; Yue, J.; Chen, J.; Chen, L.; Deng, T.; Jiang, J.; Wang, C. Fluorinated Solid Electrolyte Interphase Enables Highly Reversible Solid-State Li Metal Battery. *Sci. Adv.* **2018**, *4*, eaau9245.
- (324) Hu, A.; Chen, W.; Du, X.; Hu, Y.; Lei, T.; Wang, H.; Xue, L.; Li, Y.; Sun, H.; Yan, Y.; et al. An Artificial Hybrid Interphase for an Ultrahigh-Rate and Practical Lithium Metal Anode. *Energy Environ. Sci.* **2021**, *14*, 4115-4124.
- (325) Liu, S.; Ji, X.; Yue, J.; Hou, S.; Wang, P.; Cui, C.; Chen, J.; Shao, B.; Li, J.; Han, F.; et al. High Interfacial-Energy Interphase Promoting Safe Lithium Metal Batteries. *J. Am. Chem. Soc.* **2020**, *142*, 2438-2447.

- (326) Wang, Y.; Liu, F.; Fan, G.; Qiu, X.; Liu, J.; Yan, Z.; Zhang, K.; Cheng, F.; Chen, J. Electroless Formation of a Fluorinated Li/Na Hybrid Interphase for Robust Lithium Anodes. *J. Am. Chem. Soc.* **2021**, *143*, 2829-2837.
- (327) Yan, C.; Cheng, X. B.; Tian, Y.; Chen, X.; Zhang, X. Q.; Li, W. J.; Huang, J. Q.; Zhang, Q. Dual-Layered Film Protected Lithium Metal Anode to Enable Dendrite-Free Lithium Deposition. *Adv. Mater.* **2018**, *30*, e1707629.
- (328) Liu, S.; Xia, X.; Deng, S.; Xie, D.; Yao, Z.; Zhang, L.; Zhang, S.; Wang, X.; Tu, J. In Situ Solid Electrolyte Interphase from Spray Quenching on Molten Li: A New Way to Construct High-Performance Lithium-Metal Anodes. *Adv. Mater.* **2019**, *31*, e1806470.
- (329) Gao, Y.; Yan, Z.; Gray, J. L.; He, X.; Wang, D.; Chen, T.; Huang, Q.; Li, Y. C.; Wang, H.; Kim, S. H.; et al. Polymer-Inorganic Solid-Electrolyte Interphase for Stable Lithium Metal Batteries under Lean Electrolyte Conditions. *Nat. Mater.* **2019**, *18*, 384-389.
- (330) Shen, X.; Li, Y.; Qian, T.; Liu, J.; Zhou, J.; Yan, C.; Goodenough, J. B. Lithium Anode Stable in Air for Low-Cost Fabrication of a Dendrite-Free Lithium Battery. *Nat. Commun.* **2019**, *10*, 900.
- (331) Peled, E. The Electrochemical Behavior of Alkali and Alkaline Earth Metals in Nonaqueous Battery Systems—The Solid Electrolyte Interphase Model. *J. Electrochem. Soc.* **2019**, *126*, 2047-2051.
- (332) Peled, E.; Menkin, S. Review—SEI: Past, Present and Future. *J. Electrochem. Soc.* **2017**, *164*, A1703-A1719.
- (333) Lu, Y.; Tu, Z.; Archer, L. A. Stable Lithium Electrodeposition in Liquid and Nanoporous Solid Electrolytes. *Nat. Mater.* **2014**, *13*, 961-969.
- (334) Ko, J.; Yoon, Y. S. Recent Progress in LiF Materials for Safe Lithium Metal Anode of Rechargeable Batteries: Is LiF the Key to Commercializing Li Metal Batteries? *Ceram. Int.* **2019**, *45*, 30-49.
- (335) Yuan, Y.; Wu, F.; Chen, G.; Bai, Y.; Wu, C. Porous LiF Layer Fabricated by a Facile Chemical Method toward Dendrite-Free Lithium Metal Anode. *J. Energy Chem.* **2019**, *37*, 197-203.
- (336) Cheng, X.-B.; Yan, C.; Chen, X.; Guan, C.; Huang, J.-Q.; Peng, H.-J.; Zhang, R.; Yang, S.-T.; Zhang, Q. Implantable Solid Electrolyte Interphase in Lithium-Metal Batteries. *Chem* **2017**, *2*, 258-270.
- (337) Breuer, S.; Pregartner, V.; Lunghammer, S.; Wilkening, H. M. R. Dispersed Solid Conductors: Fast Interfacial Li-Ion Dynamics in Nanostructured LiF and LiF:γ-Al₂O₃ Composites. *J. Phys. Chem. C* **2019**, *123*, 5222-5230.
- (338) Zaban, A.; Zinigrad, E.; Aurbach, D. Impedance Spectroscopy of Li Electrodes. 4. A General Simple Model of the Li-Solution Interphase in Polar Aprotic Systems. *J. Phys. Chem.* **1996**, *100*, 3089-3101.
- (339) Rehnlund, D.; Ihrfors, C.; Maibach, J.; Nyholm, L. Dendrite-Free Lithium Electrode Cycling via Controlled Nucleation in Low LiPF₆ Concentration Electrolytes. *Mater. Today* **2018**, *21*, 1010-1018.
- (340) Jurng, S.; Brown, Z. L.; Kim, J.; Lucht, B. L. Effect of Electrolyte on the Nanostructure of the Solid Electrolyte Interphase (SEI) and Performance of Lithium Metal Anodes. *Energy Environ. Sci.* **2018**, *11*, 2600-2608.
- (341) Monroe, C.; Newman, J. The Effect of Interfacial Deformation on Electrodeposition Kinetics. *J. Electrochem. Soc.* **2004**, *151*, A880.
- (342) He, M.; Guo, R.; Hobold, G. M.; Gao, H.; Gallant, B. M. The Intrinsic Behavior of Lithium Fluoride in Solid Electrolyte Interphases on Lithium. *Proc. Natl. Acad. Sci. U.S.A.* **2020**, *117*, 73-79.
- (343) Baek, M.; Kim, J.; Jin, J.; Choi, J. W. Photochemically Driven Solid Electrolyte Interphase for Extremely Fast-Charging Lithium-Ion Batteries. *Nat. Commun.* **2021**, *12*, 6807.
- (344) Shiraishi, S.; Kanamura, K.; Takehara, Z. I. Surface Condition Changes in Lithium Metal Deposited in Nonaqueous Electrolyte Containing HF by Dissolution-Deposition Cycles. *J. Electrochem. Soc.* **2019**, *146*, 1633-1639.
- (345) Xia, J.; Petibon, R.; Xiao, A.; Lamanna, W. M.; Dahn, J. R. Some Fluorinated Carbonates as Electrolyte Additives for Li(Ni_{0.4}Mn_{0.4}Co_{0.2})O₂/Graphite Pouch Cells. *J. Electrochem. Soc.* **2016**, *163*, A1637-A1645.
- (346) Wang, J.; Liu, W.; Luo, G.; Li, Z.; Zhao, C.; Zhang, H.; Zhu, M.; Xu, Q.; Wang, X.; Zhao, C.; et al. Synergistic Effect of Well-Defined Dual Sites Boosting the Oxygen Reduction Reaction. *Energy Environ. Sci.* **2018**, *11*, 3375-3379.
- (347) Chang, W.; Park, J. H.; Steingart, D. A. Poor Man's Atomic Layer Deposition of LiF for Additive-Free Growth of Lithium Columns. *Nano Lett.* **2018**, *18*, 7066-7074.
- (348) Fan, L.; Zhuang, H. L.; Gao, L.; Lu, Y.; Archer, L. A. Regulating Li Deposition at Artificial Solid Electrolyte Interphases. *J. Mater. Chem. A* **2017**, *5*, 3483-3492.
- (349) Xie, J.; Liao, L.; Gong, Y.; Li, Y.; Shi, F.; Pei, A.; Sun, J.; Zhang, R.; Kong, B.; Subbaraman, R.; et al. Stitching H-BN by Atomic Layer Deposition of LiF as a Stable Interface for Lithium Metal Anode. *Sci. Adv.* **2017**, *3*, eaao3170.

- (350) He, M.; Li, Y.; Guo, R.; Gallant, B. M. Electrochemical Conversion of Nitrogen Trifluoride as a Gas-to-Solid Cathode in Li Batteries. *J. Phys. Chem. Lett.* **2018**, *9*, 4700-4706.
- (351) Ma, C.; Xu, F.; Song, T. Dual-Layered Interfacial Evolution of Lithium Metal Anode: SEI Analysis via TOF-SIMS Technology. *ACS Appl. Mater. Interfaces* **2022**, *14*, 20197-20207.
- (352) Zhang, Z.; Li, Y.; Xu, R.; Zhou, W.; Li, Y.; Oyakhire, S. T.; Wu, Y.; Xu, J.; Wang, H.; Yu, Z.; et al. Capturing the Swelling of Solid-Electrolyte Interphase in Lithium Metal Batteries. *Science* **2022**, *375*, 66-70.
- (353) Wu, J.; Wang, X.; Liu, Q.; Wang, S.; Zhou, D.; Kang, F.; Shanmukaraj, D.; Armand, M.; Rojo, T.; Li, B.; et al. A Synergistic Exploitation to Produce High-Voltage Quasi-Solid-State Lithium Metal Batteries. *Nat. Commun.* **2021**, *12*, 5746.
- (354) Zheng, J.; Zheng, H.; Wang, R.; Ben, L.; Lu, W.; Chen, L.; Chen, L.; Li, H. 3D Visualization of Inhomogeneous Multi-Layered Structure and Young's Modulus of the Solid Electrolyte Interphase (SEI) on Silicon Anodes for Lithium-Ion Batteries. *Phys. Chem. Chem. Phys.* **2014**, *16*, 13229-13238.
- (355) Jaumaux, P.; Wu, J.; Shanmukaraj, D.; Wang, Y.; Zhou, D.; Sun, B.; Kang, F.; Li, B.; Armand, M.; Wang, G. Non-Flammable Liquid and Quasi-Solid Electrolytes toward Highly-Safe Alkali Metal-Based Batteries. *Adv. Funct. Mater.* **2020**, *31*, 2008644.
- (356) Yildirim, H.; Kinaci, A.; Chan, M. K.; Greeley, J. P. First-Principles Analysis of Defect Thermodynamics and Ion Transport in Inorganic SEI Compounds: LiF and NaF. *ACS Appl. Mater. Interfaces* **2015**, *7*, 18985-18996.
- (357) Thomas, M.; Bruce, P.; Goodenough, J. Lithium Mobility in the Layered Oxide $\text{Li}_{1-x}\text{CoO}_2$. *Solid State Ion.* **1985**, *17*, 13-19.
- (358) Cherkashinin, G.; Nikolowski, K.; Ehrenberg, H.; Jacke, S.; Dimesso, L.; Jaegermann, W. The Stability of the SEI Layer, Surface Composition and the Oxidation State of Transition Metals at the Electrolyte-Cathode Interface Impacted by the Electrochemical Cycling: X-ray Photoelectron Spectroscopy Investigation. *Phys. Chem. Chem. Phys.* **2012**, *14*, 12321-12331.
- (359) Krueger, S.; Kloepsch, R.; Li, J.; Nowak, S.; Passerini, S.; Winter, M. How Do Reactions at the Anode/Electrolyte Interface Determine the Cathode Performance in Lithium-Ion Batteries? *J. Electrochem. Soc.* **2013**, *160*, A542-A548.
- (360) Dedryvère, R.; Foix, D.; Franger, S.; Patoux, S.; Daniel, L.; Gonbeau, D. Electrode/Electrolyte Interface Reactivity in High-Voltage Spinel $\text{LiMn}_{1.6}\text{Ni}_{0.4}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ Lithium-Ion Battery. *J. Phys. Chem. C* **2010**, *114*, 10999-11008.
- (361) Li, S. R.; Chen, C. H.; Xia, X.; Dahn, J. R. The Impact of Electrolyte Oxidation Products in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ Cells. *J. Electrochem. Soc.* **2013**, *160*, A1524-A1528.
- (362) Aurbach, D.; Markovsky, B.; Salitra, G.; Markevich, E.; Talyossef, Y.; Koltypin, M.; Nazar, L.; Ellis, B.; Kovacheva, D. Review on Electrode–Electrolyte Solution Interactions, Related to Cathode Materials for Li-Ion Batteries. *J. Power Sources* **2007**, *165*, 491-499.
- (363) Komaba, S.; Kumagai, N.; Kataoka, Y. Influence of Manganese(II), Cobalt(II), and Nickel(II) Additives in Electrolyte on Performance of Graphite Anode for Lithium-Ion Batteries. *Electrochim. Acta* **2002**, *47*, 1229-1239.
- (364) Xiong, D. J.; Petibon, R.; Nie, M.; Ma, L.; Xia, J.; Dahn, J. R. Interactions between Positive and Negative Electrodes in Li-Ion Cells Operated at High Temperature and High Voltage. *J. Electrochem. Soc.* **2016**, *163*, A546-A551.
- (365) Jung, Y. S.; Lu, P.; Cavanagh, A. S.; Ban, C.; Kim, G.-H.; Lee, S.-H.; George, S. M.; Harris, S. J.; Dillon, A. C. Unexpected Improved Performance of ALD Coated LiCoO_2 /Graphite Li-Ion Batteries. *Adv. Energy Mater.* **2013**, *3*, 213-219.
- (366) Xu, K. Electrolytes and Interphases in Li-Ion Batteries and Beyond. *Chem. Rev.* **2014**, *114*, 11503-11618.
- (367) Gauthier, M.; Carney, T. J.; Grimaud, A.; Giordano, L.; Pour, N.; Chang, H. H.; Fenning, D. P.; Lux, S. F.; Paschos, O.; Bauer, C.; et al. Electrode-Electrolyte Interface in Li-Ion Batteries: Current Understanding and New Insights. *J. Phys. Chem. Lett.* **2015**, *6*, 4653-4672.
- (368) Aurbach, D.; Markovsky, B.; Rodkin, A.; Levi, E.; Cohen, Y. S.; Kim, H. J.; Schmidt, M. On the Capacity Fading of LiCoO_2 Intercalation Electrodes. *Electrochim. Acta* **2002**, *47*, 4291-4306.
- (369) Minato, T.; Kawaura, H.; Hirayama, M.; Taminato, S.; Suzuki, K.; Yamada, N. L.; Sugaya, H.; Yamamoto, K.; Nakanishi, K.; Orikasa, Y.; et al. Dynamic Behavior at the Interface between Lithium Cobalt Oxide and an Organic Electrolyte Monitored by Neutron Reflectivity Measurements. *J. Phys. Chem. C* **2016**, *120*, 20082-20088.
- (370) Liu, B.; Zhou, H.; Yin, C.; Guan, H.; Li, J. Enhanced Electrochemical Performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode by Application of LiPF_2O_2 for Lithium Difluoro(oxalate)borate Electrolyte. *Electrochim. Acta* **2019**, *321*, 134690.

