RESEARCH ARTICLE

Recent Advances in Electrolytes for High-Voltage Cathodes of Lithium-Ion Batteries

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Abstract

With the increasing scale of energy storage, it is urgently demanding for further advancements on battery technologies in terms of energy density, cost, cycle life and safety. The development of lithium-ion batteries (LIBs) not only relies on electrodes, but also the functional electrolyte systems to achieve controllable formation of solid electrolyte interphase and high ionic conductivity. In order to satisfy the needs of higher energy density, high-voltage (> 4.3 V) cathodes such as Li-rich layered compounds, olivine $LiNiPO_4$, spinel $LiNi_{0.5}Mn_{1.5}O_4$ have been extensively studied. However, high-voltage cathode-based LIBs fade rapidly mainly owing to the anodic decomposition of electrolytes, gradually thickening of interfacial passivation layer and vast irreversible capacity loss, hence encountering huge obstacle toward practical applications. To tackle this roadblock, substantial progress has been made toward oxidation-resistant electrolytes to block its side reaction with high-voltage cathodes. In this review, we discuss degradation mechanisms of electrolytes at electrolyte/cathode interface and ideal requirements of electrolytes for high-voltage cathode, as well as summarize recent advances of oxidation-resistant electrolyte optimization mainly from solvents and additives. With these insights, it is anticipated that development of liquid electrolyte tolerable to high-voltage cathode will boost the large-scale practical applications of high-voltage cathode-based LIBs.

Keywords High-voltage cathodes · Oxidation resistance · Electrolytes optimization · Solvents · Additives

Introduction

Lithium-ion batteries (LIBs) have revolutionized the energy storage area since their advent in the market in 1991 and are developing toward the direction of higher energy density in order to meet the long duration demand. Portable electronic devices such as laptops, mobile phones, tablets and unmanned aerial vehicle need power sources with smaller volume and longer service life. Other electrical equipments, including large energy storage devices, electric vehicles, etc., are also persistently exploring lithium-ion batteries with lighter weight, smaller volume, higher output voltage and power density. Under the circumstance that energy consumption rate, battery pack volume and weight are strictly limited, its maximum working time mainly depends on the energy density of the battery. The energy density (E) is a critical parameter for rechargeable batteries and directly related to the electrode specific capacity (Q) and cell voltage (V). It can be calculated based on Eqs. (1) and (2), where Q_a and Q_c represents the specific capacity of anode and cathode electrodes, respectively, and the battery output voltage is the difference between the electrochemical potentials of cathode and anode ($V_c - V_a$) [1].

$$\frac{1}{Q} = \frac{1}{Q_a} + \frac{1}{Q_c} \tag{1}$$

$$E = (V_c - V_a) * Q \tag{2}$$

In addition to energy density, another evaluation parameter for battery is power density (P). According to Eq. (3), power density is proportional to the square of output voltage,

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thus more energy can be released correspondingly under higher working voltage.

$$P = (V_c - V_a)^2 / R \qquad (3)$$

Therefore, increasing the cutoff voltage of commercial cathodes or developing new high-voltage and high-capacity cathode materials while coordinating with low potential anodes can fundamentally improve the energy and power density of the battery. Nowadays, the majority of LIBs use graphite or lithium titanate (LTO) coupled with a high-voltage (> 4.3 V vs. Li/Li$^+$) Li$^+$ intercalation/de-intercalation cathode. As is known to us, Li metal has been recognized as ultimate anode candidate among existing anode materials owing to the most negative equilibrium potential (–3.04 V vs standard hydrogen electrode) and ultra-high capacity (3860 mAh/g). Replacing graphite with Li metal anode is regarded as one of the most meaningful approaches to enhance energy density. Despite these prominent merits, the development of rechargeable Li metal batteries has been in a dilemma due to the inferior compatibility between predominate organic carbonate solvents and Li metal, which causes unfavorable low Coulombic efficiency (< 90%) and severe capacity decay. Owing to large amount of organic species such as Li alkyl carbonate (ROCO$_2$Li) from solvent reduction, thick and fragile solid electrolyte interphase (SEI) layer with low shear modulus below 1 GPa is formed. Numerous studies have demonstrated that SEI rich in LiF, Li$_2$CO$_3$, and Li$_3$N species effectively improves the Coulombic efficiency (CE) stability [2, 3]. High-voltage lithium metal batteries are still a long way from commercialization. Relatively speaking, LTO, TiNb$_2$O$_7$ (NTO) and other negative electrodes matching with high-voltage cathode is more likely to come true. In this review, we will focus on how to construct stable cathode electrolyte interphase (CEI). Promising high-voltage cathode materials for LIBs (> 4.3 V vs Li/Li$^+$) could be classified into four major categories: lithium-rich layered oxides

(xLi$_2$MnO$_3$·(1 − x)LiMO$_2$, M = Ni, Co, Mn, etc.), nickel-rich layered oxides (LiNiO$_2$, LiNi$_{1−x}$M$_x$O$_2$, Li[Ni$_{1−x−y}$Co$_x$Mn$_y$]O$_2$, etc.), spinel oxides (LiMn$_{2−x}$MO$_4$, M = Ni, Co, Mn, etc.) and polyanionic compounds (phosphates, silicates, sulfates, etc.) [4–6]. Given that the energy density of LIBs greatly depends on the output of the specific capacity and working potential of cathodes, thus substantial efforts have been devoted to developing high-voltage cathodes. As shown in Fig. 1, in addition to layered cathodes which generally operate at voltage about 4.3 V, 5 V ultra-high-voltage cathodes such as spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$ (LNMO), olivine LiNiPO$_4$ (LNPO) and orthorhombic Li$_2$CoPO$_4$F (LCPOF) have also been extensively investigated.

However, their overall performance still cannot meet the requirements for practical application in despite of high energy density. The lifespan of these high-voltage cathodes is quite limited compared to traditional cathode materials owing to its poor interfacial stability [7]. Under high working potential, serious side reactions occur between the traditional EC (ethylene carbonate)-based electrolytes and the catalytically active surface of delithiated cathode, which will accelerate the dissolution of transition metal into electrolytes and the pulverization of cathode structure. Especially for layered cathode materials, in addition to transition metal redox, anion redox needs to be triggered by charging above 4.6 V to complete lithium storage behavior [8]. However, anionic reduction can induce the formation of O$_2^{2−}$, O$_2^−$, O$_2$ and other substances that react severely with electrolytes. Due to the restriction of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), once the working voltage range between anode and cathode exceeds the electrochemical window of the electrolyte [9], traditional carbonate electrolytes suffer from severe oxidation decomposition and thus challenge the practical energy storage applications of high-voltage cathodes. Interestingly, the actual electrochemical window of the electrolyte in a

