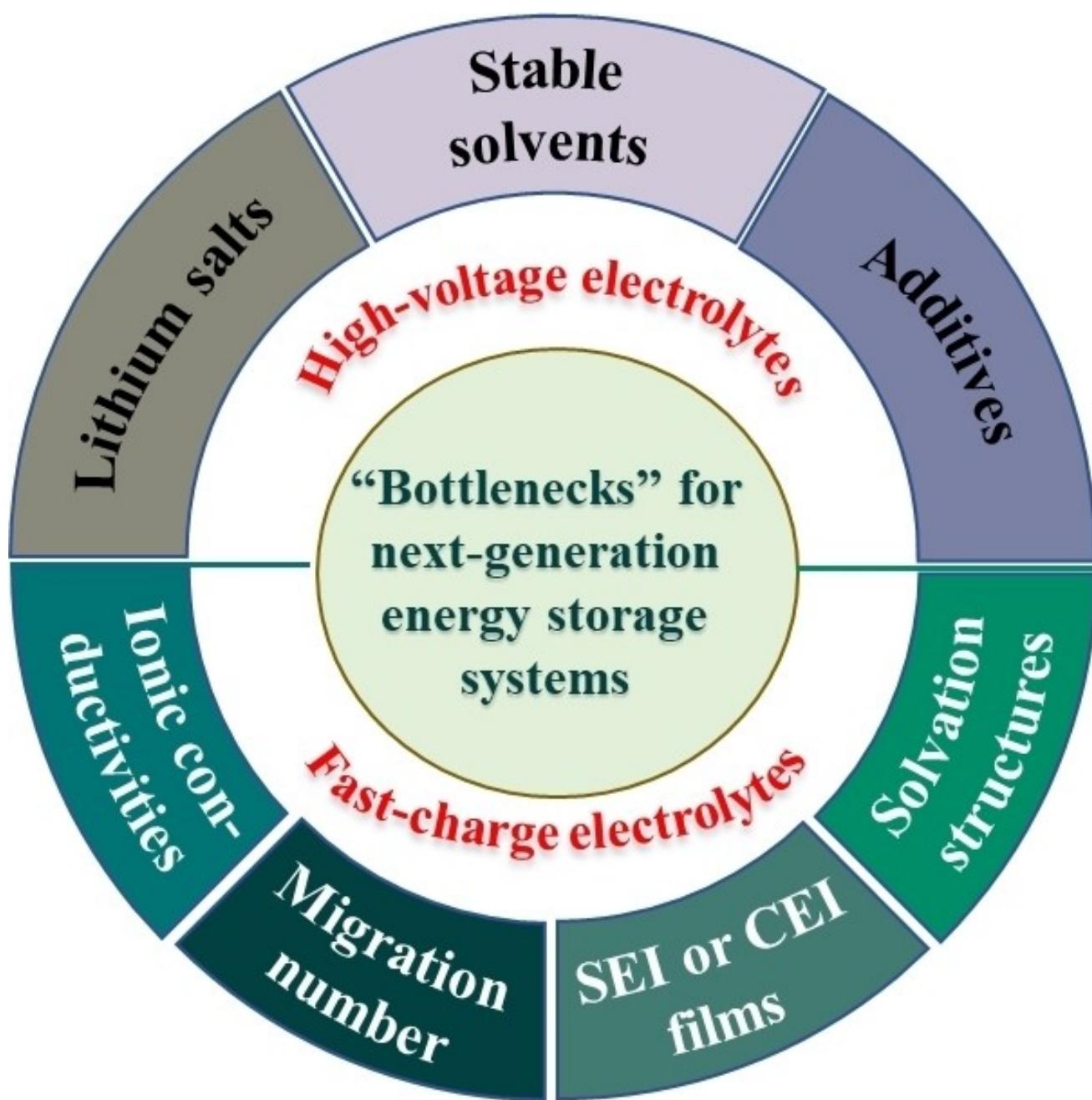


High-Voltage and Fast-Charge Electrolytes for Lithium-Ion Batteries

Shuang Wan^{+[a]}, Weiting Ma^{+[a]}, Ying Xiao,^{*[a]} and Shimou Chen^{*[a]}



Lithium-ion batteries (LIBs) with high energy density and fast-charge capability are urgently required for the ever-growing demands for electric vehicles and hybrid electric vehicles. To achieve this demand, as one of the important components, electrolytes are required to work well at a high voltage to fulfill the good performance of high energy density batteries and facilitate the fast-charge process. In this review, we mainly focus on the electrolytes design for LIBs under high-voltage and fast-

charge conditions. The bottlenecks and the typical resolving strategies referring to lithium salts, solvents, solid electrolyte interface, additives and solvent structures in electrolytes are presented in detail. Finally, we propose the challenges regarding electrolytes design insight and inspiration for LIBs under the two conditions to give a better guide for the rationale design of the high energy density and fast-charge devices in the future applications.