- (371) Meng, Y.; Chen, G.; Shi, L.; Liu, H.; Zhang, D. Operando Fourier Transform Infrared Investigation of Cathode Electrolyte Interphase Dynamic Reversible Evolution on $\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2$. *ACS Appl. Mater. Interfaces* **2019**, *11*, 45108-45117.
- (372) Wang, F.; Lin, Y.; Suo, L.; Fan, X.; Gao, T.; Yang, C.; Han, F.; Qi, Y.; Xu, K.; Wang, C. Stabilizing High Voltage LiCoO_2 Cathode in Aqueous Electrolyte with Interphase-Forming Additive. *Energy Environ. Sci.* **2016**, *9*, 3666-3673.
- (373) Song, Y.-M.; Han, J.-G.; Park, S.; Lee, K. T.; Choi, N.-S. A Multifunctional Phosphite-Containing Electrolyte for 5 V-Class $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathodes with Superior Electrochemical Performance. *J. Mater. Chem. A* **2014**, *2*, 9506-9513.
- (374) Zhang, H.; Eshetu, G. G.; Judez, X.; Li, C.; Rodriguez-Martinez, L. M.; Armand, M. Electrolyte Additives for Lithium Metal Anodes and Rechargeable Lithium Metal Batteries: Progress and Perspectives. *Angew. Chem. Int. Ed.* **2018**, *57*, 15002-15027.
- (375) Fan, X.; Chen, L.; Borodin, O.; Ji, X.; Chen, J.; Hou, S.; Deng, T.; Zheng, J.; Yang, C.; Liou, S. C.; et al. Non-flammable Electrolyte Enables Li-Metal Batteries with Aggressive Cathode Chemistries. *Nat. Nanotechnol.* **2018**, *13*, 715-722.
- (376) Cao, X.; Ren, X.; Zou, L.; Engelhard, M. H.; Huang, W.; Wang, H.; Matthews, B. E.; Lee, H.; Niu, C.; Arey, B. W.; et al. Monolithic Solid-Electrolyte Interphases Formed in Fluorinated Orthoformate-Based Electrolytes Minimize Li Depletion and Pulverization. *Nat. Energy* **2019**, *4*, 796-805.
- (377) Zhang, Z.; Yang, J.; Huang, W.; Wang, H.; Zhou, W.; Li, Y.; Li, Y.; Xu, J.; Huang, W.; Chiu, W.; et al. Cathode-Electrolyte Interphase in Lithium Batteries Revealed by Cryogenic Electron Microscopy. *Matter* **2021**, *4*, 302-312.
- (378) Zou, L.; Liu, Z.; Zhao, W.; Jia, H.; Zheng, J.; Yang, Y.; Wang, G.; Zhang, J.-G.; Wang, C. Solid-Liquid Interfacial Reaction Triggered Propagation of Phase Transition from Surface into Bulk Lattice of Ni-Rich Layered Cathode. *Chem. Mater.* **2018**, *30*, 7016-7026.
- (379) Wang, C.; Meng, Y. S.; Xu, K. Perspective—Fluorinating Interphases. *J. Electrochem. Soc.* **2018**, *166*, A5184-A5186.
- (380) Macneil, D. D.; Dahn, J. R. The Reactions of $\text{Li}_{0.5}\text{CoO}_2$ with Nonaqueous Solvents at Elevated Temperatures. *J. Electrochem. Soc.* **2002**, *149*, A912.
- (381) Baba, Y. Thermal Stability of Li_xCoO_2 Cathode for Lithium Ion Battery. *Solid State Ion.* **2002**, *148*, 311-316.
- (382) Gallus, D. R.; Wagner, R.; Wiemers-Meyer, S.; Winter, M.; Cekic-Laskovic, I. New Insights into the Structure-Property Relationship of High-Voltage Electrolyte Components for Lithium-Ion Batteries Using the pKa Value. *Electrochim. Acta* **2015**, *184*, 410-416.
- (383) Wang, F.-M.; Pradanawati, S. A.; Yeh, N.-H.; Chang, S.-C.; Yang, Y.-T.; Huang, S.-H.; Lin, P.-L.; Lee, J.-F.; Sheu, H.-S.; Lu, M.-L.; et al. Robust Benzimidazole-Based Electrolyte Overcomes High-Voltage and High-Temperature Applications in 5 V Class Lithium Ion Batteries. *Chem. Mater.* **2017**, *29*, 5537-5549.
- (384) He, M.; Su, C. C.; Peebles, C.; Feng, Z.; Connell, J. G.; Liao, C.; Wang, Y.; Shkrob, I. A.; Zhang, Z. Mechanistic Insight in the Function of Phosphite Additives for Protection of $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ Cathode in High Voltage Li-Ion Cells. *ACS Appl. Mater. Interfaces* **2016**, *8*, 11450-11458.
- (385) Mun, J.; Lee, J.; Hwang, T.; Lee, J.; Noh, H.; Choi, W. Lithium Difluoro(oxalate)borate for Robust Passivation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ in Lithium-Ion Batteries. *J. Electroanal. Chem.* **2015**, *745*, 8-13.
- (386) Wang, X. T.; Gu, Z. Y.; Li, W. H.; Zhao, X. X.; Guo, J. Z.; Du, K. D.; Luo, X. X.; Wu, X. L. Regulation of Cathode-Electrolyte Interphase via Electrolyte Additives in Lithium Ion Batteries. *Chem. Asian J.* **2020**, *15*, 2803-2814.
- (387) Wölke, C.; Diddens, D.; Heidrich, B.; Winter, M.; Cekic-Laskovic, I. Understanding the Effectiveness of Phospholane Electrolyte Additives in Lithium-Ion Batteries under High-Voltage Conditions. *ChemElectroChem* **2021**, *8*, 972-982.
- (388) Xu, N.; Shi, J.; Liu, G.; Yang, X.; Zheng, J.; Zhang, Z.; Yang, Y. Research Progress of Fluorine-Containing Electrolyte Additives for Lithium Ion Batteries. *J. Power Sources Adv.* **2021**, *7*, 100043.
- (389) Adenusi, H.; Chass, G. A.; Passerini, S.; Tian, K. V.; Chen, G. Lithium Batteries and the Solid Electrolyte Interphase (SEI)—Progress and Outlook. *Adv. Energy Mater.* **2023**, *13*, 2203307.
- (390) Lang, J.; Long, Y.; Qu, J.; Luo, X.; Wei, H.; Huang, K.; Zhang, H.; Qi, L.; Zhang, Q.; Li, Z.; et al. One-Pot Solution Coating of High Quality LiF Layer to Stabilize Li Metal Anode. *Energy Storage Mater.* **2019**, *16*, 85-90.
- (391) Stoebe, T. G. Influence of OH^- Ions on Infrared Absorption and Ionic Conductivity in Lithium Fluoride Crystals. *J. Phys. Chem. Solids* **1967**, *28*, 1375-1382.

- (392) Yuan, Y.; Wu, F.; Bai, Y.; Li, Y.; Chen, G.; Wang, Z.; Wu, C. Regulating Li Deposition by Constructing LiF-Rich Host for Dendrite-Free Lithium Metal Anode. *Energy Storage Mater.* **2019**, *16*, 411-418.
- (393) Hou, J.; Yang, M.; Wang, D.; Zhang, J. Fundamentals and Challenges of Lithium Ion Batteries at Temperatures between -40 and 60 °C. *Adv. Energy Mater.* **2020**, *10*, 1904152.
- (394) Smart, M. C.; Lucht, B. L.; Dalavi, S.; Krause, F. C.; Ratnakumar, B. V. The Effect of Additives upon the Performance of MCMB/LiNi_xCo_{1-x}O₂ Li-Ion Cells Containing Methyl Butyrate-Based Wide Operating Temperature Range Electrolytes. *J. Electrochem. Soc.* **2012**, *159*, A739-A751.
- (395) Song, G.; Yi, Z.; Su, F.; Xie, L.; Wang, Z.; Wei, X.-X.; Xu, G.; Chen, C.-M. Boosting the Low-Temperature Performance for Li-Ion Batteries in LiPF₆-Based Local High-Concentration Electrolyte. *ACS Energy Lett.* **2023**, *8*, 1336-1343.
- (396) Li, Q.; Liu, G.; Cheng, H.; Sun, Q.; Zhang, J.; Ming, J. Low-Temperature Electrolyte Design for Lithium-Ion Batteries: Prospect and Challenges. *Chemistry* **2021**, *27*, 15842-15865.
- (397) Yang, B.; Zhang, H.; Yu, L.; Fan, W.; Huang, D. Lithium Difluorophosphate as an Additive to Improve the Low Temperature Performance of LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂/graphite Cells. *Electrochim. Acta* **2016**, *221*, 107-114.
- (398) Shi, J.; Ehteshami, N.; Ma, J.; Zhang, H.; Liu, H.; Zhang, X.; Li, J.; Paillard, E. Improving the Graphite/Electrolyte Interface in Lithium-Ion Battery for Fast Charging and Low Temperature Operation: Fluorosulfonyl Isocyanate as Electrolyte Additive. *J. Power Sources* **2019**, *429*, 67-74.
- (399) Smith, K. A.; Smart, M. C.; Prakash, G. K. S.; Ratnakumar, B. V. Electrolytes Containing Fluorinated Ester Co-Solvents for Low-Temperature Li-Ion Cells. *ECS Trans.* **2008**, *11*, 91-98.
- (400) Liu, J.; Yuan, B.; He, N.; Dong, L.; Chen, D.; Zhong, S.; Ji, Y.; Han, J.; Yang, C.; Liu, Y.; et al. Reconstruction of LiF-Rich Interphases through an Anti-freezing Electrolyte for Ultralow-Temperature LiCoO₂ Batteries. *Energy Environ. Sci.* **2023**, *16*, 1024-1034.
- (401) Lu, W.; Xie, K.; Chen, Z.; Xiong, S.; Pan, Y.; Zheng, C. A New Co-Solvent for Wide Temperature Lithium-Ion Battery Electrolytes: 2,2,2-Trifluoroethyl n-Caproate. *J. Power Sources* **2015**, *274*, 676-684.
- (402) Ozhaves, Y.; Gunceler, D.; Arias, T. Stability and Surface Diffusion at Lithium-Electrolyte Interphases with Connections to Dendrite Suppression. *arXiv* **2015**, 1504.05799.
- (403) Yang, T.; Li, S.; Wang, W.; Lu, J.; Fan, W.; Zuo, X.; Nan, J. Nonflammable Functional Electrolytes with All-Fluorinated Solvents Matching Rechargeable High-Voltage Li-Metal Batteries with Ni-Rich Ternary Cathode. *J. Power Sources* **2021**, *505*, 230055.
- (404) Liao, L.; Cheng, X.; Ma, Y.; Zuo, P.; Fang, W.; Yin, G.; Gao, Y. Fluoroethylene Carbonate as Electrolyte Additive to Improve Low Temperature Performance of LiFePO₄ Electrode. *Electrochim. Acta* **2013**, *87*, 466-472.
- (405) Dong, X.; Lin, Y.; Li, P.; Ma, Y.; Huang, J.; Bin, D.; Wang, Y.; Qi, Y.; Xia, Y. High-Energy Rechargeable Metallic Lithium Battery at -70 Degrees C Enabled by a Cosolvent Electrolyte. *Angew. Chem. Int. Ed.* **2019**, *58*, 5623-5627.
- (406) Peng, Z.; Cao, X.; Gao, P.; Jia, H.; Ren, X.; Roy, S.; Li, Z.; Zhu, Y.; Xie, W.; Liu, D.; et al. High-Power Lithium Metal Batteries Enabled by High-Concentration Acetonitrile-Based Electrolytes with Vinylene Carbonate Additive. *Adv. Funct. Mater.* **2020**, *30*, 2001285.
- (407) Jiang, L. L.; Yan, C.; Yao, Y. X.; Cai, W.; Huang, J. Q.; Zhang, Q. Inhibiting Solvent Co-Intercalation in a Graphite Anode by a Localized High-Concentration Electrolyte in Fast-Charging Batteries. *Angew. Chem. Int. Ed.* **2021**, *60*, 3402-3406.
- (408) Yang, Y.; Wang, H.; Zhu, C.; Ma, J. Armor-like Inorganic-rich Cathode Electrolyte Interphase Enabled by the Pentafluorophenylboronic Acid Additive for High-voltage Li||NCM622 Batteries. *Angew. Chem. Int. Ed.* **2023**, *62*, e202300057.
- (409) Sun, Z.; Li, F.; Ding, J.; Lin, Z.; Xu, M.; Zhu, M.; Liu, J. High-Voltage and High-Temperature LiCoO₂ Operation via the Electrolyte Additive of Electron-Defect Boron Compounds. *ACS Energy Lett.* **2023**, *8*, 2478-2487.
- (410) Liu, Q.; Jiang, W.; Xu, J.; Xu, Y.; Yang, Z.; Yoo, D. J.; Pupek, K. Z.; Wang, C.; Liu, C.; Xu, K.; et al. A Fluorinated Cation Introduces New Interphasial Chemistries to Enable High-Voltage Lithium Metal Batteries. *Nat. Commun.* **2023**, *14*, 3678.
- (411) Sun, C.; Ji, X.; Weng, S.; Li, R.; Huang, X.; Zhu, C.; Xiao, X.; Deng, T.; Fan, L.; Chen, L.; et al. 50C Fast-Charge Li-Ion Batteries using a Graphite Anode. *Adv. Mater.* **2022**, *34*, e2206020.
- (412) Shin, H.; Park, J.; Sastry, A. M.; Lu, W. Effects of Fluoroethylene Carbonate (FEC) on Anode and Cathode Interfaces at Elevated Temperatures. *J. Electrochem. Soc.* **2015**, *162*, A1683-A1692.
- (413) Hu, L.; Zhang, Z.; Amine, K. Fluorinated Electrolytes for Li-Ion Battery: An FEC-Based Electrolyte for High Voltage LiNi_{0.5}Mn_{1.5}O₄/Graphite Couple. *Electrochem. commun.* **2013**, *35*, 76-79.

- (414) Ehteshami, N.; Ibing, L.; Stolz, L.; Winter, M.; Paillard, E. Ethylene Carbonate-Free Electrolytes for Li-Ion Battery: Study of the Solid Electrolyte Interphases Formed on Graphite Anodes. *J. Power Sources* **2020**, *451*, 227804.
- (415) Shen, C.; Hu, G.; Cheong, L. Z.; Huang, S.; Zhang, J. G.; Wang, D. Direct Observation of the Growth of Lithium Dendrites on Graphite Anodes by Operando EC-AFM. *Small Methods* **2017**, *2*, 1700298.
- (416) Hwang, J.-Y.; Park, S.-J.; Yoon, C. S.; Sun, Y.-K. Customizing a Li-Metal Battery That Survives Practical Operating Conditions for Electric Vehicle Applications. *Energy Environ. Sci.* **2019**, *12*, 2174-2184.
- (417) Markevich, E.; Salitra, G.; Chesneau, F.; Schmidt, M.; Aurbach, D. Very Stable Lithium Metal Stripping–Plating at a High Rate and High Areal Capacity in Fluoroethylene Carbonate-Based Organic Electrolyte Solution. *ACS Energy Lett.* **2017**, *2*, 1321-1326.
- (418) Guo, J. C.; Tan, S. J.; Zhang, C. H.; Wang, W. P.; Zhao, Y.; Wang, F.; Zhang, X. S.; Wen, R.; Zhang, Y.; Fan, M.; et al. A Self-Reconfigured, Dual-Layered Artificial Interphase Toward High-Current-Density Quasi-Solid-State Lithium Metal Batteries. *Adv. Mater.* **2023**, *35*, e2300350.
- (419) Park, S.-J.; Hwang, J.-Y.; Sun, Y.-K. Trimethylsilyl Azide (C₃H₉N₃Si): A Highly Efficient Additive for Tailoring Fluoroethylene Carbonate (FEC) Based Electrolytes for Li-Metal Batteries. *J. Mater. Chem. A* **2019**, *7*, 13441-13448.
- (420) Wang, X.; Zhang, M.; Alvarado, J.; Wang, S.; Sina, M.; Lu, B.; Bouwer, J.; Xu, W.; Xiao, J.; Zhang, J. G.; et al. New Insights on the Structure of Electrochemically Deposited Lithium Metal and Its Solid Electrolyte Interphases via Cryogenic TEM. *Nano Lett.* **2017**, *17*, 7606-7612.
- (421) Guo, L.; Huang, F.; Cai, M.; Zhang, J.; Ma, G.; Xu, S. Organic-Inorganic Hybrid SEI Induced by a New Lithium Salt for High-Performance Metallic Lithium Anodes. *ACS Appl. Mater. Interfaces* **2021**, *13*, 32886-32893.
- (422) Guo, Z.; Yang, H.; Wei, Q.; Xu, S.; Hu, G.; Bai, S.; Li, F. Dual-Additives Enable Stable Electrode-Electrolyte Interfaces for Long-Life Li-SPAN Batteries. *Chin. Chem. Lett.* **2023**, <https://doi.org/10.1016/j.cclet.2023.108622>.
- (423) Yang, H.-W.; Kang, W. S.; Kim, S.-J. A Significant Enhancement of Cycling Stability at Fast Charging Rate through Incorporation of Li₃N into LiF-Based SEI in SiO Anode for Li-Ion Batteries. *Electrochim. Acta* **2022**, *412*, 140107.
- (424) Su, H.; Chen, Z.; Li, M.; Bai, P.; Li, Y.; Ji, X.; Liu, Z.; Sun, J.; Ding, J.; Yang, M.; et al. Achieving Practical High-Energy-Density Lithium-Metal Batteries by a Dual-Anion Regulated Electrolyte. *Adv. Mater.* **2023**, *35*, e2301171.
- (425) Dong, L.; Liu, Y.; Wen, K.; Chen, D.; Rao, D.; Liu, J.; Yuan, B.; Dong, Y.; Wu, Z.; Liang, Y.; et al. High-Polarity Fluoroalkyl Ether Electrolyte Enables Solvation-Free Li⁺ Transfer for High-Rate Lithium Metal Batteries. *Adv. Sci.* **2022**, *9*, e2104699.
- (426) Yue, X.; Zhang, J.; Dong, Y.; Chen, Y.; Shi, Z.; Xu, X.; Li, X.; Liang, Z. Reversible Li Plating on Graphite Anodes through Electrolyte Engineering for Fast-Charging Batteries. *Angew. Chem. Int. Ed.* **2023**, *62*, e202302285.
- (427) Rodrigues, M.-T. F.; Babu, G.; Gullapalli, H.; Kalaga, K.; Sayed, F. N.; Kato, K.; Joyner, J.; Ajayan, P. M. A Materials Perspective on Li-Ion Batteries at Extreme Temperatures. *Nat. Energy* **2017**, *2*, 1-14.
- (428) Liu, Y.; Zhu, Y.; Cui, Y. Challenges and Opportunities towards Fast-Charging Battery Materials. *Nat. Energy* **2019**, *4*, 540-550.
- (429) Fan, X.; Ji, X.; Chen, L.; Chen, J.; Deng, T.; Han, F.; Yue, J.; Piao, N.; Wang, R.; Zhou, X.; et al. All-Temperature Batteries Enabled by Fluorinated Electrolytes with Non-polar Solvents. *Nat. Energy* **2019**, *4*, 882-890.
- (430) Liu, W.; Liu, P.; Mitlin, D. Review of Emerging Concepts in SEI Analysis and Artificial SEI Membranes for Lithium, Sodium, and Potassium Metal Battery Anodes. *Adv. Energy Mater.* **2020**, *10*, 2002297.
- (431) Dey, A. N. Lithium Anode Film and Organic and Inorganic Electrolyte Batteries. *Thin Solid Films* **1977**, *43*, 131-171.
- (432) Nazri, G.; Muller, R. H. Composition of Surface Layers on Li Electrodes in PC, LiClO₄ of Very Low Water Content. *J. Electrochem. Soc.* **2019**, *132*, 2050-2054.
- (433) Zaban, A.; Aurbach, D. Impedance Spectroscopy of Lithium and Nickel Electrodes in Propylene Carbonate Solutions of Different Lithium Salts a Comparative Study. *J. Power Sources* **1995**, *54*, 289-295.
- (434) Kanamura, K.; Tamura, H.; Shiraishi, S.; Takehara, Z. I. XPS Analysis of Lithium Surfaces Following Immersion in Various Solvents Containing LiBF₄. *J. Electrochem. Soc.* **2019**, *142*, 340-347.
- (435) Peled, E.; Golodnitsky, D.; Ardel, G. Advanced Model for Solid Electrolyte Interphase Electrodes in Liquid and Polymer Electrolytes. *J. Electrochem. Soc.* **2019**, *144*, L208-L210.
- (436) Ein-Eli, Y. A New Perspective on the Formation and Structure of the Solid Electrolyte Interface at the Graphite Anode of Li-Ion Cells. *Electrochem. Solid-State Lett.* **1999**, *2*, 212.