Fig.1 a The approximate reversible capacities and working voltage windows of commercialized and intensively investigated intercalation cathode materials. **b** Schematic illustration of electrolyte working mechanisms in LIBs. Reproduced with permission from Ref. [1]. Copyright © 2021, Royal Society of Chemistry
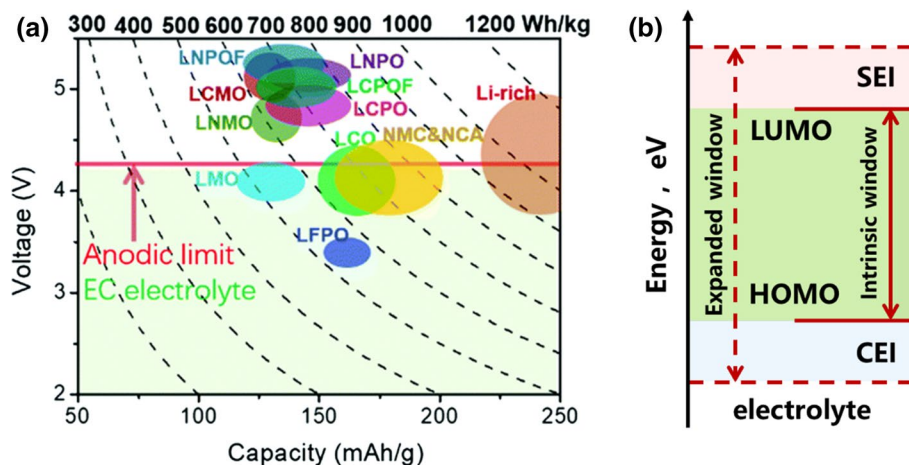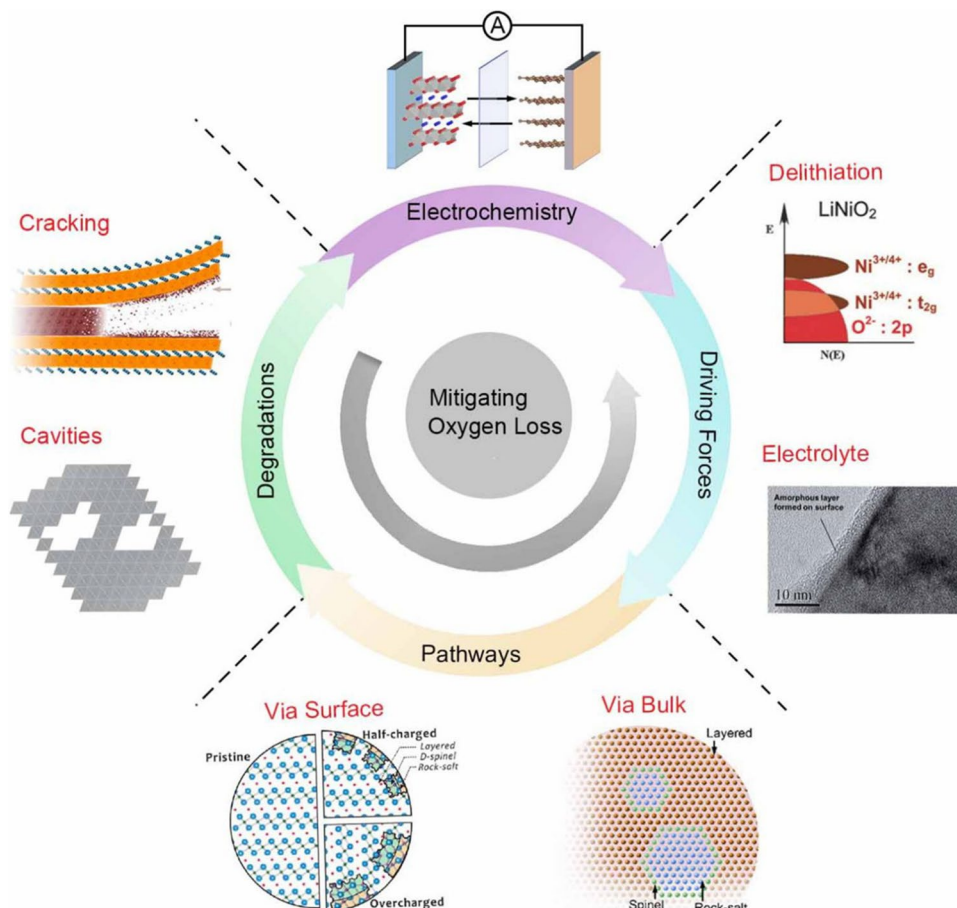
battery system could be expended by the in situ formed SEI and CEI.

Failure Mechanism of High-Voltage Cathodes Based LIBs

The commonly used cathode $LiFePO_4$ operates above the HOMO of non-aqueous electrolyte and presents satisfactory electrode/electrolyte compatibility. However, high-voltage cathodes based LIBs suffer from poor cycling capability, especially under a voltage above 4.3 V (vs Li^+/Li) or elevated temperatures. The electrochemical stable window of high-voltage cathode materials is beyond the oxidation limit of ethylene carbonate (EC)-based electrolytes, which brings about a great challenge to achieve a chemically inert interphase to guarantee the steadily cycling of the batteries. Therefore, it is indispensable to understand the degradation mechanisms for the high-voltage cathodes from a systematic view to give a wholescale assessment before their commercialization. Quantities of research works have been conducted to explore the reason behind capacity fading and there is a consensus that four following issues should take the blame for this:

Oxygen Evolution

Oxygen evolution caused by side reactions between cathode and electrolyte is one of the factors causing thermal runaway of lithium-ion batteries. During electrochemical cycling, various driving forces exist that influence the kinetics and pathways of oxygen loss (Fig. 2) [10]. Oxygen evolution takes place in both bulk and surface of cathodes. Two typical layered cathodes, namely stoichiometric layered oxides ($LiMO_2$) (M = Co, Ni) and the Li-rich compounds ($Li_{1+x}M_{1-x}O_2$) are taken as examples to elaborate the specific behavior of oxygen precipitation. In a highly delithiated state of cathode, the O-2p and M-t_{2g} bands position regulate the formation of O_2 [11]. When charging voltage reaches critical value, the O-2p and M-t_{2g} bands overlap and result in $(O_2)^{2-}$ formation and O_2 release. For the Li-rich cathode, the Li–O–M bond is easily converted into Li–O–Li, guiding the continuous aggregation of unstable electrons around the oxygen atom, and producing oxygen once the kinetic barrier is low enough [12]. The oxygen is highly oxidative and easy to be reduced by electrolyte. The side reactions consume Li and O from the cathode as reactants, thus driving the loss of Li and O. The participation of electrolyte in the side reactions leads to its partial decomposition, generating by-products on the surface of cathode or in electrolyte, including
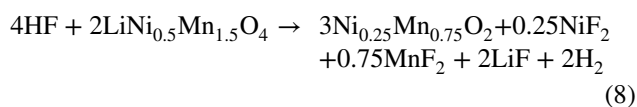
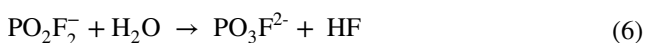**Fig. 2** Causality between the driving forces, kinetic pathways, structural degradation phenomena, and fade in electrochemical performance associated with the oxygen loss. Reproduced with permission from Ref. [10]. Copyright © 2022, American Chemical Society

CO_2, CO, H_2O, Li_2O, LiF, etc. [13]. This degradation process is also accompanied by cathode phase transition from layered structure to spinel due to the breaking of M–O transition metal bond which results in cracking and cavities [14].

Phase Transformation and Cathode Particle Cracking

Due to the restriction of uneven polarization and mass transfer, the formation of Li-rich and Li-poor domains in an electrode material induces undesirable intergranular stress, phase boundary movement, and particle pulverization [15]. Especially for nickel-rich layered oxides, Ni^{2+} (0.069 nm) and Li^+ (0.072 nm) possess similar ionic radius, thus nickel ions easily migrate to the adjacent lithium vacancies at a high degree of delithiation in cathode [16, 17]. This irreversible cation site rearrangement will cause the transformation from layered structure to spinel or rock salt phase and accelerate the attenuation of battery capacity. In the cutoff voltage range of 4.2–4.5 V, the decomposition of cathode is mainly caused by the high impedance rock salt phase generated on the surface. When the voltage is above 4.8 V, the irreversible phase transition of the bulk phase will break and form secondary particles due to mechanical stress, further aggravating the formation of the insulation layer and weakening dynamic behavior of lithium-ion intercalation/de-intercalation [18]. At present, people have carried out much research on these two problems and achieved significant progress mainly by the cathode surface coating or doping [19–24]. However, the capacity attenuation problem caused by electrolytes has not been thoroughly solved yet.

Transition Metal Dissolution and Migration

Transition metal ions (TM^{n+}) dissolution is another aging mechanism that is susceptible to the operation voltage of LIBs [25]. Up to now $LiPF_6$ is still the dominant lithium salt used in commercial lithium-ion batteries. The HF induced by the decomposition/hydrolysis of $LiPF_6$ with trace water stemming from cell materials is highly corrosive. In consequence, HF will subsequently attack cathode particles, leading to exacerbated dissolution of transition metal ions and thereby faster capacity degradation. LNMO is taken as an example to elaborate specific chemical reactions:

$$LiPF_6 + H_2O \rightarrow LiF + 2HF + POF_3 \tag{4}$$

$$POF_3 + H_2O \rightarrow PO_2F_2^- + HF \tag{5}$$

$$PO_2F_2^- + H_2O \rightarrow PO_3F^{2-} + HF \tag{6}$$

$$PO_3F^{2-} + H_2O \rightarrow PO_4^{3-} + HF \tag{7}$$

$$4HF + 2LiNi_{0.5}Mn_{1.5}O_4 \rightarrow 3Ni_{0.25}Mn_{0.75}O_2 + 0.25NiF_2 \\ +0.75MnF_2 + 2LiF + 2H_2 \tag{8}$$

Marco et al. [26] investigated the transition metal dissolution of the layered cathode material $Li_{1.04}Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ by total reflection X-ray fluorescence technique for element analysis. It turned out that the corresponding transition metal dissolution induced capacity loss at the cathode only accounts for 1.5% of overall capacity loss after 100 cycles, indicating that the dissolution of transition metal ions in the electrolyte has negligible effect on the capacity. However, once the dissolved Mn^{2+} and Ni^{2+} are deposited on the surface of anode through the electrolyte, they cause severe electrochemical performance degradation because even trace amount of transition metal cations in the SEI can lead to significant impedance increase [27–30]. Especially for lithium metal anode, the harm caused by the TM^{n+} deposition is much pronounced [31]. They trap reciprocating lithium ions in the SEI and promote lithium dendrites, which may even result in fire and safety hazards. In addition, TM ions free in the electrolyte or deposited on the electrode surface will catalyze continuous solvent decomposition due to their high reactivity.