1. Introduction

Lithium-ion batteries (LIBs) have been widely investigated and applied in our daily life due to their high energy density, long cycling life and environment-friendly.^[1] In the development history of LIBs, LiCoO₂ (LCO) was early invented by Goodenough and his group in 1980, the material has a planar Li⁺ transport channel, high ionic conductivity, and a theoretical capacity of up to 274 mAhg⁻¹.^[2] However, the real commercial application of LCO by SONY company was 1991.^[3] One of the important reasons was that no suitable electrolyte could meet the demands of LIBs until propylene carbonate (PC) was replaced by ethylene carbonate (EC),^[4] causing the big commercial application of LIBs as mobile energy in computer, communication and consumer electronics (3 C) products, electric vehicles (EVs) and hybrid electric vehicles (HEVs). Obviously, the evolutionary process of electrolytes is not only motivation but also bottleneck technology for LIBs. Especially, with the ever-increasing demands for EVs, HEVs and defense applications in extremely harsh conditions, developing advanced electrolytes with appealing performance in high-voltage and fast-charge aspects is highly desirable.^[5,6]

Although the high-voltage property is relevant to cathodes, anodes and some other components in the battery, the function of electrolytes are believed to the dominate one. On the one hand, the stability of electrolytes and the matching to electrodes decide the high-voltage application of LIBs.^[5] On the other hand, the development of high-voltage material is relatively consummate, while there are no stable and mature electrolyte systems for matching the materials, especially above 4.5 V, causing high reactive activation of cathode surfaces and the increased battery impedance.^[7] Therefore, it is significant to find high-voltage electrolytes to match the materials.

Additionally, fast charging makes the electronic devices more popular and convenient, which is also the key technology for LIBs and has exhibited extensive interests and

drawn the market's eyes these years. As well-known, the charge property of the batteries deeply depends on the migration rates of Li⁺ and electrons between the two electrodes. In the process of fast charging, the movement of high flux ions in the battery system leads to the lithium dendrites growth and the repeated growth of solid electrolyte interphase (SEI)/cathode electrolyte interphase (CEI) films, which further leads to the decreased Coulombic efficiency, enlarged potential polarization, and safety risks.^[8] However, these detrimental factors could be improved by introducing suitable electrolytes. The high ionic conductivity, high migration number, thin and uniform interface films and weak solvation of the electrolytes can enhance the Li⁺ transport rate and improve the fast-charge capacity.^[9,10]

Considering the important roles of electrolytes in improving the high-voltage and fast-charge properties of LIBs, in this review, we mainly focus on the mechanisms of electrolytes at high-voltage and fast-charge conditions to provide a unified governance framework that know the electrolytes for batteries. At first, the main challenges for high-voltage and fast-charge electrolytes are proposed. Then the mechanism analysis and failure properties from the perspectives of lithium salts, solvents, solvated structures, SEI or CEI films, interface reactions and so on are discussed in detail. Finally, we provide summary and prospects for the future development of electrolytes with high-voltage and fast-charge properties.

2. Challenges for High-Voltage and Fast-Charge Electrolytes

The traditional carbonate-based electrolytes possess a poor oxidation stability at a high-voltage, for instance, the commonly used EC solvent may decompose into polycarbonate on the cathode surface at a high-voltage up to 4.3 V and transform into Li₂CO₃ and release O₂/CO₂ gases, leading to poor connection of electrodes and battery failure.^[11] The unstable commercial carbonate-based electrolytes will form inorganic or oxygenated decomposition components on the cathode surface and largely restrict the practical application of high-voltage cathodes.^[12]

In addition, fast charging has become significant important technology for customers to accept the electromobility.^[13] In the fast-charge process, the diffusion rate of Li⁺ and porous materials determine the charging and