- (437) Wu, J.; Ihsan-Ul-Haq, M.; Chen, Y.; Kim, J.-K. Understanding Solid Electrolyte Interphases: Advanced Characterization Techniques and Theoretical Simulations. *Nano Energy* **2021**, *89*, 106489.
- (438) Kominato, A.; Yasukawa, E.; Sato, N.; Ijuuin, T.; Asahina, H.; Mori, S. Analysis of Surface Films on Lithium in Various Organic Electrolytes. *J. Power Sources* **1997**, *68*, 471-475.
- (439) Dollé, M. L.; Sannier, L.; Beaudoin, B.; Trentin, M.; Tarascon, J.-M. Live Scanning Electron Microscope Observations of Dendritic Growth in Lithium/Polymer Cells. *Electrochem. Solid-State Lett.* **2002**, *5*, A286-A289.
- (440) Sacci, R. L.; Dudney, N. J.; More, K. L.; Parent, L. R.; Arslan, I.; Browning, N. D.; Unocic, R. R. Direct Visualization of Initial SEI Morphology and Growth Kinetics During Lithium Deposition by In Situ Electrochemical Transmission Electron Microscopy. *Chem. Commun.* **2014**, *50*, 2104-2107.
- (441) Sacci, R. L.; Black, J. M.; Balke, N.; Dudney, N. J.; More, K. L.; Unocic, R. R. Nanoscale Imaging of Fundamental Li Battery Chemistry: Solid-Electrolyte Interphase Formation and Preferential Growth of Lithium Metal Nanoclusters. *Nano Lett.* **2015**, *15*, 2011-2018.
- (442) Lee, S.-B.; Pyun, S.-I. The Effect of Electrolyte Temperature on the Passivity of Solid Electrolyte Interphase Formed on a Graphite Electrode. *Carbon* **2002**, *40*, 2333-2339.
- (443) Li, Y.; Huang, W.; Li, Y.; Chiu, W.; Cui, Y. Opportunities for Cryogenic Electron Microscopy in Materials Science and Nanoscience. *ACS Nano* **2020**, *14*, 9263-9276.
- (444) Liu, Q. C.; Xu, J. J.; Yuan, S.; Chang, Z. W.; Xu, D.; Yin, Y. B.; Li, L.; Zhong, H. X.; Jiang, Y. S.; Yan, J. M.; et al. Artificial Protection Film on Lithium Metal Anode toward Long-Cycle-Life Lithium-Oxygen Batteries. *Adv. Mater.* **2015**, *27*, 5241-5247.
- (445) Li, Y.; Huang, W.; Li, Y.; Pei, A.; Boyle, D. T.; Cui, Y. Correlating Structure and Function of Battery Interphases at Atomic Resolution Using Cryoelectron Microscopy. *Joule* **2018**, *2*, 2167-2177.
- (446) Huang, W.; Boyle, D. T.; Li, Y.; Li, Y.; Pei, A.; Chen, H.; Cui, Y. Nanostructural and Electrochemical Evolution of the Solid-Electrolyte Interphase on CuO Nanowires Revealed by Cryogenic-Electron Microscopy and Impedance Spectroscopy. *ACS Nano* **2019**, *13*, 737-744.
- (447) Sheng, O.; Zheng, J.; Ju, Z.; Jin, C.; Wang, Y.; Chen, M.; Nai, J.; Liu, T.; Zhang, W.; Liu, Y.; et al. In Situ Construction of a LiF-Enriched Interface for Stable All-Solid-State Batteries and its Origin Revealed by Cryo-TEM. *Adv. Mater.* **2020**, *32*, e2000223.
- (448) Li, Y.; Zhou, W.; Li, Y.; Huang, W.; Zhang, Z.; Chen, G.; Wang, H.; Wu, G. H.; Rolston, N.; Vila, R.; et al. Unravelling Atomic Structure and Degradation Mechanisms of Organic-Inorganic Halide Perovskites by Cryo-EM. *Joule* **2019**, *3*, 2854-2866.
- (449) Huang, W.; Wang, J.; Braun, M. R.; Zhang, Z.; Li, Y.; Boyle, D. T.; McIntyre, P. C.; Cui, Y. Dynamic Structure and Chemistry of the Silicon Solid-Electrolyte Interphase Visualized by Cryogenic Electron Microscopy. *Matter* **2019**, *1*, 1232-1245.
- (450) Sayavong, P.; Zhang, W.; Oyakhire, S. T.; Boyle, D. T.; Chen, Y.; Kim, S. C.; Vila, R. A.; Holmes, S. E.; Kim, M. S.; Bent, S. F.; et al. Dissolution of the Solid Electrolyte Interphase and Its Effects on Lithium Metal Anode Cyclability. *J. Am. Chem. Soc.* **2023**, *145*, 12342-12350.
- (451) Benninghoven, A. Surface Investigation of Solids by the Statical Method of Secondary Ion Mass Spectroscopy (SIMS). *Surf. Sci.* **1973**, *35*, 427-457.
- (452) Otto, S. K.; Riegger, L. M.; Fuchs, T.; Kayser, S.; Schweitzer, P.; Burkhardt, S.; Henss, A.; Janek, J. In Situ Investigation of Lithium Metal–Solid Electrolyte Anode Interfaces with ToF-SIMS. *Adv. Mater. Interfaces* **2022**, *9*, 2102387.
- (453) Peled, E.; Bar Tow, D.; Merson, A.; Gladkikh, A.; Burstein, L.; Golodnitsky, D. Composition, Depth Profiles and Lateral Distribution of Materials in the SEI Built on HOPG-TOF SIMS and XPS Studies. *J. Power Sources* **2001**, *97-98*, 52-57.
- (454) Yamagishi, Y.; Morita, H.; Nomura, Y.; Igaki, E. Visualizing Lithiation of Graphite Composite Anodes in All-Solid-State Batteries Using Operando Time-of-Flight Secondary Ion Mass Spectrometry. *J. Phys. Chem. Lett.* **2021**, *12*, 4623-4627.
- (455) Pereira-Nabais, C.; Swiatowska, J.; Rosso, M.; Ozanam, F.; Seyeux, A.; Gohier, A.; Tran-Van, P.; Cassir, M.; Marcus, P. Effect of Lithiation Potential and Cycling on Chemical and Morphological Evolution of Si Thin Film Electrode Studied by ToF-SIMS. *ACS Appl. Mater. Interfaces* **2014**, *6*, 13023-13033.
- (456) Otto, S.-K.; Moryson, Y.; Krauskopf, T.; Pepler, K.; Sann, J.; Janek, J.; Henss, A. In-Depth Characterization of Lithium-Metal Surfaces with XPS and ToF-SIMS: Toward Better Understanding of the Passivation Layer. *Chem. Mater.* **2021**, *33*, 859-867.

- (457) Zhu, Z.; Zhou, Y.; Yan, P.; Vemuri, R. S.; Xu, W.; Zhao, R.; Wang, X.; Thevuthasan, S.; Baer, D. R.; Wang, C. M. In Situ Mass Spectrometric Determination of Molecular Structural Evolution at the Solid Electrolyte Interphase in Lithium-Ion Batteries. *Nano Lett.* **2015**, *15*, 6170-6176.
- (458) Papp, C.; Steinrück, H.-P. In Situ High-Resolution X-ray Photoelectron Spectroscopy – Fundamental Insights in Surface Reactions. *Surf. Sci. Rep.* **2013**, *68*, 446-487.
- (459) Maibach, J.; Kallquist, I.; Andersson, M.; Urpelainen, S.; Edstrom, K.; Rensmo, H.; Siegbahn, H.; Hahlin, M. Probing a Battery Electrolyte Drop with Ambient Pressure Photoelectron Spectroscopy. *Nat. Commun.* **2019**, *10*, 3080.
- (460) Xu, C.; Sun, B.; Gustafsson, T.; Edström, K.; Brandell, D.; Hahlin, M. Interface Layer Formation in Solid Polymer Electrolyte Lithium Batteries: An XPS Study. *J. Mater. Chem. A* **2014**, *2*, 7256-7264.
- (461) Oyakhire, S. T.; Gong, H.; Cui, Y.; Bao, Z.; Bent, S. F. An X-ray Photoelectron Spectroscopy Primer for Solid Electrolyte Interphase Characterization in Lithium Metal Anodes. *ACS Energy Lett.* **2022**, *7*, 2540-2546.
- (462) Zhang, J.; Wang, R.; Yang, X.; Lu, W.; Wu, X.; Wang, X.; Li, H.; Chen, L. Direct Observation of Inhomogeneous Solid Electrolyte Interphase on MnO Anode with Atomic Force Microscopy and Spectroscopy. *Nano Lett.* **2012**, *12*, 2153-2157.
- (463) Shen, C.; Wang, S.; Jin, Y.; Han, W. Q. In Situ AFM Imaging of Solid Electrolyte Interfaces on HOPG with Ethylene Carbonate and Fluoroethylene Carbonate-Based Electrolytes. *ACS Appl. Mater. Interfaces* **2015**, *7*, 25441-25447.
- (464) Shi, Y.; Yan, H. J.; Wen, R.; Wan, L. J. Direct Visualization of Nucleation and Growth Processes of Solid Electrolyte Interphase Film Using in Situ Atomic Force Microscopy. *ACS Appl. Mater. Interfaces* **2017**, *9*, 22063-22067.
- (465) Liu, R. R.; Deng, X.; Liu, X. R.; Yan, H. J.; Cao, A. M.; Wang, D. Facet-Dependent SEI Formation on the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathode Identified by In Situ Single Particle Atomic Force Microscopy. *Chem. Commun.* **2014**, *50*, 15756-15759.
- (466) Anderson, M. S. Locally Enhanced Raman Spectroscopy with an Atomic Force Microscope. *Appl. Phys. Lett.* **2000**, *76*, 3130-3132.
- (467) Zhang, R.; Zhang, Y.; Dong, Z. C.; Jiang, S.; Zhang, C.; Chen, L. G.; Zhang, L.; Liao, Y.; Aizpurua, J.; Luo, Y.; et al. Chemical Mapping of a Single Molecule by Plasmon-Enhanced Raman Scattering. *Nature* **2013**, *498*, 82-86.
- (468) Hong, L.; Li, L.; Chen-Wiegar, Y. K.; Wang, J.; Xiang, K.; Gan, L.; Li, W.; Meng, F.; Wang, F.; Wang, J.; et al. Two-Dimensional Lithium Diffusion Behavior and Probable Hybrid Phase Transformation Kinetics in Olivine Lithium Iron Phosphate. *Nat. Commun.* **2017**, *8*, 1194.
- (469) Wang, J.; Karen Chen-Wiegar, Y. C.; Eng, C.; Shen, Q.; Wang, J. Visualization of Anisotropic-Isotropic Phase Transformation Dynamics in Battery Electrode Particles. *Nat. Commun.* **2016**, *7*, 12372.
- (470) Takamatsu, D.; Nakatsutsumi, T.; Mori, S.; Orikasa, Y.; Mogi, M.; Yamashige, H.; Sato, K.; Fujimoto, T.; Takanashi, Y.; Murayama, H.; et al. Nanoscale Observation of the Electronic and Local Structures of LiCoO_2 Thin Film Electrode by Depth-Resolved X-ray Absorption Spectroscopy. *J. Phys. Chem. Lett.* **2011**, *2*, 2511-2514.
- (471) Jarry, A.; Gottis, S.; Yu, Y. S.; Roque-Rosell, J.; Kim, C.; Cabana, J.; Kerr, J.; Kostecki, R. The Formation Mechanism of Fluorescent Metal Complexes at the $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ /Carbonate Ester Electrolyte Interface. *J. Am. Chem. Soc.* **2015**, *137*, 3533-3539.
- (472) Bleith, P.; Van Beek, W.; Kaiser, H.; Novák, P.; Villevieille, C. Simultaneous in Situ X-ray Absorption Spectroscopy and X-ray Diffraction Studies on Battery Materials: The Case of $\text{Fe}_{0.5}\text{TiOPO}_4$. *J. Phys. Chem. C* **2015**, *119*, 3466-3471.
- (473) Liu, D.; Shadike, Z.; Lin, R.; Qian, K.; Li, H.; Li, K.; Wang, S.; Yu, Q.; Liu, M.; Ganapathy, S.; et al. Review of Recent Development of In Situ/Operando Characterization Techniques for Lithium Battery Research. *Adv. Mater.* **2019**, *31*, e1806620.
- (474) Rus, E. D.; Dura, J. A. In Situ Neutron Reflectometry Study of Solid Electrolyte Interface (SEI) Formation on Tungsten Thin-Film Electrodes. *ACS Appl. Mater. Interfaces* **2019**, *11*, 47553-47563.
- (475) Rus, E. D.; Dura, J. A. In Situ Neutron Reflectometry Study of a Tungsten Oxide/Li-Ion Battery Electrolyte Interface. *ACS Appl. Mater. Interfaces* **2023**, *15*, 2832-2842.
- (476) Huang, Z.; Ren, J.; Zhang, W.; Xie, M.; Li, Y.; Sun, D.; Shen, Y.; Huang, Y. Protecting the Li-Metal Anode in a Li- O_2 Battery by using Boric Acid as an SEI-Forming Additive. *Adv. Mater.* **2018**, *30*, e1803270.
- (477) Fan, L.; Ma, R.; Zhang, Q.; Jia, X.; Lu, B. Graphite Anode for a Potassium-Ion Battery with Unprecedented Performance. *Angew. Chem. Int. Ed.* **2019**, *58*, 10500-10505.