Oxidation of the Electrolytes on the High-Voltage Cathodes

Electrolyte decomposition, particularly at the interface between the electrolyte and cathode, is the critical issue of electrochemical performance decay. The deteriorative electrolyte decomposition at higher upper cutoff voltage is driven mainly by two reasons: the intrinsic anodic instability of electrolyte and the formation of highly catalytic surface of high-voltage cathodes [32]. Ether solvents possess good compatibility for lithium metal, and the Coulombic efficiency is more than 99%. However, most of this electrolyte system can only match 4.3 V cathodes. Due to its intrinsic oxidation intolerance caused by the molecular structure, only a few systems can cycle stably under 4.5 V [33–35]. Generally, electrolytes for high-voltage cathodes based LIBs are non-aqueous systems (ethylene carbonate (EC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC)) and lithium salts (e.g. $LiPF_6$, LiTFSI (lithium bis(trifluoromethane sulfonimide)), $LiBF_4$). Such electrolyte systems are designed and optimized for LIBs operated at cutoff voltages ≤ 4.2 V. Understandably, 1 mol/L $LiPF_6$ in carbonates tend to occur violent side reactions with the delithiated cathode material under high-voltage (> 4.3 V) systems [36]. In the highly delithiated cathode state, the valence of the transition metal increases accordingly, corresponding surface with high chemical activity and catalytic

capability will directly accelerate the decomposition of the electrolyte. Although the common component EC has good SEI film forming ability and improves the interface compatibility between the electrolyte and the graphite anode, the EC decomposition by-products resulting from three main ways of nucleophilic reaction, dehydrogenation reaction and ring-opening polymerization cannot form a stable CEI [37, 38]. The oxidation behavior of carbonate is closely related to the surface state of cathode [39]. Theoretical calculation and electrochemical tests, such as linear sweep voltammetry, show that the carbonate electrolyte has no obvious oxidation on the inert metal surface even at high voltage above 5.0 V. However, once contacting the highly delithiated cathode surface (Fig. 3), its decomposition at a lower potential is significantly accelerated due to catalytic action of TM ions [40].

Optimization Strategies on the Anti-Oxidative Electrolytes

The Coulombic efficiency of conventional carbonate electrolyte is difficult to exceed 98.5%; the cycle life of lithium metal battery decreases more sharply when it is coupled with high-voltage cathodes. In the traditional low-concentration electrolyte (~ 1 mol/L), lithium ions and anions are fully dispersed among solvent molecules. As for high-concentration electrolyte, due to the limited number of solvent molecules, lithium salts cannot be completely dissociated, as shown in Fig. 4, contact ion pairs (CIPs, anion coordinates with a Li^+) and aggregation ion pairs (AGGs, anion coordinates with two or more Li^+) will be formed [41, 42]. High-concentration electrolytes are often employed for solvent systems with poor anode film forming ability, such as carbonate, nitrile, and phosphate ester. By reducing the solvent molecules in free state and forming anion-dominated SEI, high-concentration electrolytes not only allow high reversible Li^+ intercalation into the graphite without participation of EC or other film-formation enablers, but also notably improve the anodic stability of the electrolytes on high-voltage cathodes [43, 44]. However, its application is limited by high viscosity, low conductivity and high cost [45, 46]. In addition, the sudden reduction of battery capacity caused by electrolyte depletion after long time cycle is also one indispensable problem needs to be settled.

According to above discussion, the degradation mechanism in high-voltage LIBs can be summarized into four major categories: (I) oxygen evolution; (II) phase transformation and cathode particle cracking; (III) transition metal dissolution and migration; (IV) oxidation of the electrolytes on the high-voltage cathodes. The design of electrolytes used in high-voltage LIBs mainly seeks to address the latter two categories of the degradation processes. As is known, the EC-based electrolytes present poor oxidation resistance

which hinders the application of high-voltage cathode materials. To cater for the aggressive cathodes with higher voltage, extensive works been conducted in the field of new solvents with high anti-oxidative ability and film-forming additives to stabilize the CEI [47], both of which are proven to improve the compatibility of electrolytes against high-voltage cathodes.

Solvents with High Anti-Oxidative Ability

Fluorinated Carbonates

Compared with EC-based electrolyte, fluorinated carbonates possess lower HOMO and LUMO levels due to the electron-withdrawing effect of fluorine atoms, which means that the electrolyte is more likely to be reduced and involve in SEI formation at the negative electrode as well as oxidation resistance at the high-voltage cathodes. Especially for cyclic carbonates, partial fluorine substitution can effectively reduce their melting point, improve the interface passivation ability and flame retardation [48]. As shown in Table 1, on the basis of EC molecular structure, the melting point (T_m), boiling point (T_b), flash point (T_f) and dielectric constant decrease simultaneously with the increase in fluorination degree, as a result of increased polarity and less intermolecular interaction induced by electron-withdrawing F groups [49]. Due to steric hindrance, the viscosity of FEC (fluoroethylene carbonate) and DFEC (difluoroethylene carbonate) is obviously higher than that of EC. Nevertheless, despite steric hindrance result from high fluorination degree, the decreased intermolecular force makes its viscosity lower than EC instead. In terms of ions transportation, fluoridation also brings some disadvantages. Due to the weakening of intermolecular interaction, the dissociation ability of solvent to lithium salt becomes weaker, which is quantitatively reflected as the dielectric constant decreases from 90.5 to 18. Moreover, the diffusion coefficient of Li^+ (D_{Li}^+) increases with fluorination degree, but the anion diffusion coefficient, solvent diffusion coefficient and Li^+ transference number (t^+) showed no obvious correlation.

Li et al. [50] found that trace amount (~ 1 vol.%) of FEC electrolyte additive can improve the electrochemical performance of Li-rich high-voltage cathode materials. Liu et al. [51] mixed FEC, EMC and DEC with the volume ratio of 3:3:4 and applied this electrolyte system to $LiNi_{0.5}Mn_{1.5}O_4$/ $Li_4Ti_5O_{12}$ (LTO) pouch cell with 8 A·h capacity. They explored the gas production behavior of FEC and SEI formation mechanism on the surface of single electrode of LTO. The electrolyte with FEC showed better electrochemical performance than that without FEC, and the capacity retention reached 93.5% after 500 cycles. However, the introduction of FEC leads to more gas and apparent Mn^{2+} deposition, which may be caused by the metadecomposition reaction
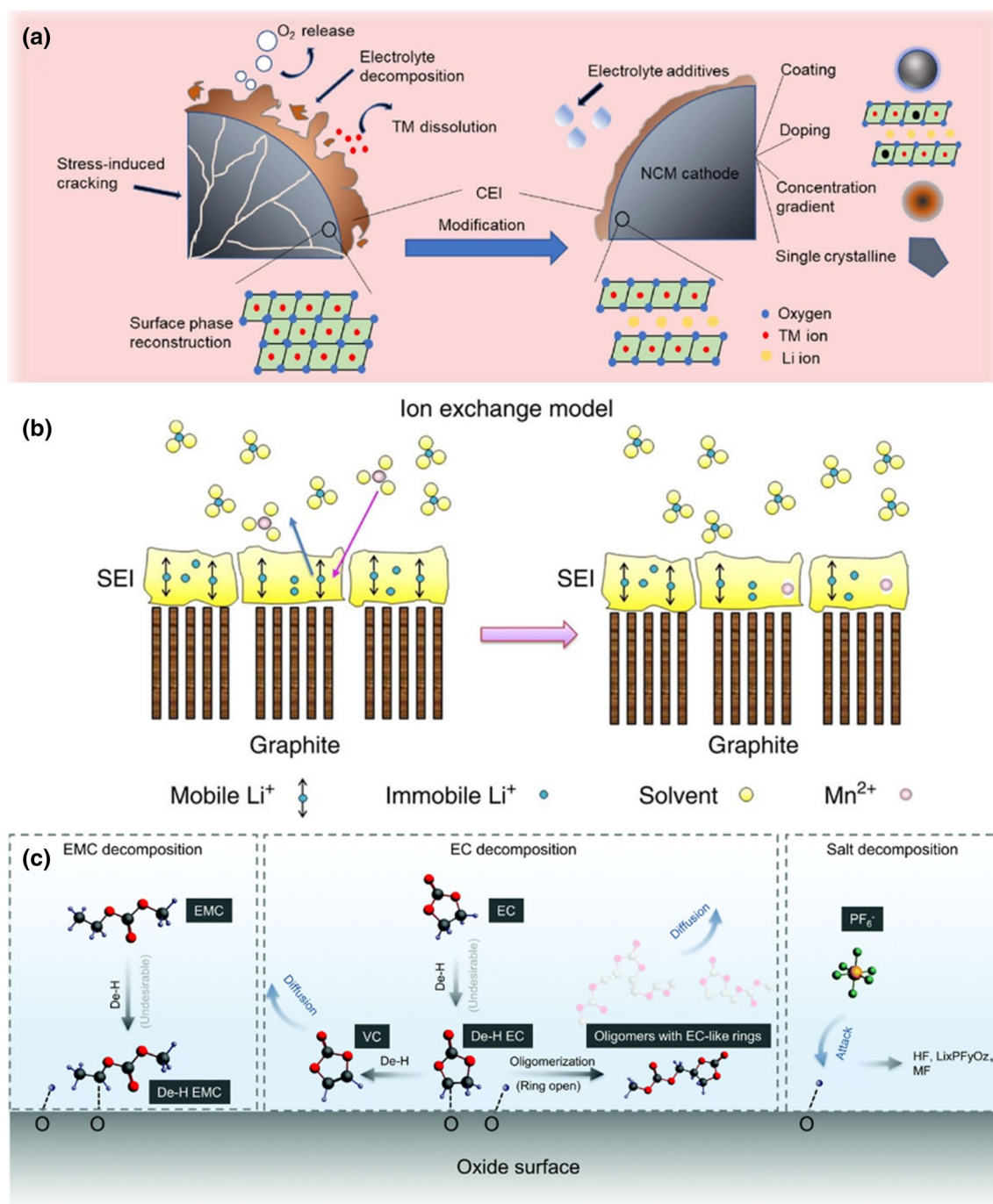
Fig. 3 a A schematic view of problems and countermeasures of NCM ($LiNi_xCo_yMn_{1-x-y}O_2$) materials when operating at high voltages. Reproduced with permission from Ref. [17]. Copyright © 2020, Wiley. **b** Proposed ion-exchange model for the Mn deposition on the graphite anode during the Mn dissolution, migration and deposition process in the graphite/LMO ($LiMn_2O_4$) cell. Reproduced with permission from Ref. [31]. Copyright © 2013, Springer Nature. **c** Proposed mechanism and pathways of electrolyte decompositions on NMC811. Reproduced with permission from Ref. [38]. Copyright © 2020, The Royal Society of Chemistry