- (478) Sun, Y.; Ren, Y. In Situ Synchrotron X-Ray Techniques for Real-Time Probing of Colloidal Nanoparticle Synthesis. *Part. Part Syst. Charact.* **2013**, *30*, 399-419.
- (479) Yu, C.; Ganapathy, S.; Eck, E.; Wang, H.; Basak, S.; Li, Z.; Wagemaker, M. Accessing the Bottleneck in All-Solid State Batteries, Lithium-Ion Transport over the Solid-Electrolyte-Electrode Interface. *Nat. Commun.* **2017**, *8*, 1086.
- (480) Langdon, J.; Manthiram, A. Crossover Effects in Batteries with High-Nickel Cathodes and Lithium-Metal Anodes. *Adv. Funct. Mater.* **2021**, *31*, 2010267.
- (481) Zhu, Y.; Hilty, C.; Savukov, I. Dynamic Nuclear Polarization Enhanced Nuclear Spin Optical Rotation. *Angew. Chem. Int. Ed.* **2021**, *60*, 8823-8826.
- (482) Gunnarsdóttir, A. B.; Vema, S.; Menkin, S.; Marbella, L. E.; Grey, C. P. Investigating the Effect of a Fluoroethylene Carbonate Additive on Lithium Deposition and the Solid Electrolyte Interphase in Lithium Metal Batteries Using In Situ NMR Spectroscopy. *J. Mater. Chem. A* **2020**, *8*, 14975-14992.
- (483) Kolesov, D. V.; Gorelkin, P. V.; Prelovskaya, A. O.; Erofeev, A. S. Scanning Electrochemical Microscopy for the Study of Energy Accumulators: Principles, Equipment, and Application. *Mosc. Univ. Phys. Bull.* **2023**, *77*, 801-810.
- (484) Ventosa, E.; Schuhmann, W. Scanning Electrochemical Microscopy of Li-Ion Batteries. *Phys. Chem. Chem. Phys.* **2015**, *17*, 28441-28450.
- (485) Zoski, C. G. Review—Advances in Scanning Electrochemical Microscopy (SECM). *J. Electrochem. Soc.* **2015**, *163*, H3088-H3100.
- (486) Bulter, H.; Peters, F.; Schwenzel, J.; Wittstock, G. Spatiotemporal Changes of the Solid Electrolyte Interphase in Lithium-Ion Batteries Detected by Scanning Electrochemical Microscopy. *Angew. Chem. Int. Ed.* **2014**, *53*, 10531-10535.
- (487) Shan, X.; Zhong, Y.; Zhang, L.; Zhang, Y.; Xia, X.; Wang, X.; Tu, J. A Brief Review on Solid Electrolyte Interphase Composition Characterization Technology for Lithium Metal Batteries: Challenges and Perspectives. *J. Phys. Chem. C* **2021**, *125*, 19060-19080.
- (488) Verma, P.; Maire, P.; Novák, P. A Review of the Features and Analyses of the Solid Electrolyte Interphase in Li-Ion Batteries. *Electrochim. Acta* **2010**, *55*, 6332-6341.
- (489) Wang, A.; Kadam, S.; Li, H.; Shi, S.; Qi, Y. Review on Modeling of the Anode Solid Electrolyte Interphase (SEI) for Lithium-Ion Batteries. *Npj Comput. Mater.* **2018**, *4*, 15.
- (490) Chen, J.; Li, Q.; Pollard, T. P.; Fan, X.; Borodin, O.; Wang, C. Electrolyte design for Li metal-free Li batteries. *Mater. Today* **2020**, *39*, 118-126.
- (491) Yao, N.; Chen, X.; Fu, Z. H.; Zhang, Q. Applying Classical, Ab Initio, and Machine-Learning Molecular Dynamics Simulations to the Liquid Electrolyte for Rechargeable Batteries. *Chem. Rev.* **2022**, *122*, 10970-11021.
- (492) Li, Y.; Li, Y.; Pei, A.; Yan, K.; Sun, Y.; Wu, C. L.; Joubert, L. M.; Chin, R.; Koh, A. L.; Yu, Y.; et al. Atomic Structure of Sensitive Battery Materials and Interfaces Revealed by Cryo-Electron Microscopy. *Science* **2017**, *358*, 506-510.
- (493) Huang, W.; Attia, P. M.; Wang, H.; Renfrew, S. E.; Jin, N.; Das, S.; Zhang, Z.; Boyle, D. T.; Li, Y.; Bazant, M. Z.; et al. Evolution of the Solid-Electrolyte Interphase on Carbonaceous Anodes Visualized by Atomic-Resolution Cryogenic Electron Microscopy. *Nano Lett.* **2019**, *19*, 5140-5148.
- (494) Tu, Z.; Zachman, M. J.; Choudhury, S.; Khan, K. A.; Zhao, Q.; Kourkoutis, L. F.; Archer, L. A. Stabilizing Protic and Aprotic Liquid Electrolytes at High-Bandgap Oxide Interphases. *Chem. Mater.* **2018**, *30*, 5655-5662.
- (495) Xiaobing, L.; Holland, J.; Burgess, S.; Bhadare, S.; Yamaguchi, S.; Birtwistle, D.; Statham, P.; Rowlands, N. Detection of Lithium X-rays by EDS. *Microsc. Microanal.* **2013**, *19*, 1136-1137.
- (496) Hubaud, A. A.; Yang, Z.; Schroeder, D. J.; Dogan, F.; Trahey, L.; Vaughey, J. T. Interfacial Study of the Role of SiO₂ on Si Anodes Using Electrochemical Quartz Crystal Microbalance. *J. Power Sources* **2015**, *282*, 639-644.
- (497) Dargel, V.; Shpigel, N.; Sigalov, S.; Nayak, P.; Levi, M. D.; Daikhin, L.; Aurbach, D. In Situ Real-Time Gravimetric and Viscoelastic Probing of Surface Films Formation on Lithium Batteries Electrodes. *Nat. Commun.* **2017**, *8*, 1389.
- (498) Levi, M. D.; Shpigel, N.; Sigalov, S.; Dargel, V.; Daikhin, L.; Aurbach, D. In Situ Porous Structure Characterization of Electrodes for Energy Storage and Conversion by EQCM-D: a Review. *Electrochim. Acta* **2017**, *232*, 271-284.
- (499) Munoz, R. a. A.; Toma, S. H.; Toma, H. E.; Araki, K.; Angnes, L. Investigation of Interfacial Processes at Tetra-ruthenated Zinc Porphyrin Films Using Electrochemical Surface Plasmon Resonance and Electrochemical Quartz Crystal Microbalance. *Electrochim. Acta* **2009**, *54*, 2971-2976.

- (500) Levi, M. D.; Levy, N.; Sigalov, S.; Salitra, G.; Aurbach, D.; Maier, J. Electrochemical Quartz Crystal Microbalance (EQCM) Studies of Ions and Solvents Insertion into Highly Porous Activated Carbons. *J. Am. Chem. Soc.* **2010**, *132*, 13220-13222.
- (501) Griffin, J. M.; Forse, A. C.; Tsai, W. Y.; Taberna, P. L.; Simon, P.; Grey, C. P. In Situ NMR and Electrochemical Quartz Crystal Microbalance Techniques Reveal the Structure of the Electrical Double Layer in Supercapacitors. *Nat. Mater.* **2015**, *14*, 812-819.
- (502) Song, X.; Liu, T.; Amine, J.; Duan, Y.; Zheng, J.; Lin, Y.; Pan, F. In-Situ Mass-Electrochemical Study of Surface Redox Potential and Interfacial Chemical Reactions of Li(Na)FePO₄ Nanocrystals for Li(Na)-Ion Batteries. *Nano Energy* **2017**, *37*, 90-97.
- (503) Shpigel, N.; Levi, M. D.; Sigalov, S.; Girshevitz, O.; Aurbach, D.; Daikhin, L.; Pikma, P.; Marandi, M.; Janes, A.; Lust, E.; et al. In Situ Hydrodynamic Spectroscopy for Structure Characterization of Porous Energy Storage Electrodes. *Nat. Mater.* **2016**, *15*, 570-575.
- (504) Fang, C.; Li, J.; Zhang, M.; Zhang, Y.; Yang, F.; Lee, J. Z.; Lee, M. H.; Alvarado, J.; Schroeder, M. A.; Yang, Y.; et al. Quantifying Inactive Lithium in Lithium Metal Batteries. *Nature* **2019**, *572*, 511-515.
- (505) Kasahara, S.; Ogose, T.; Ikemiya, N.; Yamamoto, T.; Natsui, K.; Yokota, Y.; Wong, R. A.; Iizuka, S.; Hoshi, N.; Tateyama, Y.; et al. In Situ Spectroscopic Study on the Surface Hydroxylation of Diamond Electrodes. *Anal. Chem.* **2019**, *91*, 4980-4986.
- (506) Sherwood, P. M. A. Photoelectron Spectroscopic Studies of Electrode and Related Surfaces. *Chem. Soc. Rev.* **1985**, *14*, 1.
- (507) Bagus, P. S.; Ilton, E. S.; Nelin, C. J. The Interpretation of XPS Spectra: Insights into Materials Properties. *Surf. Sci. Rep.* **2013**, *68*, 273-304.
- (508) Wang, J. G.; Zhang, Y.; Yu, X.; Hua, X.; Wang, F.; Long, Y. T.; Zhu, Z. Direct Molecular Evidence of Proton Transfer and Mass Dynamics at the Electrode-Electrolyte Interface. *J. Phys. Chem. Lett.* **2019**, *10*, 251-258.
- (509) Zhou, Y.; Su, M.; Yu, X.; Zhang, Y.; Wang, J. G.; Ren, X.; Cao, R.; Xu, W.; Baer, D. R.; Du, Y.; et al. Real-Time Mass Spectrometric Characterization of the Solid-Electrolyte Interphase of a Lithium-Ion Battery. *Nat. Nanotechnol.* **2020**, *15*, 224-230.
- (510) Zhang, Y.; Wang, J.-G.; Yu, X.; Baer, D. R.; Zhao, Y.; Mao, L.; Wang, F.; Zhu, Z. Potential-Dynamic Surface Chemistry Controls the Electrocatalytic Processes of Ethanol Oxidation on Gold Surfaces. *ACS Energy Lett.* **2018**, *4*, 215-221.
- (511) Liu, X.; Wang, D.; Wan, L. Progress of Electrode/Electrolyte Interfacial Investigation of Li-Ion Batteries via In Situ Scanning Probe Microscopy. *Sci. Bull.* **2015**, *60*, 839-849.
- (512) Kumar, R.; Tokranov, A.; Sheldon, B. W.; Xiao, X.; Huang, Z.; Li, C.; Mueller, T. In Situ and Operando Investigations of Failure Mechanisms of the Solid Electrolyte Interphase on Silicon Electrodes. *ACS Energy Lett.* **2016**, *1*, 689-697.
- (513) Nanda, J.; Yang, G.; Hou, T.; Voylov, D. N.; Li, X.; Ruther, R. E.; Naguib, M.; Persson, K.; Veith, G. M.; Sokolov, A. P. Unraveling the Nanoscale Heterogeneity of Solid Electrolyte Interphase Using Tip-Enhanced Raman Spectroscopy. *Joule* **2019**, *3*, 2001-2019.
- (514) Stöckle, R. M.; Suh, Y. D.; Deckert, V.; Zenobi, R. Nanoscale Chemical Analysis by Tip-Enhanced Raman Spectroscopy. *Chem. Phys. Lett.* **2000**, *318*, 131-136.
- (515) Hayazawa, N.; Inouye, Y.; Sekkat, Z.; Kawata, S. Metallized Tip Amplification of Near-Field Raman Scattering. *Opt. Commun.* **2000**, *183*, 333-336.
- (516) Steinhauer, M.; Stich, M.; Kurniawan, M.; Seidlhofer, B. K.; Trapp, M.; Bund, A.; Wagner, N.; Friedrich, K. A. In Situ Studies of Solid Electrolyte Interphase (SEI) Formation on Crystalline Carbon Surfaces by Neutron Reflectometry and Atomic Force Microscopy. *ACS Appl. Mater. Interfaces* **2017**, *9*, 35794-35801.
- (517) Akai, T.; Ota, H.; Namita, H.; Yamaguchi, S.; Nomura, M. XANES Study on Solid Electrolyte Interface of Li Ion Battery. *Phys. Scr.* **2005**, *2005*, 408.
- (518) Ota, H.; Akai, T.; Namita, H.; Yamaguchi, S.; Nomura, M. XAFS and TOF-SIMS Analysis of SEI Layers on Electrodes. *J. Power Sources* **2003**, *119-121*, 567-571.
- (519) Ruther, R. E.; Zhou, H.; Dhital, C.; Saravanan, K.; Kercher, A. K.; Chen, G.; Huq, A.; Delnick, F. M.; Nanda, J. Synthesis, Structure, and Electrochemical Performance of High Capacity Li₂Cu_{0.5}Ni_{0.5}O₂ Cathodes. *Chem. Mater.* **2015**, *27*, 6746-6754.
- (520) Schellenberger, M.; Golnak, R.; Quevedo Garzon, W. G.; Risse, S.; Seidel, R. Accessing the Solid Electrolyte Interphase on Silicon Anodes for Lithium-Ion Batteries In-Situ through Transmission Soft X-ray Absorption Spectroscopy. *Mater. Today Adv.* **2022**, *14*, 100215.

- (521) Wei, C.; Bard, A. J. Scanning Electrochemical Microscopy: XXIX . In Situ Monitoring of Thickness Changes of Thin Films on Electrodes. *J. Electrochem. Soc.* **2019**, *142*, 2523-2527.
- (522) Aurbach, D.; Ein-Ely, Y.; Zaban, A. The Surface Chemistry of Lithium Electrodes in Alkyl Carbonate Solutions. *J. Electrochem. Soc.* **2019**, *141*, L1-L3.
- (523) Geschwind, G. Anion Reduced Ionic Conductivity in LiF. *J. Phys. Chem. Solids* **1969**, *30*, 1631-1635.
- (524) Pan, J.; Cheng, Y.-T.; Qi, Y. General Method to Predict Voltage-Dependent Ionic Conduction in a Solid Electrolyte Coating on Electrodes. *Phys. Rev. B* **2015**, *91*, 134116.
- (525) Zachman, M. J.; Tu, Z.; Archer, L. A.; Kourkoutis, L. F. Nanoscale Elemental Mapping of Intact Solid–Liquid Interfaces and Reactive Materials in Energy Devices Enabled by Cryo-FIB/SEM. *ACS Energy Lett.* **2020**, *5*, 1224-1232.
- (526) Zachman, M. J.; Tu, Z.; Choudhury, S.; Archer, L. A.; Kourkoutis, L. F. Cryo-STEM Mapping of Solid–Liquid Interfaces and Dendrites in Lithium-Metal Batteries. *Nature* **2018**, *560*, 345-349.
- (527) Zhang, X.; Su, Q.; Du, G.; Xu, B.; Wang, S.; Chen, Z.; Wang, L.; Huang, W.; Pang, H. Stabilizing Solid-state Lithium Metal Batteries through In Situ Generated Janus-heterarchical LiF-rich SEI in Ionic Liquid Confined 3D MOF/Polymer Membranes. *Angew. Chem. Int. Ed.* **2023**, *62*, e202304947.
- (528) Han, B.; Zou, Y.; Xu, G.; Hu, S.; Kang, Y.; Qian, Y.; Wu, J.; Ma, X.; Yao, J.; Li, T.; et al. Additive Stabilization of SEI on Graphite Observed Using Cryo-Electron Microscopy. *Energy Environ. Sci.* **2021**, *14*, 4882-4889.
- (529) Lu, X.; Cheng, Y.; Li, M.; Zou, Y.; Zhen, C.; Wu, D.; Wei, X.; Li, X.; Yang, X.; Gu, M. A Stable Polymer-based Solid-State Lithium Metal Battery and its Interfacial Characteristics Revealed by Cryogenic Transmission Electron Microscopy. *Adv. Funct. Mater.* **2023**, *33*, 2212847.
- (530) Jabbari, V.; Yurkiv, V.; Rasul, M. G.; Phakatkar, A. H.; Mashayek, F.; Shahbazian-Yassar, R. In Situ Formation of Stable Solid Electrolyte Interphase with High Ionic Conductivity for Long Lifespan All-Solid-State Lithium Metal Batteries. *Energy Storage Mater.* **2023**, *57*, 1-13.
- (531) Han, B.; Zhang, Z.; Zou, Y.; Xu, K.; Xu, G.; Wang, H.; Meng, H.; Deng, Y.; Li, J.; Gu, M. Poor Stability of Li_2CO_3 in the Solid Electrolyte Interphase of a Lithium-Metal Anode Revealed by Cryo-Electron Microscopy. *Adv. Mater.* **2021**, *33*, e2100404.
- (532) Sheng, O.; Jin, C.; Chen, M.; Ju, Z.; Liu, Y.; Wang, Y.; Nai, J.; Liu, T.; Zhang, W.; Tao, X. Platinum Nano-Interlayer Enhanced Interface for Stable All-Solid-State Batteries Observed via Cryo-Transmission Electron Microscopy. *J. Mater. Chem. A* **2020**, *8*, 13541-13547.
- (533) Liu, T.; Zheng, J.; Hu, H.; Sheng, O.; Ju, Z.; Lu, G.; Liu, Y.; Nai, J.; Wang, Y.; Zhang, W.; et al. In-Situ Construction of a Mg-Modified Interface to Guide Uniform Lithium Deposition for Stable All-Solid-State Batteries. *J. Energy Chem.* **2021**, *55*, 272-278.
- (534) Alvarado, J.; Schroeder, M. A.; Pollard, T. P.; Wang, X.; Lee, J. Z.; Zhang, M.; Wynn, T.; Ding, M.; Borodin, O.; Meng, Y. S.; et al. Bisalt Ether Electrolytes: A Pathway towards Lithium Metal Batteries with Ni-Rich Cathodes. *Energy Environ. Sci.* **2019**, *12*, 780-794.
- (535) Li, Y.; Wang, K.; Zhou, W.; Li, Y.; Vila, R.; Huang, W.; Wang, H.; Chen, G.; Wu, G. H.; Tsao, Y.; et al. Cryo-EM Structures of Atomic Surfaces and Host-Guest Chemistry in Metal-Organic Frameworks. *Matter* **2019**, *1*, 428-438.
- (536) Wang, J.; Huang, W.; Pei, A.; Li, Y.; Shi, F.; Yu, X.; Cui, Y. Improving Cyclability of Li Metal Batteries at Elevated Temperatures and Its Origin Revealed by Cryo-Electron Microscopy. *Nat. Energy* **2019**, *4*, 664-670.
- (537) Huang, W.; Wang, H.; Boyle, D. T.; Li, Y.; Cui, Y. Resolving Nanoscopic and Mesoscopic Heterogeneity of Fluorinated Species in Battery Solid-Electrolyte Interphases by Cryogenic Electron Microscopy. *ACS Energy Lett.* **2020**, *5*, 1128-1135.
- (538) Liu, T.; Lin, L.; Bi, X.; Tian, L.; Yang, K.; Liu, J.; Li, M.; Chen, Z.; Lu, J.; Amine, K.; et al. In Situ Quantification of Interphasial Chemistry in Li-Ion Battery. *Nat. Nanotechnol.* **2019**, *14*, 50-56.
- (539) Voinova, M. V.; Rodahl, M.; Jonson, M.; Kasemo, B. Viscoelastic Acoustic Response of Layered Polymer Films at Fluid-Solid Interfaces: Continuum Mechanics Approach. *Phys. Scr.* **1999**, *59*, 391-396.
- (540) Broussely, M.; Biensan, P.; Bonhomme, F.; Blanchard, P.; Herreyre, S.; Nechev, K.; Staniewicz, R. J. Main Aging Mechanisms in Li Ion Batteries. *J. Power Sources* **2005**, *146*, 90-96.
- (541) Heiskanen, S. K.; Kim, J.; Lucht, B. L. Generation and Evolution of the Solid Electrolyte Interphase of Lithium-Ion Batteries. *Joule* **2019**, *3*, 2322-2333.
- (542) Tan, J.; Matz, J.; Dong, P.; Shen, J.; Ye, M. A Growing Appreciation for the Role of LiF in the Solid Electrolyte Interphase. *Adv. Energy Mater.* **2021**, *11*, 2100046.