and decomposition mechanism. In contrast, the change of physicochemical properties caused by fluorination of linear carbonate is not as prominent as that of cyclic carbonate (Table 2).

Although it is numerically reflected that the dielectric constant increases with fluorination, the electrostatic interaction between fluorinated solvent and lithium salt weakens, and the solvation ability decreases, thus ionic conductivity decreases instead [52]. Fan et al. [20] designed a
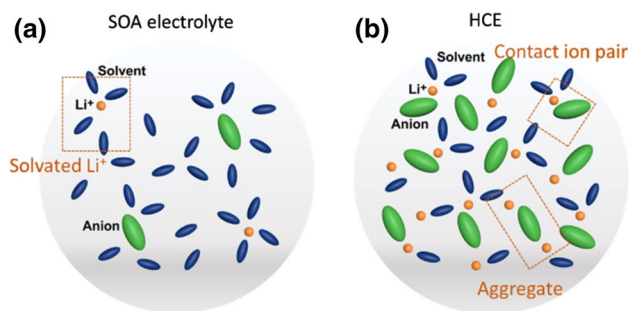
Fig. 4 Solvation structure diagram of a traditional electrolyte (SOA). **b** Solvation structure diagram of high-concentration electrolyte (HCE). Reproduced with permission from Ref. [41]. Copyright © 2020, The Electrochemical Society

non-combustible electrolyte with high-voltage resistance of 5 V by combining the advantages of cyclic and linear fluorinated carbonates, which consisted of FEC/FEMC (methyl trifluoroethyl carbonate)/HFE (1H,1H,5H-perfluoropentyl-1,1,2,2-tetrafluoroethylether) (mass ratio = 1:3:1). Combined with high-voltage and high-capacity cathode material LCPO and low-concentration lithium salt (1 mol/L $LiPF_6$), corresponding LIBs showed excellent cycling stability (capacity retention of 93% after 1000 cycles) (Fig. 5). The system forms a stable interface with low impedance on lithium metal anode. Surface analysis and quantum chemistry calculations further showed that the anode stability under ultra-high voltages is due to the fluorine-rich interfacial layer with only a few nanometers thickness. This FEC/FEMC/HFE system matches with 5.3 V LCMO cathode and takes on cycling stability more than 1000 cycles. General properties (T_m, T_b, T_f, etc.) and corresponding electrochemical properties of

solvents have been extensively studied. However, there is still a lack of systematic exploration and summary of the design rules for molecular structure [53].

Sulfone Electrolytes

Sulfone is an economical by-product produced by many chemical plants in tons and commonly used in high-temperature industries as extraction and reaction solvents for organic and inorganic preparations, as well as for metal and fungicide treatments. If these by-products can be used as high value-added chemicals in the field of lithium batteries, it will be very meaningful. Compared with ordinary carbonate and ether-based electrolyte, sulfone group possesses lower HOMO level, high flame point and high oxidation resistance due to its strong electron absorption ability [54–56]. Xu Kang et al. [57] first employed sulfone as electrolyte solvent of LIBs, and the electrochemical window reached 5.5 V (vs. Li^+/Li), which realized a remarkable progress in the anti-oxidation stability of organic electrolytes. A series of cyclic sulfone and linear sulfone solvents were synthesized and their physicochemical properties were analyzed and explored. It has been observed that these molecules generally do not undergo oxidation reactions around 5 V, but the solution of high viscosity and incompatibility with graphite and lithium metal anode still need to rely on grafting functional groups or blending with other solvents.

A. Abouimrane et al. [54] mixed ethyl methyl sulfone (EMS) and tetramethyl sulfone (TMS) by equal volume and applied to $Li_4Ti_5O_{12}/LiNi_{0.5}Mn_{1.5}O_4$ lithium battery system. Under high operating voltage, it can cycle stably for more than 1000 times at 2 C rate. In the combustion experiment, the electrolyte only took on faint flame for 45 s after

Table 1 Relevant physicochemical properties of EC, FEC, DFEC and F_3EC [49]

Chemical structure	T_m (℃)	T_b (℃)	T_f (℃)	Density (25 ℃) (g/cm³)	Dielectric constant (20 ℃)	Viscosity (20 ℃) (×10⁻³ Pa•s)	Conductivity (27 ℃) (mS/cm)	D_{Li}^+ (×10⁻⁶ cm³/s)
EC	37.5	238	145	1.32	90.5	1.94	6.9	1.12
FEC	20	210	130	1.48	79.7	4.40	4.2	1.46
DFEC	8.5	129	65	1.52	35.4	2.70	2.0	1.75
F_3EC	−54.5	91	-	1.60	18.0	1.28	-	-

Table 2 Physicochemical properties of linear carbonates namely DEC, F_1DEC, F_4DEC [49]

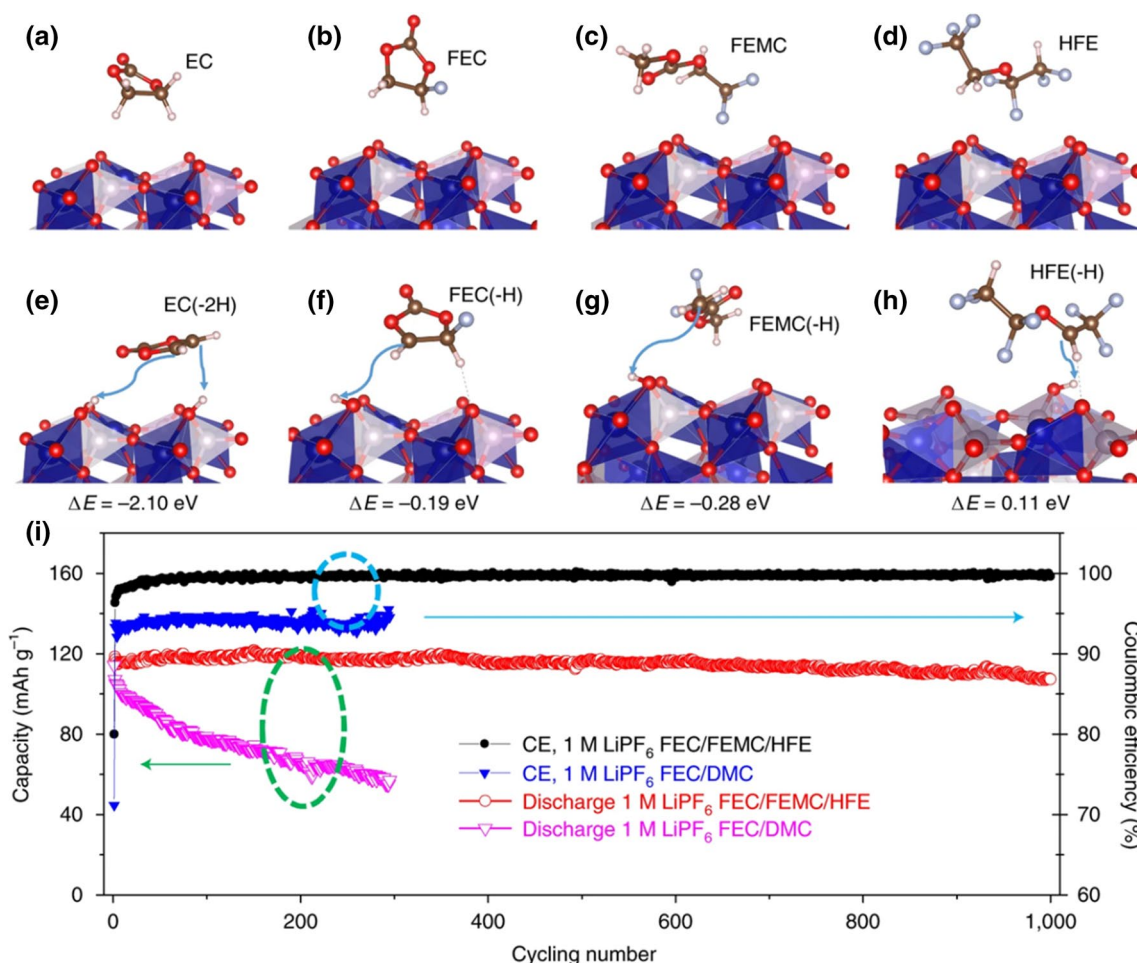| Chemical structure	T_m (℃)	T_b (℃)	T_f (℃)	Density (25 ℃) (g/cm³)	Dielectric constant (20 ℃)	Viscosity (20 ℃) (×10⁻³ Pa•s)
DEC	−75.0	126.0	40	0.98	2.8	0.82
F_1DEC	–	135.0	50	1.06	7.5	1.21
F_4DEC	−28.5	127.5	60	1.18	8.3	1.87

Fig. 5 a–h Reactivity of EC, FEC, FEMC and HFE solvents at the fully charged CoPO$_4$ (010) surface from PBE+U density functional theoretical calculations. Initial (**a–d**) and final (**e–h**) configurations and reaction energies. **i** Cycling stability of Li∥LCP cells using 1 mol/L LiPF$_6$ FEC/DMC and 1 mol/L LiPF$_6$ FEC/FEMC/HFE electrolyte when cycled at 1 C. Reproduced with permission from Ref. [20]. Copyright © 2018, Springer Nature

contacting with the fire, indicating flame retardation is much higher than traditional EC/EMC carbonate.

The sulfone eutectic mixture of EMS has been employed to investigate the solubility of lithium salts at room temperature, but the solvent still appears crystallization behavior as the temperature decreases gradually. Sun et al. [58] introduced ethoxyl into EMS ($T_m = 36.5$ °C), and the melting point and electrochemical window of new sulfone were both lower than non-functional EMS. The reason is that the ether group after functionalized modification is easy to oxidize under high voltage, resulting in lower oxidation potential. With the introduction of ether-oxygen chain, the melting point of solvent decreases to below room temperature, but the lithium solubility decreases simultaneously.

In addition to introducing ether-oxygen chain and alkyl branch chain, fluorination can further solve the problem of partial melting point and solvent molecules co-embedding in the graphite interlayer. For high-voltage electrolyte, the prerequisite is inhibiting the corrosion of aluminum current collector. LiPF$_6$ react with Al/Al$_2$O$_3$ under high voltage and form an effective passivation layer AlF$_3$, but lithium difluorosulfonimide (LiFSI) can not form a stable passivation layer, requiring extra use of aluminum-coating cathode cap. In order to solve the problem of aluminum corrosion, the TFPMS (structural formula is shown in Fig. 6) solvent obtained by local fluorination can achieve good passivation performance in the system of low concentration (molar ratio LiFSI: TFPMS = 1:8) (Fig. 7), and no obvious aluminum corrosion signal is observed through the infrared spectrum at 4.7 V [59].

DFT calculations show that C–S bonds are more likely to break, and lithium ions can form sulfonyl groups by extracting hydrogen atoms from solvents. The methyl sulfonyl group is relatively stable, while the trifluoromethyl group dissociates into sulfur dioxide and a trifluoromethyl radical. The free radicals further react with the solvent molecules,
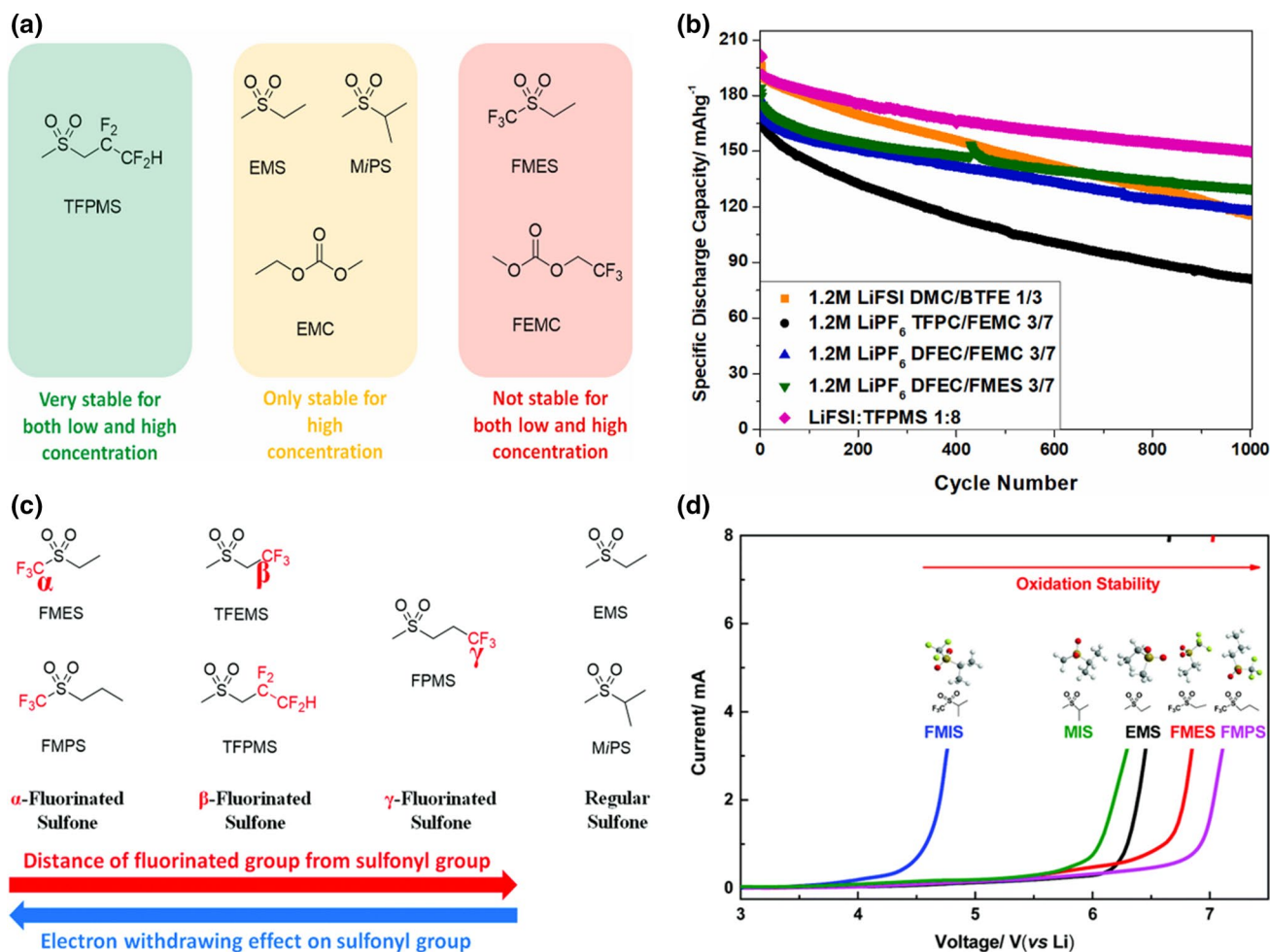
Fig. 6 a Structural formula of TFPMS, EMS, MiPS, FMES, EMC, FEMC. b Cycling performance of graphite‖NMC622 cells using various reported electrolyte formulations at room temperature. Reproduced with permission from Ref. [59]. Copyright © 2021, Elsevier. c Sulfones with fluorinated group in different position. Reproduced with permission from Ref. [60]. Copyright ©2021, The Royal Society of Chemistry. d Linear sweep voltammetry of the fluorinated sulfones and their non-fluorinated counterparts. Reproduced with permission from Ref. [61]. Copyright ©2017, The Royal Society of Chemistry

causing continuous solvent decomposition on the electrode surface [49]. Designing and synthesizing new molecules that can be employed as electrolyte solvents is a longtime struggle. Researchers often focus on one particular property and end up synthesizing molecules that are outstanding for that aspect, while ignoring other important properties that may be crucial to the stable operation of lithium-ion batteries. For example, fluorinated sulfones have excellent anodic stability because of strong electron-absorbing trifluoromethyl attached directly to the sulfoxide group. However, such a strong electron-withdrawing effect significantly increases the reduction potential of α-fluorinated sulfone, making it unstable to the graphite anode. The β-fluorinated sulfone (TFPMS) synthesized by Su et al. [60] not only has sufficient oxidation stability to withstand the high-voltage cathode of NMC622, but also takes on reduction stability to the graphite anode.