- (543) Kitz, P. G.; Lacey, M. J.; Novak, P.; Berg, E. J. Operando EQCM-D with Simultaneous in Situ EIS: New Insights into Interphase Formation in Li Ion Batteries. *Anal. Chem.* **2019**, *91*, 2296-2303.
- (544) Edström, K.; Herstedt, M.; Abraham, D. P. A New Look at the Solid Electrolyte Interphase on Graphite Anodes in Li-Ion Batteries. *J. Power Sources* **2006**, *153*, 380-384.
- (545) Malmgren, S.; Ciosek, K.; Hahlin, M.; Gustafsson, T.; Gorgoi, M.; Rensmo, H.; Edström, K. Comparing Anode and Cathode Electrode/Electrolyte Interface Composition and Morphology Using Soft and Hard X-ray Photoelectron Spectroscopy. *Electrochim. Acta* **2013**, *97*, 23-32.
- (546) Aurbach, D.; Markovsky, B.; Levi, M. D.; Levi, E.; Schechter, A.; Moshkovich, M.; Cohen, Y. New Insights into the Interactions between Electrode Materials and Electrolyte Solutions for Advanced Nonaqueous Batteries. *J. Power Sources* **1999**, *81-82*, 95-111.
- (547) Laruelle, S.; Pilard, S.; Guenot, P.; Grugeon, S.; Tarascon, J. M. Identification of Li-Based Electrolyte Degradation Products Through DEI and ESI High-Resolution Mass Spectrometry. *J. Electrochem. Soc.* **2004**, *151*, A1202.
- (548) Zhang, Z.; Smith, K.; Jervis, R.; Shearing, P. R.; Miller, T. S.; Brett, D. J. L. Operando Electrochemical Atomic Force Microscopy of Solid-Electrolyte Interphase Formation on Graphite Anodes: The Evolution of SEI Morphology and Mechanical Properties. *ACS Appl. Mater. Interfaces* **2020**, *12*, 35132-35141.
- (549) Campana, F. P.; Buqa, H.; Novák, P.; Kötz, R.; Siegenthaler, H. In Situ Atomic Force Microscopy Study of Exfoliation Phenomena on Graphite Basal Planes. *Electrochem. commun.* **2008**, *10*, 1590-1593.
- (550) Jerliu, B.; Dorner, L.; Huger, E.; Borchardt, G.; Steitz, R.; Geckle, U.; Oberst, V.; Bruns, M.; Schneider, O.; Schmidt, H. Neutron Reflectometry Studies on the Lithiation of Amorphous Silicon Electrodes in Lithium-Ion Batteries. *Phys. Chem. Chem. Phys.* **2013**, *15*, 7777-7784.
- (551) Schulz, N.; Hausbrand, R.; Wittich, C.; Dimesso, L.; Jaegermann, W. XPS-Surface Analysis of SEI Layers on Li-Ion Cathodes: Part II. SEI-Composition and Formation inside Composite Electrodes. *J. Electrochem. Soc.* **2018**, *165*, A833-A846.
- (552) Zhang, H.; Wang, D.; Shen, C. In-Situ EC-AFM and Ex-Situ XPS Characterization to Investigate the Mechanism of SEI Formation in Highly Concentrated Aqueous Electrolyte for Li-Ion Batteries. *Appl. Surf. Sci.* **2020**, *507*, 145059.
- (553) Li, J.-T.; Światowska, J.; Maurice, V.; Seyeux, A.; Huang, L.; Sun, S.-G.; Marcus, P. XPS and ToF-SIMS Study of Electrode Processes on Sn-Ni Alloy Anodes for Li-Ion Batteries. *J. Phys. Chem. C* **2011**, *115*, 7012-7018.
- (554) Leroy, S.; Blanchard, F.; Dedryvère, R.; Martinez, H.; Carré, B.; Lemordant, D.; Gonbeau, D. Surface Film Formation on a Graphite Electrode in Li-Ion Batteries: AFM and XPS Study. *Surf. Interface Anal.* **2005**, *37*, 773-781.
- (555) Li, J.-T.; Światowska, J.; Seyeux, A.; Huang, L.; Maurice, V.; Sun, S.-G.; Marcus, P. XPS and ToF-SIMS Study of Sn-Co Alloy Thin Films as Anode for Lithium Ion Battery. *J. Power Sources* **2010**, *195*, 8251-8257.
- (556) Hope, M. A.; Rinkel, B. L. D.; Gunnarsdottir, A. B.; Marker, K.; Menkin, S.; Paul, S.; Sergeyev, I. V.; Grey, C. P. Selective NMR Observation of the SEI-Metal Interface by Dynamic Nuclear Polarisation from Lithium Metal. *Nat. Commun.* **2020**, *11*, 2224.
- (557) Benninghoven, A. Die Analyse Monomolekularer Festkörperoberflächenschichten mit Hilfe der Sekundärionenemission. *Z. anorg. allg. Chem.* **1970**, *230*, 403-417.
- (558) Shotyk, W.; Metson, J. B. Secondary Ion Mass Spectrometry (SIMS) and Its Application to Chemical Weathering. *Rev. Geophys.* **1994**, *32*, 197.
- (559) Benninghoven, A.; Loebach, E. Analysis of Monomolecular Layers of Solids by the Static Method of Secondary Ion Mass Spectroscopy (SIMS). *J. Radioanal. Chem.* **1972**, *12*, 95-99.
- (560) Menkin, S.; O'keefe, C. A.; Gunnarsdottir, A. B.; Dey, S.; Pesci, F. M.; Shen, Z.; Agüero, A.; Grey, C. P. Toward an Understanding of SEI Formation and Lithium Plating on Copper in Anode-Free Batteries. *J. Phys. Chem. C* **2021**, *125*, 16719-16732.
- (561) Xu, H.; Li, Z.; Liu, T.; Han, C.; Guo, C.; Zhao, H.; Li, Q.; Lu, J.; Amine, K.; Qiu, X. Impacts of Dissolved Ni²⁺ on the Solid Electrolyte Interphase on a Graphite Anode. *Angew. Chem. Int. Ed.* **2022**, *61*, e202202894.
- (562) Ota, H.; Sakata, Y.; Inoue, A.; Yamaguchi, S. Analysis of Vinylene Carbonate Derived SEI Layers on Graphite Anode. *J. Electrochem. Soc.* **2004**, *151*, A1659.
- (563) Zhao, D.; Wang, J.; Wang, P.; Liu, H.; Li, S. Regulating the Composition Distribution of Layered SEI Film on Li-Ion Battery Anode by LiDFBOP. *Electrochim. Acta* **2020**, *337*, 135745.

- (564) Pereira-Nabais, C.; Światowska, J.; Chagnes, A.; Ozanam, F.; Gohier, A.; Tran-Van, P.; Cojocaru, C.-S.; Cassir, M.; Marcus, P. Interphase Chemistry of Si Electrodes Used as Anodes in Li-Ion Batteries. *Appl. Surf. Sci.* **2013**, *266*, 5-16.
- (565) Bordes, A.; De Vito, E.; Haon, C.; Boulineau, A.; Montani, A.; Marcus, P. Multiscale Investigation of Silicon Anode Li Insertion Mechanisms by Time-of-Flight Secondary Ion Mass Spectrometer Imaging Performed on an In Situ Focused Ion Beam Cross Section. *Chem. Mater.* **2016**, *28*, 1566-1573.
- (566) Zhou, L.; Zuo, T.; Li, C.; Zhang, Q.; Janek, J.; Nazar, L. F. $\text{Li}_{3-x}\text{Zr}_x(\text{Ho/Lu})_{1-x}\text{Cl}_6$ Solid Electrolytes Enable Ultrahigh-Loading Solid-State Batteries with a Prelithiated Si Anode. *ACS Energy Lett.* **2023**, *8*, 3102-3111.
- (567) Kim, M.; Harvey, S. P.; Huey, Z.; Han, S.-D.; Jiang, C.-S.; Son, S.-B.; Yang, Z.; Bloom, I. A New Mechanism of Stabilizing SEI of Si Anode Driven by Crosstalk Behavior and Its Potential for Developing High Performance Si-Based Batteries. *Energy Storage Mater.* **2023**, *55*, 436-444.
- (568) Huo, H.; Chen, Y.; Li, R.; Zhao, N.; Luo, J.; Pereira Da Silva, J. G.; Mücke, R.; Kaghazchi, P.; Guo, X.; Sun, X. Design of a Mixed Conductive Garnet/Li Interface for Dendrite-Free Solid Lithium Metal Batteries. *Energy Environ. Sci.* **2020**, *13*, 127-134.
- (569) Paul-Orecchio, A. G.; Weeks, J. A.; Dolocan, A.; Mullins, C. B. High-Stability Lithium Metal Batteries Enabled by a Tetrahydrofuran-Based Electrolyte Mixture. *ACS Appl. Energy Mater.* **2022**, *5*, 9437-9446.
- (570) Fang, R.; Xu, B.; Grundish, N. S.; Xia, Y.; Li, Y.; Lu, C.; Liu, Y.; Wu, N.; Goodenough, J. B. Li_2S_6 -Integrated PEO-Based Polymer Electrolytes for All-Solid-State Lithium-Metal Batteries. *Angew. Chem. Int. Ed.* **2021**, *60*, 17701-17706.
- (571) Sun, H.-H.; Dolocan, A.; Weeks, J. A.; Rodriguez, R.; Heller, A.; Mullins, C. B. In Situ Formation of a Multicomponent Inorganic-Rich SEI Layer Provides a Fast Charging and High Specific Energy Li-Metal Battery. *J. Mater. Chem. A* **2019**, *7*, 17782-17789.
- (572) Tu, H.; Li, L.; Wang, Z.; Wang, J.; Lin, H.; Wang, M.; Yan, C.; Liu, M. Tailoring Electrolyte Solvation for LiF-Rich Solid Electrolyte Interphase toward a Stable Li Anode. *ACS Nano* **2022**, *16*, 16898-16908.
- (573) Jin, Y.; Kneusels, N. H.; Magusin, P.; Kim, G.; Castillo-Martinez, E.; Marbella, L. E.; Kerber, R. N.; Howe, D. J.; Paul, S.; Liu, T.; et al. Identifying the Structural Basis for the Increased Stability of the Solid Electrolyte Interphase Formed on Silicon with the Additive Fluoroethylene Carbonate. *J. Am. Chem. Soc.* **2017**, *139*, 14992-15004.
- (574) Shadike, Z.; Lee, H.; Borodin, O.; Cao, X.; Fan, X.; Wang, X.; Lin, R.; Bak, S. M.; Ghose, S.; Xu, K.; et al. Identification of LiH and Nanocrystalline LiF in the Solid-Electrolyte Interphase of Lithium Metal Anodes. *Nat. Nanotechnol.* **2021**, *16*, 549-554.
- (575) V Cresce, A.; Russell, S. M.; Baker, D. R.; Gaskell, K. J.; Xu, K. In Situ and Quantitative Characterization of Solid Electrolyte Interphases. *Nano Lett.* **2014**, *14*, 1405-1412.
- (576) Liu, X. R.; Wang, L.; Wan, L. J.; Wang, D. In Situ Observation of Electrolyte-Concentration-Dependent Solid Electrolyte Interphase on Graphite in Dimethyl Sulfoxide. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9573-9580.
- (577) Wang, X.; Huang, S. C.; Huang, T. X.; Su, H. S.; Zhong, J. H.; Zeng, Z. C.; Li, M. H.; Ren, B. Tip-Enhanced Raman Spectroscopy for Surfaces and Interfaces. *Chem. Soc. Rev.* **2017**, *46*, 4020-4041.
- (578) Veith, G. M.; Browning, K. L.; Doucet, M.; Browning, J. F. Solid Electrolyte Interphase Architecture Determined through In Situ Neutron Scattering. *J. Electrochem. Soc.* **2021**, *168*, 060523.
- (579) Veith, G. M.; Doucet, M.; Sacci, R. L.; Vacaliuc, B.; Baldwin, J. K.; Browning, J. F. Determination of the Solid Electrolyte Interphase Structure Grown on a Silicon Electrode Using a Fluoroethylene Carbonate Additive. *Sci. Rep.* **2017**, *7*, 6326.
- (580) Veith, G. M.; Doucet, M.; Baldwin, J. K.; Sacci, R. L.; Fears, T. M.; Wang, Y.; Browning, J. F. Direct Determination of Solid-Electrolyte Interphase Thickness and Composition as a Function of State of Charge on a Silicon Anode. *J. Phys. Chem. C* **2015**, *119*, 20339-20349.
- (581) Fears, T. M.; Doucet, M.; Browning, J. F.; Baldwin, J. K.; Winiarz, J. G.; Kaiser, H.; Taub, H.; Sacci, R. L.; Veith, G. M. Evaluating the Solid Electrolyte Interphase Formed on Silicon Electrodes: A Comparison of Ex Situ X-ray Photoelectron Spectroscopy and In Situ Neutron Reflectometry. *Phys. Chem. Chem. Phys.* **2016**, *18*, 13927-13940.
- (582) Takamatsu, D.; Orikasa, Y.; Mori, S.; Nakatsutsumi, T.; Yamamoto, K.; Koyama, Y.; Minato, T.; Hirano, T.; Tanida, H.; Arai, H.; et al. Effect of an Electrolyte Additive of Vinylene Carbonate on the Electronic Structure at the Surface of a Lithium Cobalt Oxide Electrode under Battery Operating Conditions. *J. Phys. Chem. C* **2015**, *119*, 9791-9797.