Nitrile Electrolytes

As previously stated, the oxidative stability of sulfone solvents is derived from the intrinsic antioxidant properties of the sulfone group at high voltage when used as bulk electrolyte solvents. In contrast, the anodic stability of nitriles electrolytes results from the selective chemisorption of cyanogroup with transition metal on the high-voltage cathode surface, which generates a layer of —C≡N–TM complexes. The oxidation voltage of nitrile solvent can reach more than 5 V, which surpasses the working voltage window of the existing mainstream cathode materials. Nitriles possess strong lithium dissociation ability, and the electron-withdrawing group –CN can effectively decrease the HOMO energy level of molecules. However, LUMO orbital also decreases with serious reduction instability, thus nitrile solvents cannot be applied to lithium metal batteries with
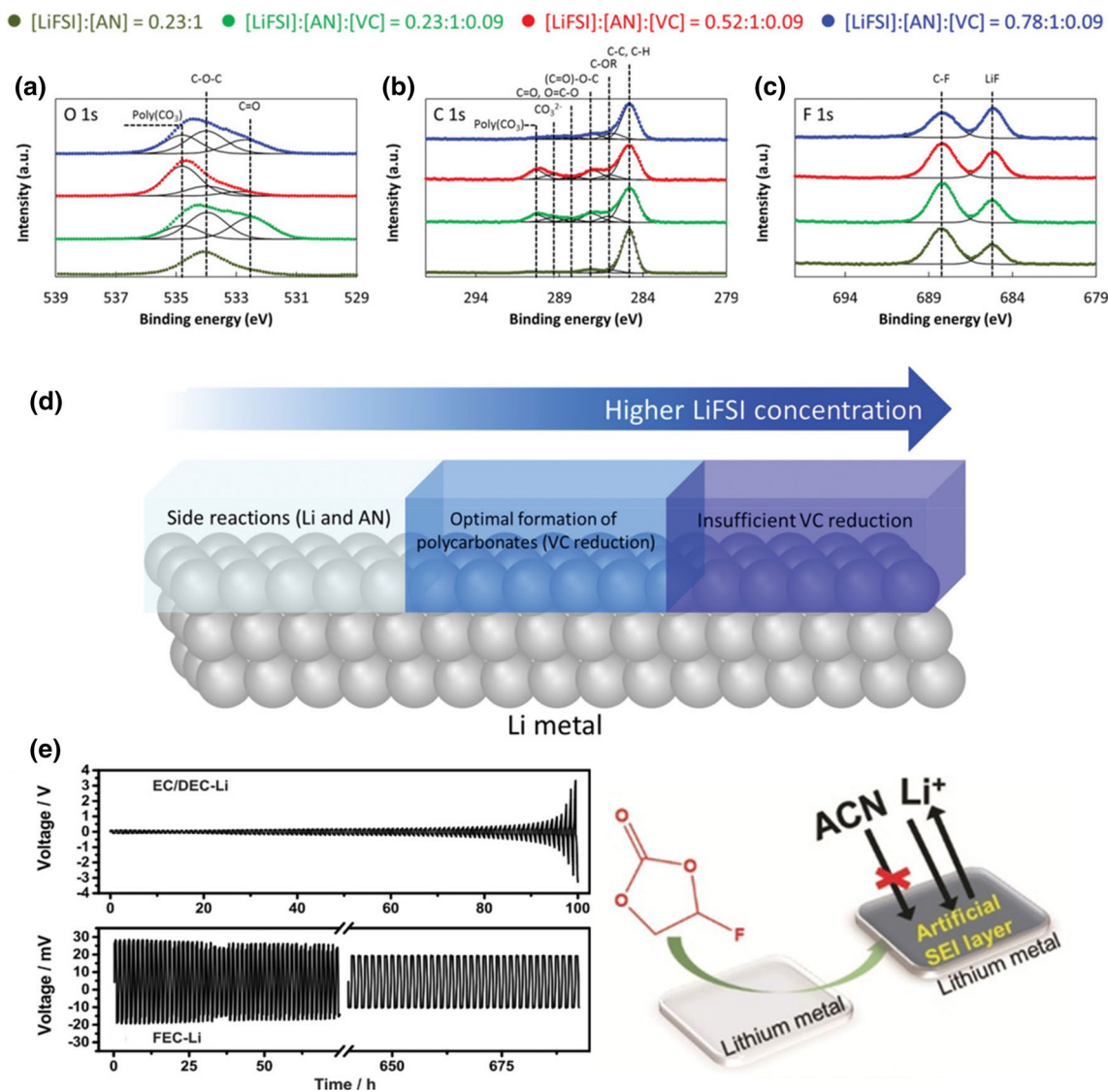
Fig. 7 **a–c** XPS spectra of a) O 1 s, b) C 1 s, and c) F 1 s for cycled Li surfaces in the LAV electrolytes of [LiFSI]:[AN]:[VC] = X:1:0.09 where X = 0.23, 0.52, and 0.78, and a VC-free electrolyte of [LiFSI]:[AN] = 0.23:1. **d** Schematic diagram of VC oxidation degree on lithium metal surface varying with LiFSI salt concentra-

tion. Reproduced with permission from Ref. [62]. Copyright © 2020, Wiley. **e** Voltage–time profiles of Li-symmetrical cells at 0.1 mA/cm² for 30 min per half cycle for EC/DEC-Li and FEC-Li in 1 mol/L LiPF₆/ACN at a temperature of 30 °C. Reproduced with permission from Ref. [63]. Copyright © 2018, Wiley

low concentration of single solvent system. Peng et al. [62] dissolved LiFSI (lithium difluoride sulfonimide) in acetonitrile (AN) to produce a high-concentration electrolyte (~ 10 mol/L). Due to the low viscosity of acetonitrile and the high dissociation ability of LiFSI, the non-aqueous electrolyte system showed excellent intrinsic ionic conductivity. The weak interaction between solvated Li⁺ and FSI⁻ results in higher electrical conductivity than dilute concentration carbonate electrolyte.

Ngoc Duc Trinh et al. [63] soaked lithium foils in FEC (vinyl fluoride carbonate) for 12 h in advance to construct a stable interfacial passivation film, and assembled Li//

Li symmetrical battery with 1 mol/L LiPF₆/AN electrolyte, which could be stably cycled over 1500 h. Borodin et al. [64] found that the solvation structure of cations was not as uniform as expected under high concentrations (10–21 mol/kg), and about 40% of lithium ions participated in the construction of three-dimensional fast ion conducting network. However, the Coulombic efficiency of Li–Cu measured by Aurbach method is only 14% even under such particular conditions. A trace amount of vinyl carbonate (VC) is introduced as an additive to stabilize the negative electrode interface.

In the exploration of high-voltage solvent, in addition to the structural design of bulk solvent molecules, the advantages of different solvents can also be combined. For example, FEC and FEMC are the key anti-oxidation components in FEC/FEMC/HFE full-fluorinated solvent system designed by Fan et al. [65], among which FEC has highest dielectric constant and high dissociation ability to lithium salt. As the most fluorinated component, HFE forms a LiF-rich SEI on the surface of lithium metal through reduction reaction.

Constructing Stable CEI

Based on the four failure mechanisms of high-voltage cathode-based LIBs described above, it can be determined that if the electrolyte under research can provide higher CEI stability than conventional electrolytes. For example, the interface film forming additives will help improve electrochemical performance. In addition, the use of additives with H_2O, HF and free radical scavenging capabilities, as well as strong chelating with transition metal ions, will also improve the interfacial compatibility between the high-voltage electrode and the electrolyte.