- (583) Khalid, S.; Caliebe, W.; Siddons, P.; So, I.; Clay, B.; Lenhard, T.; Hanson, J.; Wang, Q.; Frenkel, A. I.; Marinkovic, N.; et al. Quick Extended X-ray Absorption Fine Structure Instrument with Millisecond Time Scale, Optimized for In Situ Applications. *Rev. Sci. Instrum.* **2010**, *81*, 015105.
- (584) Stotzel, J.; Lutzenkirchen-Hecht, D.; Fonda, E.; De Oliveira, N.; Briois, V.; Frahm, R. Novel Angular Encoder for a Quick-Extended X-ray Absorption Fine Structure Monochromator. *Rev. Sci. Instrum.* **2008**, *79*, 083107.
- (585) Ventosa, E.; Wilde, P.; Zinn, A. H.; Trautmann, M.; Ludwig, A.; Schuhmann, W. Understanding Surface Reactivity of Si Electrodes in Li-ion Batteries by In Operando Scanning Electrochemical Microscopy. *Chem. Commun.* **2016**, *52*, 6825-6828.
- (586) Takahashi, T.; Iwahara, H.; Ishikawa, T. Ionic Conductivity of Doped Cerium Trifluoride. *J. Electrochem. Soc.* **2019**, *124*, 280-284.
- (587) Rongeat, C.; Anji Reddy, M.; Diemant, T.; Behm, R. J.; Fichtner, M. Development of New Anode Composite Materials for Fluoride Ion Batteries. *J. Mater. Chem. A* **2014**, *2*, 20861-20872.
- (588) Grenier, A.; Porras-Gutierrez, A. G.; Body, M.; Legein, C.; Chrétien, F.; Raymundo-Piñero, E.; Dollé, M.; Groult, H.; Dambournet, D. Solid Fluoride Electrolytes and Their Composite with Carbon: Issues and Challenges for Rechargeable Solid State Fluoride-Ion Batteries. *J. Phys. Chem. C* **2017**, *121*, 24962-24970.
- (589) Li, X.; Tang, Y.; Zhu, J.; Lv, H.; Xu, Y.; Wang, W.; Zhi, C.; Li, H. Initiating a Room-Temperature Rechargeable Aqueous Fluoride-Ion Battery with Long Lifespan through a Rational Buffering Phase Design. *Adv. Energy Mater.* **2021**, *11*, 2003714.
- (590) Zhang, D.; Yamamoto, K.; Wang, Y.; Gao, S.; Uchiyama, T.; Watanabe, T.; Takami, T.; Matsunaga, T.; Nakanishi, K.; Miki, H.; et al. Reversible and Fast (De)fluorination of High-Capacity Cu_2O Cathode: One Step Toward Practically Applicable All-Solid-State Fluoride-Ion Battery. *Adv. Energy Mater.* **2021**, *11*, 2102285.
- (591) Hou, X.; Zhang, Z.; Shen, K.; Cheng, S.; He, Q.; Shi, Y.; Yu, D. Y. W.; Su, C.-Y.; Li, L.-J.; Chen, F. An Aqueous Rechargeable Fluoride Ion Battery with Dual Fluoride Electrodes. *J. Electrochem. Soc.* **2019**, *166*, A2419-A2424.
- (592) Zhang, S.; Wang, T.; Zhang, J.; Miao, Y.; Yin, Q.; Wu, Z.; Wu, Y.; Yuan, Q.; Han, J. A Zero-Strain Insertion Cathode Material for Room-Temperature Fluoride-Ion Batteries. *ACS Appl. Mater. Interfaces* **2022**, *14*, 24518-24525.
- (593) Clemens, O.; Rongeat, C.; Reddy, M. A.; Giehr, A.; Fichtner, M.; Hahn, H. Electrochemical Fluorination of Perovskite Type $\text{BaFeO}_{2.5}$. *Dalton Trans.* **2014**, *43*, 15771-15778.
- (594) Andrews, J. L.; McClure, E. T.; Jew, K. K.; Preefer, M. B.; Irshad, A.; Lertola, M. J.; Robertson, D. D.; Salamat, C. Z.; Brady, M. J.; Piper, L. F. J.; et al. Room-Temperature Electrochemical Fluoride (De)insertion into CsMnFeF_6 . *ACS Energy Lett.* **2022**, *7*, 2340-2348.
- (595) Nowroozi, M. A.; Ivlev, S.; Rohrer, J.; Clemens, O. La_2CoO_4 : A New Intercalation Based Cathode Material for Fluoride Ion Batteries with Improved Cycling Stability. *J. Mater. Chem. A* **2018**, *6*, 4658-4669.
- (596) Nowroozi, M. A.; Wissel, K.; Donzelli, M.; Hosseinpourkavaz, N.; Plana-Ruiz, S.; Kolb, U.; Schoch, R.; Bauer, M.; Malik, A. M.; Rohrer, J.; et al. High Cycle Life All-Solid-State Fluoride Ion Battery with $\text{La}_2\text{NiO}_{4+d}$ High Voltage Cathode. *Commun. Mater.* **2020**, *1*, 27.
- (597) Roos, A.; Vandepol, F.; Keim, R.; Schoonman, J. Ionic Conductivity in Tysonite-Type Solid Solutions $\text{La}_{1-x}\text{Ba}_x\text{F}_{3-x}$. *Solid State Ion.* **1984**, *13*, 191-203.
- (598) Dieudonne, B.; Chable, J.; Body, M.; Legein, C.; Durand, E.; Mauvy, F.; Fourcade, S.; Leblanc, M.; Maisonneuve, V.; Demourgues, A. The Key Role of the Composition and Structural Features in Fluoride Ion Conductivity in Tysonite $\text{Ce}_{1-x}\text{Sr}_x\text{F}_{3-x}$ Solid Solutions. *Dalton Trans.* **2017**, *46*, 3761-3769.
- (599) Dieudonné, B.; Chable, J.; Mauvy, F.; Fourcade, S.; Durand, E.; Lebraud, E.; Leblanc, M.; Legein, C.; Body, M.; Maisonneuve, V.; et al. Exploring the $\text{Sm}_{1-x}\text{Ca}_x\text{F}_{3-x}$ Tysonite Solid Solution as a Solid-State Electrolyte: Relationships between Structural Features and F⁻ Ionic Conductivity. *J. Phys. Chem. C* **2015**, *119*, 25170-25179.
- (600) Tran, Q. C.; Bui, V. T.; Dao, V. D.; Lee, J. K.; Choi, H. S. Ionic Liquid-Based Polymer Electrolytes via Surfactant-Assisted Polymerization at the Plasma-Liquid Interface. *ACS Appl. Mater. Interfaces* **2016**, *8*, 16125-16135.
- (601) Liu, J.; Yi, L.; Zeng, P.; Zou, C.; Chen, X.; Tao, X.; Liu, X.; Yang, L.; Zang, Z.; Chang, B.; et al. Point Defect Engineering Enabled the High Ionic Conductivity of BaSnF_4 for Solid-State Fluoride-Ion Batteries at Room Temperature. *Energy Fuels* **2022**, *36*, 15258-15267.
- (602) Wang, J.; Hao, J.; Duan, C.; Wang, X.; Wang, K.; Ma, C. A Fluoride-Ion-Conducting Solid Electrolyte with Both High Conductivity and Excellent Electrochemical Stability. *Small* **2022**, *18*, e2104508.

- (603) Yu, Y.; Lei, M.; Li, D.; Li, C. Near-Room-Temperature Quasi-Solid-State F-Ion Batteries with High Conversion Reversibility Based on Layered Structured Electrolyte. *Adv. Energy Mater.* **2023**, *13*, 2203168.
- (604) Rongeat, C.; Reddy, M. A.; Witter, R.; Fichtner, M. Nanostructured Fluorite-Type Fluorides as Electrolytes for Fluoride Ion Batteries. *J. Phys. Chem. C* **2013**, *117*, 4943-4950.
- (605) Mori, K.; Mineshige, A.; Emoto, T.; Sugiura, M.; Saito, T.; Namba, K.; Otomo, T.; Abe, T.; Fukunaga, T. Electrochemical, Thermal, and Structural Features of BaF₂-SnF₂ Fluoride-Ion Electrolytes. *J. Phys. Chem. C* **2021**, *125*, 12568-12577.
- (606) Murakami, M.; Morita, Y.; Mizuno, M. ¹⁹F/¹¹⁹Sn/²⁰⁷Pb NMR Studies on Ion Dynamics in Tetragonal PbSnF₄: Spectroscopic Evidence for Defect-Driven Conductivity. *J. Phys. Chem. C* **2017**, *121*, 2627-2634.
- (607) Murakami, M.; Morita, Y.; Yonemura, M.; Shimoda, K.; Mori, M.; Koyama, Y.; Kawaguchi, T.; Fukuda, K.; Ishikawa, Y.; Kamiyama, T.; et al. High Anionic Conductive Form of Pb_xSn_{2-x}F₄. *Chem. Mater.* **2019**, *31*, 7704-7710.
- (608) Denes, G.; Birchall, T.; Sayer, M.; Bell, M. BaSnF₄ — a New Fluoride Ionic Conductor with the α-PbSnF₄ Structure. *Solid State Ion.* **1984**, *13*, 213-219.
- (609) Liu, L.; Yang, L.; Liu, M.; Li, X.; Shao, D.; Luo, K.; Wang, X.; Luo, Z. SnF₂-Based Fluoride Ion Electrolytes MSnF₄ (M = Ba, Pb) for the Application of Room-Temperature Solid-State Fluoride Ion Batteries. *J. Alloys Compd.* **2020**, *819*, 152983.
- (610) Liu, L.; Yang, L.; Shao, D.; Luo, K.; Zou, C.; Luo, Z.; Wang, X. Nd³⁺ Doped BaSnF₄ Solid Electrolyte for Advanced Room-Temperature Solid-State Fluoride Ion Batteries. *Ceram. Int.* **2020**, *46*, 20521-20528.
- (611) Bachman, J. C.; Muy, S.; Grimaud, A.; Chang, H. H.; Pour, N.; Lux, S. F.; Paschos, O.; Maglia, F.; Lupart, S.; Lamp, P.; et al. Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction. *Chem. Rev.* **2016**, *116*, 140-162.
- (612) Mohammad, I.; Witter, R.; Fichtner, M.; Anji Reddy, M. Room-Temperature, Rechargeable Solid-State Fluoride-Ion Batteries. *ACS Appl. Energy Mater.* **2018**, *1*, 4766-4775.
- (613) Mohammad, I.; Witter, R.; Fichtner, M.; Reddy, M. A. Introducing Interlayer Electrolytes: Toward Room-Temperature High-Potential Solid-State Rechargeable Fluoride Ion Batteries. *ACS Appl. Energy Mater.* **2019**, *2*, 1553-1562.
- (614) Davis, V. K.; Munoz, S.; Kim, J.; Bates, C. M.; Momčilović, N.; Billings, K. J.; Miller, T. F.; Grubbs, R. H.; Jones, S. C. Fluoride-Ion Solvation in Non-aqueous Electrolyte Solutions. *Mater. Chem. Front.* **2019**, *3*, 2721-2727.
- (615) Kobayashi, S.; Nakamoto, H.; Yokoe, D.; Kuwabara, A.; Abe, T.; Ikuhara, Y. Nanoscale Defluorination Mechanism and Solid Electrolyte Interphase of a MgF₂ Anode in Fluoride-Shuttle Batteries. *ACS Appl. Energy Mater.* **2021**, *4*, 996-1003.
- (616) Celik Kucuk, A.; Yamanaka, T.; Yokoyama, Y.; Abe, T. Low-Cost Fluoride Source for Organic Liquid Electrolyte-Based Fluoride Shuttle Battery. *J. Electrochem. Soc.* **2021**, *168*.
- (617) Kawasaki, M.; Morigaki, K.-I.; Kano, G.; Nakamoto, H.; Takekawa, R.; Kawamura, J.; Minato, T.; Abe, T.; Ogumi, Z. Lactone-Based Liquid Electrolytes for Fluoride Shuttle Batteries. *J. Electrochem. Soc.* **2021**, *168*.
- (618) Okazaki, K.-I.; Uchimoto, Y.; Abe, T.; Ogumi, Z. Charge–Discharge Behavior of Bismuth in a Liquid Electrolyte for Rechargeable Batteries Based on a Fluoride Shuttle. *ACS Energy Lett.* **2017**, *2*, 1460-1464.
- (619) Yamamoto, T.; Matsumoto, K.; Hagiwara, R.; Nohira, T. Room-Temperature Fluoride Shuttle Batteries Based on a Fluorohydrogenate Ionic Liquid Electrolyte. *ACS Appl. Energy Mater.* **2019**, *2*, 6153-6157.
- (620) Yamamoto, T.; Matsumoto, K.; Hagiwara, R.; Nohira, T. Charge–Discharge Performance of Copper Metal Positive Electrodes in Fluorohydrogenate Ionic Liquids for Fluoride-Shuttle Batteries. *J. Electrochem. Soc.* **2021**, *168*, 040530.
- (621) Darolles, I.; Weiss, C. M.; Alam, M. M.; Tiruvannamalai, A.; Jones, S. C. Fluoride Ion Battery Compositions. *United States* **2015**, US9166249B2.
- (622) Lee, H. S.; Yang, X. Q.; Xiang, C. L.; Mcbreen, J.; Choi, L. S. The Synthesis of a New Family of Boron-Based Anion Receptors and the Study of Their Effect on Ion Pair Dissociation and Conductivity of Lithium Salts in Nonaqueous Solutions. *J. Electrochem. Soc.* **2019**, *145*, 2813-2818.
- (623) Lee, H. S.; Sun, X.; Yang, X. Q.; Mcbreen, J. Synthesis and Study of New Cyclic Boronate Additives for Lithium Battery Electrolytes. *J. Electrochem. Soc.* **2002**, *149*, A1460.
- (624) Li, L. F.; Lee, H. S.; Li, H.; Yang, X. Q.; Nam, K. W.; Yoon, W. S.; Mcbreen, J.; Huang, X. J. New Electrolytes for Lithium Ion Batteries Using LiF Salt and Boron Based Anion Receptors. *J. Power Sources* **2008**, *184*, 517-521.

- (625) Xie, B.; Lee, H. S.; Li, H.; Yang, X. Q.; Mcbreen, J.; Chen, L. Q. New Electrolytes Using Li_2O or Li_2O_2 Oxides and Tris(pentafluorophenyl) Borane as Boron-Based Anion Receptor for Lithium Batteries. *Electrochem. commun.* **2008**, *10*, 1195-1197.
- (626) Chen, Z.; Amine, K. Computational Estimates of Fluoride Affinity of Boron-Based Anion Receptors. *J. Electrochem. Soc.* **2009**, *156*, A672.
- (627) Konishi, H.; Minato, T.; Abe, T.; Ogumi, Z. Electrochemical Performance of a Lead Fluoride Electrode Mixed with Carbon in an Electrolyte Containing Triphenylboroxine as an Anion Acceptor for Fluoride Shuttle Batteries. *Mater. Chem. Phys.* **2019**, *226*, 1-5.
- (628) Konishi, H.; Minato, T.; Abe, T.; Ogumi, Z. Reversible Electrochemical Reaction of a Fluoride Shuttle Battery with a Bismuth(III) Fluoride Electrode and Electrolyte Containing Triphenylboroxine as an Anion Acceptor. *ChemistrySelect* **2020**, *5*, 6237-6241.
- (629) Konishi, H.; Minato, T.; Abe, T.; Ogumi, Z. Triphenylboroxine and Triphenylborane as Anion Acceptors for Electrolyte in Fluoride Shuttle Batteries. *Chem. Lett.* **2018**, *47*, 1346-1349.
- (630) Konishi, H.; Takekawa, R.; Minato, T.; Ogumi, Z.; Abe, T. Effect of Anion Acceptor Added to the Electrolyte on the Electrochemical Performance of Bismuth(III) Fluoride in a Fluoride Shuttle Battery. *Chem. Phys. Lett.* **2020**, *755*, 137785.
- (631) Konishi, H.; Minato, T.; Abe, T.; Ogumi, Z. Reactivity of the Anion Acceptor in Electrolyte: An Important Factor in Achieving High Electrochemical Performance of a Lead (II) Fluoride Electrode in a Fluoride Shuttle Battery. *J. Electroanal. Chem.* **2020**, *871*, 114103.
- (632) Konishi, H.; Minato, T.; Abe, T.; Ogumi, Z. Electrochemical Performance of a Bismuth Fluoride Electrode in a Reserve-Type Fluoride Shuttle Battery. *J. Electrochem. Soc.* **2017**, *164*, A3702-A3708.
- (633) Konishi, H.; Minato, T.; Abe, T.; Ogumi, Z. Improvement of Cycling Performance in Bismuth Fluoride Electrodes by Controlling Electrolyte Composition in Fluoride Shuttle Batteries. *J. Appl. Electrochem.* **2018**, *48*, 1205-1211.
- (634) Celik Kucuk, A.; Abe, T. Borolan-2-yl Involving Anion Acceptors for Organic Liquid Electrolyte-Based Fluoride Shuttle Batteries. *J. Fluor. Chem.* **2020**, *240*.
- (635) Celik Kucuk, A.; Yamanaka, T.; Abe, T. Using Siloxane-Based Liquid Electrolytes with High Stability for Fluoride Shuttle Batteries. *J. Mater. Chem. A* **2020**, *8*, 22134-22142.
- (636) Konishi, H.; Minato, T.; Abe, T.; Ogumi, Z. Influence of Electrolyte Composition on the Electrochemical Reaction Mechanism of Bismuth Fluoride Electrode in Fluoride Shuttle Battery. *J. Phys. Chem. C* **2019**, *123*, 10246-10252.
- (637) Celik Kucuk, A.; Minato, T.; Yamanaka, T.; Abe, T. Effects of LiBOB on Salt Solubility and BiF_3 Electrode Electrochemical Properties in Fluoride Shuttle Batteries. *J. Mater. Chem. A* **2019**, *7*, 8559-8567.
- (638) Kawauchi, S.; Nakamoto, H.; Takekawa, R.; Kobayashi, T.; Abe, T. Electrolytes for Room-Temperature Rechargeable Fluoride Shuttle Batteries. *ACS Appl. Energy Mater.* **2022**, *5*, 2096-2103.
- (639) Celik Kucuk, A.; Yamanaka, T.; Minato, T.; Abe, T. Influence of LiBOB as an Electrolyte Additive on the Performance of BiF_3/C for Fluoride Shuttle Batteries. *J. Electrochem. Soc.* **2020**, *167*, 120508.
- (640) Yamanaka, T.; Kucuk, A. C.; Ogumi, Z.; Abe, T. Evolution of Fluoride Shuttle Battery Reactions of BiF_3 Microparticles in a $\text{CsF}/\text{LiBOB}/\text{Tetraglyme}$ Electrolyte: Dependence on Structure, Size, and Shape. *ACS Appl. Energy Mater.* **2020**, *3*, 9390-9400.
- (641) Celik Kucuk, A.; Yamanaka, T.; Abe, T. Fluoride Shuttle Batteries: On the Performance of the BiF_3 Electrode in Organic Liquid Electrolytes Containing a Mixture of Lithium Bis(oxalato)borate and Triphenylboroxin. *Solid State Ion.* **2020**, *357*, 115499.
- (642) Celik-Kucuk, A.; Abe, T. Electrochemical Behavior of CuF_2 as Reversible Cathode in an Organic Liquid Electrolyte for Room-Temperature Fluoride-Shuttle Batteries. *J. Power Sources* **2021**, *496*, 229828.
- (643) Celik Kucuk, A.; Abe, T. Influence of Conductive Additives on the Electrochemical Compatibility of Copper Fluoride Cathode for FSB. *J. Electroanal. Chem.* **2021**, *900*, 115744.
- (644) Chen, J.; Huang, Z.; Wang, C.; Porter, S.; Wang, B.; Lie, W.; Liu, H. K. Sodium-Difluoro(oxalato)borate (NaDFOB): A New Electrolyte Salt for Na-Ion Batteries. *Chem. Commun.* **2015**, *51*, 9809-9812.
- (645) Zavalij, P. Y.; Yang, S.; Whittingham, M. S. Structures of Potassium, Sodium and Lithium Bis(oxalato)borate Salts from Powder Diffraction Data. *Acta Crystallogr. B* **2003**, *59*, 753-759.
- (646) Ge, C.; Wang, L.; Xue, L.; Wu, Z.-S.; Li, H.; Gong, Z.; Zhang, X.-D. Synthesis of Novel Organic-Ligand-Doped Sodium Bis(oxalato)-Borate Complexes with Tailored Thermal Stability and Enhanced Ion Conductivity for Sodium Ion Batteries. *J. Power Sources* **2014**, *248*, 77-82.

- (647) Gallagher, T. C.; Sandstrom, S. K.; Wu, C. Y.; Stickle, W.; Fulkerson, C. R.; Hagglund, L.; Ji, X. Copper Metal Electrode Reversibly Hosts Fluoride in a 16 m KF Aqueous Electrolyte. *Chem. Commun.* **2022**, 58, 10218-10220.
- (648) Fang, Z.; Li, M.; Wang, L.; Duan, X.; Zhao, H. A Long-Life Aqueous Fluoride-Ion Battery Based on Water-in-Salt Electrolyte. *Inorg. Chem. Commun.* **2023**, 148, 110275.
- (649) Alshangiti, O.; Galatolo, G.; Rees, G. J.; Guo, H.; Quirk, J. A.; Dawson, J. A.; Pasta, M. Solvent-in-Salt Electrolytes for Fluoride Ion Batteries. *ACS Energy Lett.* **2023**, 8, 2668-2673.
- (650) Ali, G.; Oh, S. H.; Kim, S. Y.; Kim, J. Y.; Cho, B. W.; Chung, K. Y. An Open-Framework Iron Fluoride and Reduced Graphene Oxide Nanocomposite as a High-Capacity Cathode Material for Na-Ion Batteries. *J. Mater. Chem. A* **2015**, 3, 10258-10266.
- (651) Lemoine, K.; Hemon-Ribaud, A.; Leblanc, M.; Lhoste, J.; Tarascon, J. M.; Maisonneuve, V. Fluorinated Materials as Positive Electrodes for Li- and Na-Ion Batteries. *Chem. Rev.* **2022**, 122, 14405-14439.
- (652) Zhang, N.; Xiao, X.; Pang, H. Transition Metal (Fe, CO, Ni) Fluoride-Based Materials for Electrochemical Energy Storage. *Nanoscale Horiz.* **2019**, 4, 99-116.
- (653) He, K.; Zhou, Y.; Gao, P.; Wang, L.; Pereira, N.; Amatucci, G. G.; Nam, K. W.; Yang, X. Q.; Zhu, Y.; Wang, F.; et al. Sodiation via Heterogeneous Disproportionation in FeF₂ Electrodes for Sodium-Ion Batteries. *ACS Nano* **2014**, 8, 7251-7259.
- (654) Ni, D.; Sun, W.; Lu, C.; Wang, Z.; Qiao, J.; Cai, H.; Liu, C.; Sun, K. Improved Rate and Cycling Performance of FeF₂-rGO Hybrid Cathode with Poly (Acrylic Acid) Binder for Sodium Ion Batteries. *J. Power Sources* **2019**, 413, 449-458.
- (655) Zu, C.-X.; Li, H. Thermodynamic Analysis on Energy Densities of Batteries. *Energy Environ. Sci.* **2011**, 4, 2614.
- (656) Kang, J.; Ahn, J.; Park, H.; Ko, W.; Lee, Y.; Lee, S.; Lee, S.; Jung, S. K.; Kim, J. Highly Stable Fe²⁺/Ti³⁺-Based Fluoride Cathode Enabling Low-Cost and High-Performance Na-Ion Batteries. *Adv. Funct. Mater.* **2022**, 32, 2201816.
- (657) Zhu, J.; Deng, D. Wet-Chemical Synthesis of Phase-Pure FeOF Nanorods as High-Capacity Cathodes for Sodium-Ion Batteries. *Angew. Chem. Int. Ed.* **2015**, 54, 3079-3083.
- (658) Zhou, Y.-N.; Sina, M.; Pereira, N.; Yu, X.; Amatucci, G. G.; Yang, X.-Q.; Cosandey, F.; Nam, K.-W. FeO_{0.7}F_{1.3}/C Nanocomposite as a High-Capacity Cathode Material for Sodium-Ion Batteries. *Adv. Funct. Mater.* **2015**, 25, 696-703.
- (659) Dey, U. K.; Barman, N.; Ghosh, S.; Sarkar, S.; Peter, S. C.; Senguttuvan, P. Topochemical Bottom-Up Synthesis of 2D- and 3D-Sodium Iron Fluoride Frameworks. *Chem. Mater.* **2019**, 31, 295-299.
- (660) Foley, E. E.; Wu, V. C.; Jin, W.; Cui, W.; Yoshida, E.; Manche, A.; Clement, R. J. Polymorphism in Weberite Na₂Fe₂F₇ and its Effects on Electrochemical Properties as a Na-Ion Cathode. *Chem. Mater.* **2023**, 35, 3614-3627.
- (661) Peschel, B.; Molinier, M.; Babel, D. Kristallstrukturbestimmungen an Vier Monoklinen Weberiten Na₂M^{II}M^{III}F₇ (M^{II} = Fe, Co; M^{III} = V, Cr). *Z. Physik* **1995**, 621, 1573-1581.
- (662) Peschel, B.; Babel, D. Die Kristallstrukturen der Vanadium-Weberite Na₂M^{II}V^{III}F₇ (M^{II} = Mn, Ni, Cu) und von NaVF₄. *Z. Physik* **1997**, 623, 1614-1620.
- (663) Liao, J.; Han, J.; Xu, J.; Du, Y.; Sun, Y.; Duan, L.; Zhou, X. Scalable Synthesis of Na₂MVF₇ (M = Mn, Fe, and Co) as High-Performance Cathode Materials for Sodium-Ion Batteries. *Chem. Commun.* **2021**, 57, 11497-11500.
- (664) Leblanc, M.; Ferey, G.; Chevallier, P.; Calage, Y.; De Pape, R. Hexagonal Tungsten Bronze-Type Fe^{III} Fluoride: (H₂O)_{0.33}FeF₃; Crystal Structure, Magnetic Properties, Dehydration to a New Form of Iron Trifluoride. *J. Solid State Chem.* **1983**, 47, 53-58.
- (665) Zhang, R.; Wang, X.; Wang, X.; Liu, M.; Wei, S.; Wang, Y.; Hu, H. Iron Fluoride Packaged into 3D Order Mesoporous Carbons as High-Performance Sodium-Ion Battery Cathode Material. *J. Electrochem. Soc.* **2018**, 165, A89-A96.
- (666) Li, C.; Yin, C.; Mu, X.; Maier, J. Top-Down Synthesis of Open Framework Fluoride for Lithium and Sodium Batteries. *Chem. Mater.* **2013**, 25, 962-969.
- (667) Liu, M.; Wang, Q.; Chen, B.; Lei, H.; Liu, L.; Wu, C.; Wang, X.; Yang, Z. Band-Gap Engineering of FeF₃·0.33H₂O Nanosphere via Ni Doping as a High-Performance Lithium-Ion Battery Cathode. *ACS Sustain. Chem. Eng.* **2020**, 8, 15651-15660.

- (668) Wei, S.; Wang, X.; Yu, R.; Zhang, R.; Liu, M.; Yang, Z.; Hu, H. Ti-Doped $\text{Fe}_{1-x}\text{Ti}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ Nanocomposite as an Ultrahigh Rate Capability Cathode Materials of Lithium Ion Batteries. *J. Alloys Compd.* **2017**, *702*, 372-380.
- (669) Yang, Z.; Zhang, Z.; Yuan, Y.; Huang, Y.; Wang, X.; Chen, X.; Wei, S. First-Principles Study of Ti Doping in $\text{FeF}_3 \cdot 0.33\text{H}_2\text{O}$. *Curr. Appl. Phys.* **2016**, *16*, 905-913.
- (670) Ding, J.; Zhou, X.; Wang, H.; Yang, J.; Gao, Y.; Tang, J. Mn-Doped $\text{Fe}_{1-x}\text{Mn}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}/\text{C}$ Cathodes for Li-Ion Batteries: First-Principles Calculations and Experimental Study. *ACS Appl. Mater. Interfaces* **2019**, *11*, 3852-3860.
- (671) Zhang, C.; Yan, M.; Li, W.; Han, C.; Li, J.; Zhao, H.; Jia, G.; An, S.; Qiu, X. Cr-Doped $\text{Fe}_{1-x}\text{Cr}_x\text{F}_3 \cdot 0.33\text{H}_2\text{O}$ Nanomaterials as Cathode Materials for Sodium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 48653-48660.
- (672) Eshetu, G. G.; Elia, G. A.; Armand, M.; Forsyth, M.; Komaba, S.; Rojo, T.; Passerini, S. Electrolytes and Interphases in Sodium-Based Rechargeable Batteries: Recent Advances and Perspectives. *Adv. Energy Mater.* **2020**, *10*, 2000093.
- (673) Bommier, C.; Ji, X. Electrolytes, SEI Formation, and Binders: A Review of Nonelectrode Factors for Sodium-Ion Battery Anodes. *Small* **2018**, *14*, e1703576.
- (674) Lin, Z.; Xia, Q.; Wang, W.; Li, W.; Chou, S. Recent Research Progresses in Ether- and Ester-Based Electrolytes for Sodium-Ion Batteries. *InfoMat* **2019**, *1*, 376-389.
- (675) Komaba, S.; Ishikawa, T.; Yabuuchi, N.; Murata, W.; Ito, A.; Ohsawa, Y. Fluorinated Ethylene Carbonate as Electrolyte Additive for Rechargeable Na Batteries. *ACS Appl. Mater. Interfaces* **2011**, *3*, 4165-4168.
- (676) Dahbi, M.; Nakano, T.; Yabuuchi, N.; Fujimura, S.; Chihara, K.; Kubota, K.; Son, J.-Y.; Cui, Y.-T.; Oji, H.; Komaba, S. Effect of Hexafluorophosphate and Fluoroethylene Carbonate on Electrochemical Performance and the Surface Layer of Hard Carbon for Sodium-Ion Batteries. *ChemElectroChem* **2016**, *3*, 1856-1867.
- (677) Yi, Q.; Lu, Y.; Sun, X.; Zhang, H.; Yu, H.; Sun, C. Fluorinated Ether Based Electrolyte Enabling Sodium-Metal Batteries with Exceptional Cycling Stability. *ACS Appl. Mater. Interfaces* **2019**, *11*, 46965-46972.
- (678) Zheng, X.; Gu, Z.; Liu, X.; Wang, Z.; Wen, J.; Wu, X.; Luo, W.; Huang, Y. Bridging the Immiscibility of an All-Fluoride Fire Extinguishant with Highly-Fluorinated Electrolytes toward Safe Sodium Metal Batteries. *Energy Environ. Sci.* **2020**, *13*, 1788-1798.
- (679) Nimkar, A.; Shpigel, N.; Malchik, F.; Bublil, S.; Fan, T.; Penki, T. R.; Tsubery, M. N.; Aurbach, D. Unraveling the Role of Fluorinated Alkyl Carbonate Additives in Improving Cathode Performance in Sodium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 46478-46487.
- (680) Wang, C.; Sun, Z.; Liu, L.; Ni, H.; Hou, Q.; Fan, J.; Yuan, R.; Zheng, M.; Dong, Q. A Rooted Interphase on Sodium via In Situ Pre-implantation of Fluorine Atoms for High-Performance Sodium Metal Batteries. *Energy Environ. Sci.* **2023**, *16*, 3098-3109.
- (681) Guo, X. F.; Yang, Z.; Zhu, Y. F.; Liu, X. H.; He, X. X.; Li, L.; Qiao, Y.; Chou, S. L. High-Voltage, Highly Reversible Sodium Batteries Enabled by Fluorine-Rich Electrode/Electrolyte Interphases. *Small Methods* **2022**, *6*, e2200209.
- (682) Zou, Y.; Shen, Y.; Wu, Y.; Xue, H.; Guo, Y.; Liu, G.; Wang, L.; Ming, J. A Designed Durable Electrolyte for High-Voltage Lithium-Ion Batteries and Mechanism Analysis. *Chemistry* **2020**, *26*, 7930-7936.
- (683) Zheng, X.; Cao, Z.; Gu, Z.; Huang, L.; Sun, Z.; Zhao, T.; Yu, S.; Wu, X.-L.; Luo, W.; Huang, Y. Toward High Temperature Sodium Metal Batteries via Regulating the Electrolyte/Electrode Interfacial Chemistries. *ACS Energy Lett.* **2022**, *7*, 2032-2042.
- (684) Feng, Y.; Zhou, L.; Ma, H.; Wu, Z.; Zhao, Q.; Li, H.; Zhang, K.; Chen, J. Challenges and Advances in Wide-Temperature Rechargeable Lithium Batteries. *Energy Environ. Sci.* **2022**, *15*, 1711-1759.
- (685) Zhou, X.; Chen, X.; Yang, Z.; Liu, X.; Hao, Z.; Jin, S.; Zhang, L.; Wang, R.; Zhang, C.; Li, L.; et al. Anion Receptor Weakens ClO_4^- Solvation for High-Temperature Sodium-Ion Batteries. *Adv. Funct. Mater.* **2023**, <https://doi.org/10.1002/adfm.202302281>.
- (686) Wu, J.; Tian, Y.; Gao, Y.; Gao, Z.; Meng, Y.; Wang, Y.; Wang, X.; Zhou, D.; Kang, F.; Li, B.; et al. Rational Electrolyte Design toward Cyclability Remedy for Room-Temperature Sodium-Sulfur Batteries. *Angew. Chem. Int. Ed.* **2022**, *61*, e202205416.
- (687) Zheng, J.; Chen, S.; Zhao, W.; Song, J.; Engelhard, M. H.; Zhang, J.-G. Extremely Stable Sodium Metal Batteries Enabled by Localized High-Concentration Electrolytes. *ACS Energy Lett.* **2018**, *3*, 315-321.
- (688) Jin, Y.; Xu, Y.; Le, P. M. L.; Vo, T. D.; Zhou, Q.; Qi, X.; Engelhard, M. H.; Matthews, B. E.; Jia, H.; Nie, Z.; et al. Highly Reversible Sodium Ion Batteries Enabled by Stable Electrolyte-Electrode Interphases. *ACS Energy Lett.* **2020**, *5*, 3212-3220.