Assorted additives have been developed for the commercial electrolytes to stabilize the key interfacial chemistries for desired electrochemical performance, although the detailed underlying mechanism remains unclear in most cases. Considering the promoting effect on the electrochemical performance and the low cost of these additives, it is believed that the prevailed carbonate electrolytes with
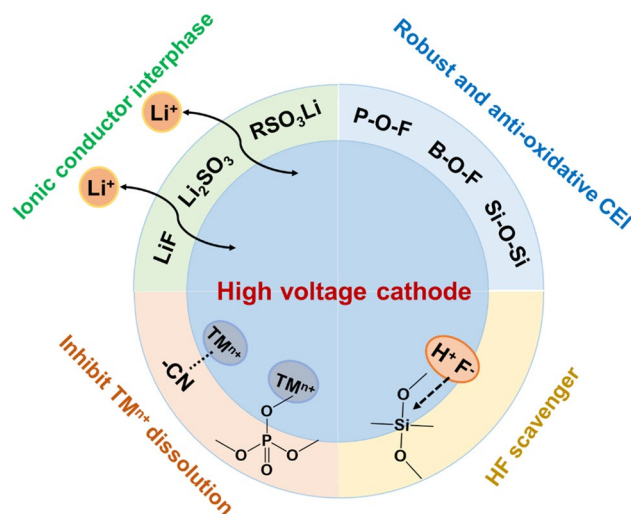

Fig. 8 The functions of different additives on high-voltage cathodes. Reproduced with permission from Ref. [5]. Copyright © 2022, Wiley

diversified additives will dominate the electrolyte infrastructures in the foreseeable future. These electrolyte additives could be divided into several categories according to their functions, such as SEI/CEI forming improver, HF scavenger, transition metal ion complexing agent, and salt stabilizer (Fig. 8). For example, the commonly used film-forming additive VC (vinyl carbonate) has the selective adsorption ability on cathode surface [66], and the interfacial protective
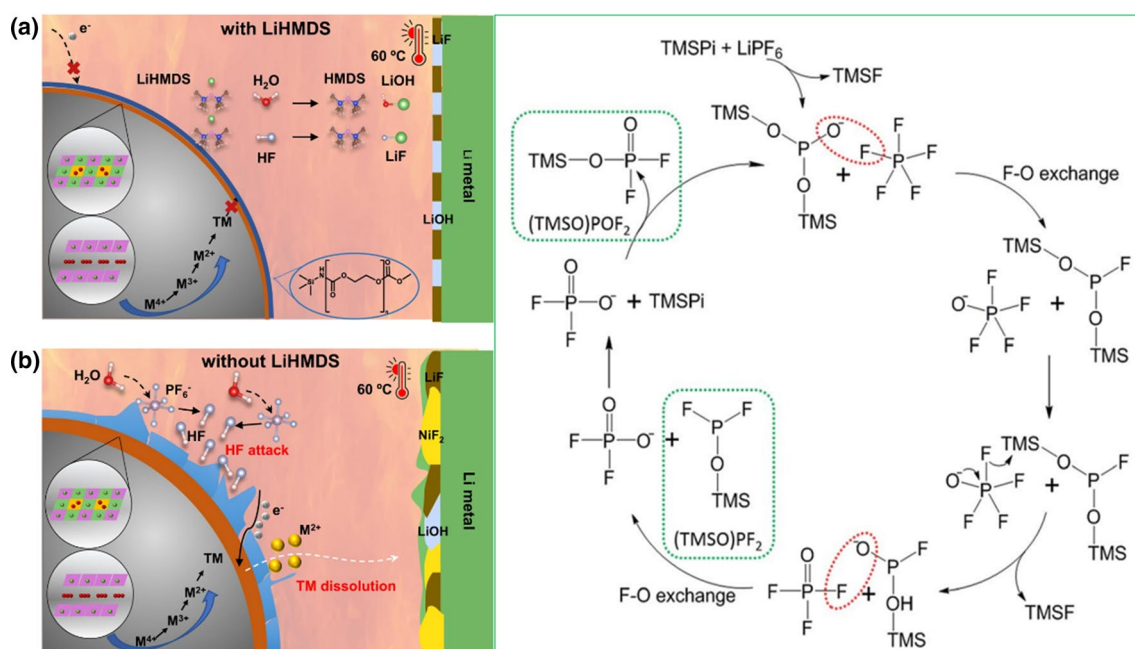

Fig.9 a–b Working mechanism of Li||NCM811 cells with/without LiHMDS cells at 60 °C. Reproduced with permission from Ref. [69]. Copyright © 2022, Springer nature. **c** Reaction mechanism between TMSPi and $LiPF_6$ in anhydrous and anaerobic conditions. Reproduced with permission from Ref. [70]. Copyright © 2016, The Royal Society of Chemistry

layer formed by ring-opening polymerization can block electron conduction between the cathode and electrolytes. The amount of unsaturated carbonate additives with similar structure should be controlled in a certain proportion. Overdose will lead to increased impedance and limited Li^+ conduction due to the formation of organic layer interface film.

Functional additives decompose preferentially before solvents and lithium salts in high-voltage systems, such as those containing fluorine, sulfur and phosphorus [67]. They can not only form highly ion-conductive interfaces in lithium fluoride and lithium sulfite, but also broaden the voltage window over 5 V. The decomposition by-products of phosphorus-containing additives [68], boron-containing additives and silicon-containing additives builds up O-rich anti-oxidative interphase to prevent further interfacial side reactions.

Through quantitative analysis and theoretical calculation, Zhang et al. [69] found that lithium hexamethyldisilazide (LiHMDS) could not only completely eliminates different contents of HF and H_2O in the electrolyte, but also inhibit the hydrolysis of $LiPF_6$. Under low oxidation potential, it could construct stable CEI on the surface of high-nickel cathode materials before electrolytes oxidation. The LiHMDS-derived CEI significantly prevents the Ni dissolution of NCM811, mitigates the irreversible phase transformation from layered structure to rock-salt

phase (Fig. 9a–b). As shown in Fig. 9c, the bifunctional additive TMSPi (tri (trimethylsilane) phosphite) can not only participate in the film formation of CEI, but also capture hydrogen fluoride produced during the aging process of the electrolyte [70]. Strong electrophilic TMS groups serve as anionic acceptors and react directly with $LiPF_6$ or its hydrolyzed products by forming Si–O groups. At present, TMSPi is usually applied to the electrolyte in a small amount (~ 1 wt%). Due to its continuous consumption in these two reaction routes, the ability of the battery to clean hydrogen fluoride would decay after long time circulation.

Due to the electron-deficit effect of central boron atom, boron-containing additives can cooperate with cations to stabilize carbonate. People initially scheduled to use $LiBF_4$, LiDFOB (lithium difluoroxalate borate), LiBOB (lithium dioxalate borate) [71, 72] as lithium salts. With the development of research, it was found that their HOMO energies were higher than that of common lithium salts and solvents, and the CEI formed in first circle as sacrificial salt decomposition was rich in B–O, B–F, b–O–B bonds (Fig. 10). It preferentially forms a dense protective layer rich in boron on the surface of the positive electrode. Therefore, these borate salts are extensively explored as the anti-oxidative electrolyte additive in recent years.