- (689) Barnes, P.; Smith, K.; Parrish, R.; Jones, C.; Skinner, P.; Storch, E.; White, Q.; Deng, C.; Karsann, D.; Lau, M. L.; et al. A Non-aqueous Sodium Hexafluorophosphate-Based Electrolyte Degradation Study: Formation and Mitigation of Hydrofluoric Acid. *J. Power Sources* **2020**, *447*, 227363.
- (690) Terborg, L.; Nowak, S.; Passerini, S.; Winter, M.; Karst, U.; Haddad, P. R.; Nesterenko, P. N. Ion Chromatographic Determination of Hydrolysis Products of Hexafluorophosphate Salts in Aqueous Solution. *Anal. Chim. Acta* **2012**, *714*, 121-126.
- (691) Ould, D. M. C.; Menkin, S.; Smith, H. E.; Riesgo-Gonzalez, V.; Jonsson, E.; O'keefe, C. A.; Coowar, F.; Barker, J.; Bond, A. D.; Grey, C. P.; et al. Sodium Borates: Expanding the Electrolyte Selection for Sodium-Ion Batteries. *Angew. Chem. Int. Ed.* **2022**, *61*, e202202133.
- (692) Xu, X.; Zhou, D.; Qin, X.; Lin, K.; Kang, F.; Li, B.; Shanmukaraj, D.; Rojo, T.; Armand, M.; Wang, G. A Room-Temperature Sodium-Sulfur Battery with High Capacity and Stable Cycling Performance. *Nat. Commun.* **2018**, *9*, 3870.
- (693) Yang, C.; Feng, J.; Lv, F.; Zhou, J.; Lin, C.; Wang, K.; Zhang, Y.; Yang, Y.; Wang, W.; Li, J.; et al. Metallic Graphene-Like VSe₂ Ultrathin Nanosheets: Superior Potassium-Ion Storage and Their Working Mechanism. *Adv. Mater.* **2018**, *30*, e1800036.
- (694) Fan, L.; Hu, Y.; Rao, A. M.; Zhou, J.; Hou, Z.; Wang, C.; Lu, B. Prospects of Electrode Materials and Electrolytes for Practical Potassium-Based Batteries. *Small Methods* **2021**, *5*, e2101131.
- (695) Chihara, K.; Katogi, A.; Kubota, K.; Komaba, S. KVPO₄F and KVOPO₄ Toward 4 Volt-Class Potassium-Ion Batteries. *Chem. Commun.* **2017**, *53*, 5208-5211.
- (696) Tan, H.; Du, X.; Huang, J. Q.; Zhang, B. KVPO₄F as a Novel Insertion-Type Anode for Potassium Ion Batteries. *Chem. Commun.* **2019**, *55*, 11311-11314.
- (697) Liao, J.; Hu, Q.; He, X.; Mu, J.; Wang, J.; Chen, C. A long lifespan potassium-ion full battery based on KVPO₄F cathode and VPO₄ anode. *J. Power Sources* **2020**, *451*, 227739.
- (698) Fedotov, S. S.; Luchinin, N. D.; Aksyonov, D. A.; Morozov, A. V.; Ryazantsev, S. V.; Gaboardi, M.; Plaisier, J. R.; Stevenson, K. J.; Abakumov, A. M.; Antipov, E. V. Titanium-Based Potassium-Ion Battery Positive Electrode with Extraordinarily High Redox Potential. *Nat. Commun.* **2020**, *11*, 1484.
- (699) Kim, H.; Seo, D. H.; Bianchini, M.; Clément, R. J.; Kim, H.; Kim, J. C.; Tian, Y.; Shi, T.; Yoon, W. S.; Ceder, G. A New Strategy for High-Voltage Cathodes for K-Ion Batteries: Stoichiometric KVPO₄F. *Adv. Energy Mater.* **2018**, *8*, 1801591.
- (700) Dong, J.; Liao, J.; He, X.; Hu, Q.; Yu, Y.; Chen, C. Graphene Encircled KFeSO₄F Cathode Composite for High Energy Density Potassium-Ion Batteries. *Chem. Commun.* **2020**, *56*, 10050-10053.
- (701) Recham, N.; Rousse, G.; Sougrati, M. T.; Chotard, J.-N.; Frayret, C.; Mariyappan, S.; Melot, B. C.; Jumas, J.-C.; Tarascon, J.-M. Preparation and Characterization of a Stable FeSO₄F-Based Framework for Alkali Ion Insertion Electrodes. *Chem. Mater.* **2012**, *24*, 4363-4370.
- (702) Ling, C.; Mizuno, F. Mechanistic Study of the Electrochemical Extraction of K⁺ from KFeSO₄F. *J. Mater. Chem. A* **2013**, *1*, 8000.
- (703) Jian, Z.; Luo, W.; Ji, X. Carbon Electrodes for K-Ion Batteries. *J. Am. Chem. Soc.* **2015**, *137*, 11566-11569.
- (704) Zhou, M.; Bai, P.; Ji, X.; Yang, J.; Wang, C.; Xu, Y. Electrolytes and Interphases in Potassium Ion Batteries. *Adv. Mater.* **2021**, *33*, e2003741.
- (705) Xu, Y.; Ding, T.; Sun, D.; Ji, X.; Zhou, X. Recent Advances in Electrolytes for Potassium-Ion Batteries. *Adv. Funct. Mater.* **2022**, *33*, 2211290.
- (706) Xiao, N.; McCulloch, W. D.; Wu, Y. Reversible Dendrite-Free Potassium Plating and Stripping Electrochemistry for Potassium Secondary Batteries. *J. Am. Chem. Soc.* **2017**, *139*, 9475-9478.
- (707) Zhang, W.; Wu, Z.; Zhang, J.; Liu, G.; Yang, N.-H.; Liu, R.-S.; Pang, W. K.; Li, W.; Guo, Z. Unraveling the Effect of Salt Chemistry on Long-Durability High-Phosphorus-Concentration Anode for Potassium Ion Batteries. *Nano Energy* **2018**, *53*, 967-974.
- (708) Zhang, W.; Pang, W. K.; Sencadas, V.; Guo, Z. Understanding High-Energy-Density Sn₄P₃ Anodes for Potassium-Ion Batteries. *Joule* **2018**, *2*, 1534-1547.
- (709) Xie, J.; Li, X.; Lai, H.; Zhao, Z.; Li, J.; Zhang, W.; Xie, W.; Liu, Y.; Mai, W. A Robust Solid Electrolyte Interphase Layer Augments the Ion Storage Capacity of Bimetallic-Sulfide-Containing Potassium-Ion Batteries. *Angew. Chem. Int. Ed.* **2019**, *58*, 14740-14747.
- (710) Zhang, Q.; Mao, J.; Pang, W. K.; Zheng, T.; Sencadas, V.; Chen, Y.; Liu, Y.; Guo, Z. Boosting the Potassium Storage Performance of Alloy-Based Anode Materials via Electrolyte Salt Chemistry. *Adv. Energy Mater.* **2018**, *8*, 1703288.

- (711) Wang, H.; Wang, H.; Chen, S.; Zhang, B.; Yang, G.; Gao, P.; Liu, J.; Fan, X.; Huang, Y.; Lin, J.; et al. A Depth-Profiling Study on the Solid Electrolyte Interface: Bis(fluorosulfonyl)imide Anion toward Improved K^+ Storage. *ACS Appl. Energy Mater.* **2019**, *2*, 7942-7951.
- (712) Deng, L.; Zhang, Y.; Wang, R.; Feng, M.; Niu, X.; Tan, L.; Zhu, Y. Influence of KPF_6 and KFSI on the Performance of Anode Materials for Potassium-Ion Batteries: A Case Study of MoS_2 . *ACS Appl. Mater. Interfaces* **2019**, *11*, 22449-22456.
- (713) Wang, H.; Yu, D.; Wang, X.; Niu, Z.; Chen, M.; Cheng, L.; Zhou, W.; Guo, L. Electrolyte Chemistry Enables Simultaneous Stabilization of Potassium Metal and Alloying Anode for Potassium-Ion Batteries. *Angew. Chem. Int. Ed.* **2019**, *58*, 16451-16455.
- (714) Liu, S.; Mao, J.; Zhang, Q.; Wang, Z.; Pang, W. K.; Zhang, L.; Du, A.; Sencadas, V.; Zhang, W.; Guo, Z. An Intrinsically Non-flammable Electrolyte for High-Performance Potassium Batteries. *Angew. Chem. Int. Ed.* **2020**, *59*, 3638-3644.
- (715) Nie, P.; Liu, M.; Qu, W.; Hou, M.; Chang, L.; Wu, Z.; Wang, H.; Jiang, J. Unravelling the Solvation Structure and Interfacial Mechanism of Fluorinated Localized High Concentration Electrolytes in K-ion Batteries. *Adv. Funct. Mater.* **2023**, *33*, 2302235.
- (716) Yang, H.; Chen, C. Y.; Hwang, J.; Kubota, K.; Matsumoto, K.; Hagiwara, R. Potassium Difluorophosphate as an Electrolyte Additive for Potassium-Ion Batteries. *ACS Appl. Mater. Interfaces* **2020**, *12*, 36168-36176.
- (717) Qin, L.; Xiao, N.; Zheng, J.; Lei, Y.; Zhai, D.; Wu, Y. Localized High-Concentration Electrolytes Boost Potassium Storage in High-Loading Graphite. *Adv. Energy Mater.* **2019**, *9*, 1902618.
- (718) Jiang, X.; Zhang, T.; Yang, L.; Li, G.; Lee, J. Y. A Fe/Mn-Based Prussian Blue Analogue as a K-Rich Cathode Material for Potassium-Ion Batteries. *ChemElectroChem* **2017**, *4*, 2237-2242.
- (719) Bie, X.; Kubota, K.; Hosaka, T.; Chihara, K.; Komaba, S. A Novel K-ion Battery: Hexacyanoferrate(ii)/Graphite Cell. *J. Mater. Chem. A* **2017**, *5*, 4325-4330.
- (720) Yuan, F.; Li, Z.; Zhang, D.; Wang, Q.; Wang, H.; Sun, H.; Yu, Q.; Wang, W.; Wang, B. Fundamental Understanding and Research Progress on the Interfacial Behaviors for Potassium-Ion Battery Anode. *Adv. Sci.* **2022**, *9*, e2200683.
- (721) Xu, C.; Li, B.; Du, H.; Kang, F. Energetic Zinc Ion Chemistry: The Rechargeable Zinc Ion Battery. *Angew. Chem. Int. Ed.* **2012**, *51*, 933-935.
- (722) Yang, Y.; Liu, C.; Lv, Z.; Yang, H.; Zhang, Y.; Ye, M.; Chen, L.; Zhao, J.; Li, C. C. Synergistic Manipulation of Zn^{2+} Ion Flux and Desolvation Effect Enabled by Anodic Growth of a 3D ZnF_2 Matrix for Long-Lifespan and Dendrite-Free Zn Metal Anodes. *Adv. Mater.* **2021**, *33*, e2007388.
- (723) Cao, L.; Li, D.; Pollard, T.; Deng, T.; Zhang, B.; Yang, C.; Chen, L.; Vatamanu, J.; Hu, E.; Hourwitz, M. J.; et al. Fluorinated Interphase Enables Reversible Aqueous Zinc Battery Chemistries. *Nat. Nanotechnol.* **2021**, *16*, 902-910.
- (724) Li, D.; Cao, L.; Deng, T.; Liu, S.; Wang, C. Design of a Solid Electrolyte Interphase for Aqueous Zn Batteries. *Angew. Chem. Int. Ed.* **2021**, *60*, 13035-13041.
- (725) Sun, W.; Wang, F.; Zhang, B.; Zhang, M.; Kupers, V.; Ji, X.; Theile, C.; Bieker, P.; Xu, K.; Wang, C.; et al. A Rechargeable Zinc-Air Battery Based on Zinc Peroxide Chemistry. *Science* **2021**, *371*, 46-51.
- (726) Rubio, S.; Liang, Z.; Liu, X.; Lavela, P.; Tirado, J. L.; Stoyanova, R.; Zhecheva, E.; Liu, R.; Zuo, W.; Yang, Y.; et al. Reversible Multi-Electron Storage Enabled by $Na_5V(PO_4)_2F_2$ for Rechargeable Magnesium Batteries. *Energy Storage Mater.* **2021**, *38*, 462-472.
- (727) Tang, X.; Zhou, D.; Zhang, B.; Wang, S.; Li, P.; Liu, H.; Guo, X.; Jaumaux, P.; Gao, X.; Fu, Y.; et al. A Universal Strategy towards High-Energy Aqueous Multivalent-Ion Batteries. *Nat. Commun.* **2021**, *12*, 2857.
- (728) Zhao-Karger, Z.; Liu, R.; Dai, W.; Li, Z.; Diemant, T.; Vinayan, B. P.; Bonatto Minella, C.; Yu, X.; Manthiram, A.; Behm, R. J.; et al. Toward Highly Reversible Magnesium-Sulfur Batteries with Efficient and Practical $Mg[B(hfip)_4]_2$ Electrolyte. *ACS Energy Lett.* **2018**, *3*, 2005-2013.
- (729) Sun, Y.; Zou, Q.; Wang, W.; Lu, Y.-C. Non-passivating Anion Adsorption Enables Reversible Magnesium Redox in Simple Non-nucleophilic Electrolytes. *ACS Energy Lett.* **2021**, *6*, 3607-3613.
- (730) Hou, S.; Ji, X.; Gaskell, K.; Wang, P. F.; Wang, L.; Xu, J.; Sun, R.; Borodin, O.; Wang, C. Solvation Sheath Reorganization Enables Divalent Metal Batteries with Fast Interfacial Charge Transfer Kinetics. *Science* **2021**, *374*, 172-178.
- (731) Li, Z.; Fuhr, O.; Fichtner, M.; Zhao-Karger, Z. Towards Stable and Efficient Electrolytes for Room-Temperature Rechargeable Calcium Batteries. *Energy Environ. Sci.* **2019**, *12*, 3496-3501.
- (732) Song, H.; Su, J.; Wang, C. Hybrid Solid Electrolyte Interphases Enabled Ultralong Life Ca-Metal Batteries Working at Room Temperature. *Adv. Mater.* **2021**, *33*, e2006141.

- (733) Kotobuki, M.; Lu, L.; Savilov, S. V.; Aldoshin, S. M. Poly(vinylidene fluoride)-Based Al Ion Conductive Solid Polymer Electrolyte for Al Battery. *J. Electrochem. Soc.* **2017**, *164*, A3868-A3875.
- (734) Xu, Z. L.; Park, J.; Wang, J.; Moon, H.; Yoon, G.; Lim, J.; Ko, Y. J.; Cho, S. P.; Lee, S. Y.; Kang, K. A New High-Voltage Calcium Intercalation Host for Ultra-Stable and High-Power Calcium Rechargeable Batteries. *Nat. Commun.* **2021**, *12*, 3369.
- (735) Fan, J.; Zhang, Z.; Liu, Y.; Wang, A.; Li, L.; Yuan, W. An Excellent Rechargeable PP₁₄TFSI Ionic Liquid Dual-Ion Battery. *Chem. Commun.* **2017**, *53*, 6891-6894.
- (736) Zhang, L.; Li, J.; Huang, Y.; Zhu, D.; Wang, H. Synergetic Effect of Ethyl Methyl Carbonate and Trimethyl Phosphate on BF₄⁻ Intercalation into a Graphite Electrode. *Langmuir* **2019**, *35*, 3972-3979.
- (737) Özmen-Monkul, B.; Lerner, M. M. The First Graphite Intercalation Compounds Containing Tris(pentafluoroethyl)trifluorophosphate. *Carbon* **2010**, *48*, 3205-3210.
- (738) Xiang, L.; Ou, X.; Wang, X.; Zhou, Z.; Li, X.; Tang, Y. Highly Concentrated Electrolyte towards Enhanced Energy Density and Cycling Life of Dual-Ion Battery. *Angew. Chem. Int. Ed.* **2020**, *59*, 17924-17930.
- (739) Wang, M.; Jiang, C.; Zhang, S.; Song, X.; Tang, Y.; Cheng, H. M. Reversible Calcium Alloying Enables a Practical Room-Temperature Rechargeable Calcium-Ion Battery with a High Discharge Voltage. *Nat. Chem.* **2018**, *10*, 667-672.
- (740) Yu, D.; Zhu, Q.; Cheng, L.; Dong, S.; Zhang, X.; Wang, H.; Yang, N. Anion Solvation Regulation Enables Long Cycle Stability of Graphite Cathodes. *ACS Energy Lett.* **2021**, *6*, 949-958.
- (741) Sun, Z.; Zhu, K.; Liu, P.; Chen, X.; Li, H.; Jiao, L. Fluorination Treatment of Conjugated Protonated Polyanilines for High-Performance Sodium Dual-Ion Batteries. *Angew. Chem. Int. Ed.* **2022**, *61*, e202211866.
- (742) Read, J. A.; Cresce, A. V.; Ervin, M. H.; Xu, K. Dual-Graphite Chemistry Enabled by a High-Voltage Electrolyte. *Energy Environ. Sci.* **2014**, *7*, 617-620.
- (743) Wang, Y.; Zhang, Y.; Wang, S.; Dong, S.; Dang, C.; Hu, W.; Yu, D. Y. W. Ultrafast Charging and Stable Cycling Dual-Ion Batteries Enabled via an Artificial Cathode–Electrolyte Interface. *Adv. Funct. Mater.* **2021**, *31*, 2102360.
- (744) Wang, Y.; Zhang, Y.; Dong, S.; Zhou, W.; Lee, P. K.; Peng, Z.; Dang, C.; Sit, P. H. L.; Guo, J.; Yu, D. Y. W. An All-Fluorinated Electrolyte Toward High Voltage and Long Cycle Performance Dual-Ion Batteries. *Adv. Energy Mater.* **2022**, *12*, 2103360.
- (745) Zhu, J.; Xu, Y.; Fu, Y.; Xiao, D.; Li, Y.; Liu, L.; Wang, Y.; Zhang, Q.; Li, J.; Yan, X. Hybrid Aqueous/Nonaqueous Water-in-Bisalt Electrolyte Enables Safe Dual Ion Batteries. *Small* **2020**, *16*, e1905838.
- (746) Wrogemann, J. M.; Künne, S.; Heckmann, A.; Rodríguez-Pérez, I. A.; Siozios, V.; Yan, B.; Li, J.; Winter, M.; Beltrop, K.; Placke, T. Development of Safe and Sustainable Dual-Ion Batteries Through Hybrid Aqueous/Nonaqueous Electrolytes. *Adv. Energy Mater.* **2020**, *10*, 1902709.
- (747) Rodríguez-Pérez, I. A.; Zhang, L.; Wrogemann, J. M.; Driscoll, D. M.; Sushko, M. L.; Han, K. S.; Fulton, J. L.; Engelhard, M. H.; Balasubramanian, M.; Viswanathan, V. V.; et al. Enabling Natural Graphite in High-Voltage Aqueous Graphite || Zn Metal Dual-Ion Batteries. *Adv. Energy Mater.* **2020**, *10*, 2001256.
- (748) Zhang, Z.; Hu, X.; Zhou, Y.; Wang, S.; Yao, L.; Pan, H.; Su, C.-Y.; Chen, F.; Hou, X. Aqueous Rechargeable Dual-Ion Battery Based on Fluoride Ion and Sodium Ion Electrochemistry. *J. Mater. Chem. A* **2018**, *6*, 8244-8250.
- (749) Yang, C.; Chen, J.; Ji, X.; Pollard, T. P.; Lu, X.; Sun, C. J.; Hou, S.; Liu, Q.; Liu, C.; Qing, T.; et al. Aqueous Li-Ion Battery Enabled by Halogen Conversion-Intercalation Chemistry in Graphite. *Nature* **2019**, *569*, 245-250.
- (750) Wang, H.; Sun, Y.; Li, M.; Li, G.; Xue, K.; Chen, Z.; Yu, D. Y. W. Engineering Solvation Complex-Membrane Interaction to Suppress Cation Crossover in 3 V Cu-Al Battery. *Small* **2020**, *16*, e2003438.
- (751) Yu, M.; Sui, Y.; Sandstrom, S. K.; Wu, C. Y.; Yang, H.; Stickle, W.; Luo, W.; Ji, X. Reversible Copper Cathode for Nonaqueous Dual-Ion Batteries. *Angew. Chem. Int. Ed.* **2022**, *61*, e202212191.