The functional additives with cyanide and phosphorus atom react with TM ions to produce complexes that suppress the
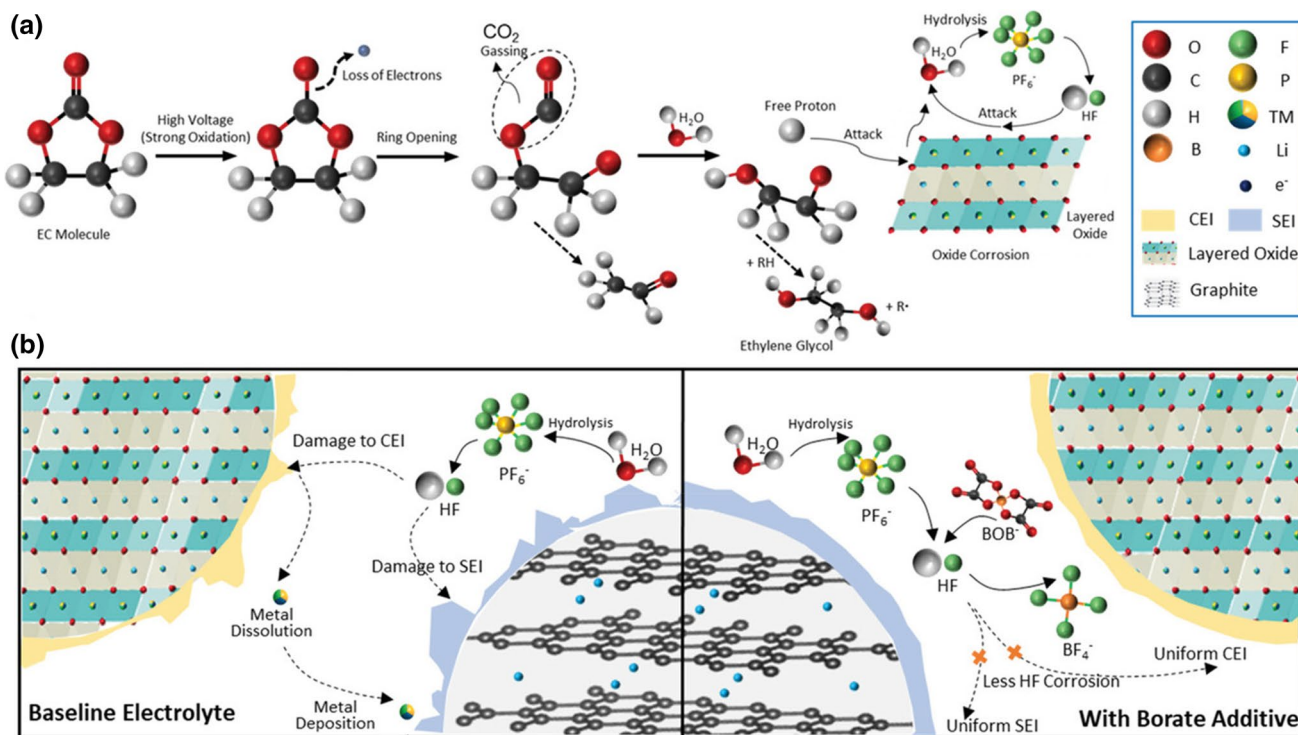

Fig.10 a Decomposition mechanism of EC-based carbonate electrolyte at high voltage. **b** Improved high-voltage stability brought by LiBOB as additive. Reproduced with permission from Ref. [73]. Copyright © 2022, Wiley

Fig.11 a Schematic diagram of adiponitrile as bifunctional additive in Lithium/ NCMA battery system. **b–c** Cycle life test of the Li/FCG73 batteries with different amounts of the electrolyte at a current density of 1.8 mA/cm² with 100 μL electrolyte and 25 μL electrolyte. Reproduced with permission from Ref. [76]. Copyright © 2019, Wiley
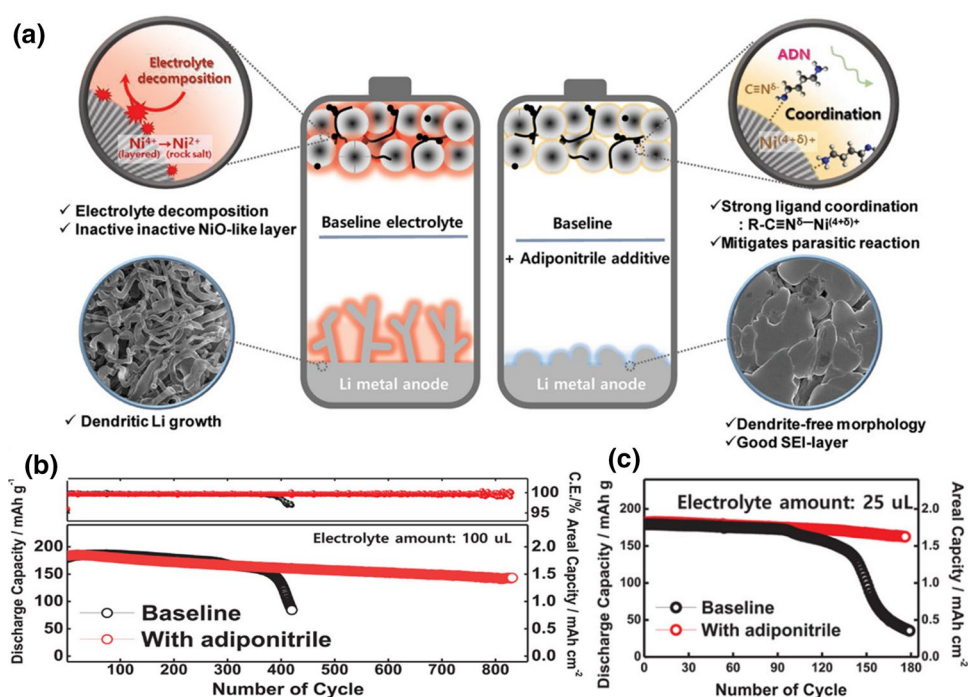
further dissolution of TM^{n+} [74]. As pure solvents, nitriles have been regarded as one of the promising solvated molecules for LIBs thanks to their high stability on the high-voltage cathodes and favorable dielectric factor [75]. Besides this, it is believed that some nitriles can also be utilized as additives with trace amount in the commercial carbonate electrolytes, stabilizing the carbonate electrolytes against oxidation under high voltages. Sun et al. [76] added 1 wt% adiponitrile into FEC/EMC ($v/v = 1:3$) carbonate system and matched with high-nickel cathode Li[$Ni_{0.73}Co_{0.1}Mn_{0.15}Al_{0.02}$]$O_2$. On the one hand, adiponitrile inhibited low-valence Ni ions deposition on the anode surface with strong bond coordination (Fig. 11). On the other hand, it could form LiF-rich SEI to promote the uniform deposition of lithium metal. They further explored the effect of electrolyte dosage on electrochemical performance, only 25 uL of electrolyte (a quarter of the original amount) can allow 180 stable cycles.

Summary and Perspective

This review systematically highlighted several promising opportunities offered by the high-voltage electrolyte chemistries to further boost up energy densities for next generation batteries. To cater for the hash requirements of high-voltage cathodes, breakthrough research has been conducted to widen voltage window of the conventional EC-based electrolytes, such as fluorinated carbonates, nitrile, sulfone electrolytes, and electrolytes, with multifunctional additives. For

the further development of electrolytes used in high-voltage LIBs, several suggestions have been put forward as follows:

Design of Electrolyte Additives

Varieties of additives are still the mainstream therapy for liquid electrolyte due to the feasibility and effectiveness of additives, such as silicon-containing, phosphate-containing, sacrificial lithium salts, and unsaturated carbonate. The research community want to obtain bifunctional or multifunctional additives, which can form anti-oxidation interfacial film through self-decomposition or interfacial interactions. The design principles of functional additives should include: (1) lower oxidation potential than EC solvent; (2) lower reduction potential than the SEI film forming agent, which does not affect the preference of EC or FEC to participate in SEI formation; (3) strong coordination with transition metal ions, which prevents deposition on the anode surface to further catalyze electrolyte decomposition; (4) it can scavenge HF, H_2O and other harmful substances produced in the aging process of electrolyte.

However, most reported additives achieve function by self-decomposition. When the additives are completely consumed, the long-term operation of the battery cannot be guaranteed. It is necessary to figure out the by-products formation process. In order to maximize electrochemical performance, specific additive formulations are required to embrace any changes in battery composition. However, none additive has been able to meet all of these demanding requirements. Therefore, the formulation of multiple

additives is becoming the mainstream to withstand high-voltage corrosion. Even for an additive, there should be different functional groups, which results in different free radicals and compositions of the anti-oxidative interphase.

Design of Electrolyte Solvents

At present, the use of additives in traditional carbonate electrolyte has obvious advantages, especially for the fast charging, low cost and so on. However, given the high safety requirements for future applications, more efforts should be devoted into other electrolyte systems with stronger anti-oxidation ability and flame retardancy. In the high-voltage electrolyte systems, sulfones, fluorinated carbonate, and phosphate ester-based electrolytes have intrinsic flame retardant and antioxidant advantages, which need to be further explored. Electron-withdrawing groups, such as nitrile and sulfone group, can reduce the HOMO and LUMO levels of molecules at the same time, resulting in even worse capacity decay. In terms of performance, it is difficult to take various factors (viscosity, conductivity, dipole, wettability, etc.) into account. What's more, polymer solid electrolyte is also an important direction for the construction of high-voltage lithium battery system in consideration of its high mechanical strength and high security [77, 78].

The change in solvent intrinsically alters the properties of the electrolyte, including HOMO and LUMO energy, as well as the interactions with lithium ions, anions, and solvents, all of which are closely related to the performance of the SEI/CEI layer on the electrode. In these promising EC-free solvent systems, fluorinated electrolytes (sulfones, nitriles, carbonates) have better anode stability, good passivation ability to most electrodes, good ionic conductivity and low flammability. Despite the relatively high cost of fluorinated electrolytes, it is believed that it will create a new market. In addition, the penetration of LIBs in multiple application areas will further promote the development of anti-oxidation fluorinated electrolytes.

Declarations

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