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discharging time, thereby affecting the fast-charge capability of the battery. The low diffusion rate of Li^+ in cells will cause ohmic polarization and concentration polarization, which eventually leads to the energy loss and heat generation, bringing about thermal runaway and overcharge.^[9] Besides, the non-uniform and fast lithium plating will induce the generation of lithium dendrite and battery short circuit. Generally, the morphology of the lithium deposit is highly dependent on the charge rates and temperature in the practical application. Big charge rate may cause the rapid deposition of lithium and the generation of huge heat in the battery. These adverse factors may change the conductivity of the electrolyte and lead to the degradation of lifetime.^[14,15] The relationship between degradation mechanism and thermal safety characteristics was showed orderly in Figure 1.^[15]

3. High-Voltage Electrolytes

In order to realize the high energy density, the high-voltage electrolytes are required to be stable at the range of working potentials and inert to other components within the battery, which should have good electrical conductivity and electronic insulation as well as the ability of fast ion transport.^[16] In this part, we summarize the recent progress of high-voltage electrolytes from the perspectives of lithium salts, solvents, ionic liquids and additives to provide ideas for designing high-voltage electrolytes of LIBs.

3.1. Optimizing lithium salts

LiPF_6 is the most widely commercialized lithium salt in carbonate solvents with high dielectric constant (such as in PC/EC) and low viscosity, such as in DMC (dimethyl carbonate)/

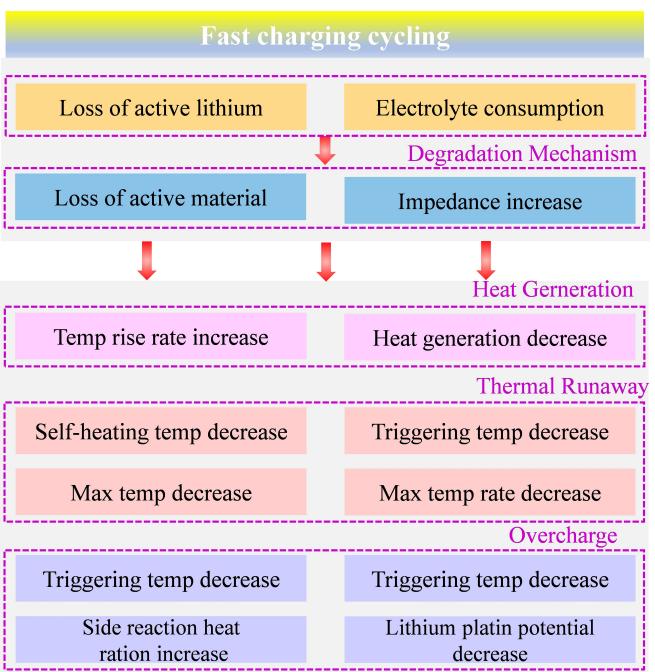


Figure 1. Relationship between degradation mechanism and thermal safety characteristics caused by fast-charge cycling. Reproduced with permission from Ref. [15]. Copyright (2022) American Chemical Society.

EMC (ethyl methyl carbonate)/DEC (diethyl carbonate).^[17] However, LiPF_6 is not the perfect salt due to the unstable thermal properties and high trace moisture sensitivity. At harsh operated conditions, LiPF_6 can generate unfavorable products including POF_3 and HF, resulting in the corrosion of protective films on the electrodes, the dissolution of cations from cathodes and the decomposition of solvents.^[18,19] Thus, some thermally and chemically stable lithium salts such as lithium imides (LiTFSI , LiFSI) and lithium borates (LiDFOB , LiBOB) have



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been proposed to replace the traditional LiPF₆ at high-voltage operation. Except for their high cost, the lithium borates salts have low solubility in carbonate solvents, while lithium imides have a high solubility but strong corrosion of aluminum (Al)-foil current collector beyond 4 V. Combining LiBOB with other lithium salts are demonstrated to be efficient to prevent the corrosion phenomenon (Figure 2a) and enhance the high-voltage performance.^[20] According to the previous reports, the mixture of LiTFSI, Li(CF₃SO₂)₂ and LiBOB in nitrile groups-based solvents could exhibit a wide voltage window of 6.0 V vs. Li⁺/Li. The 1 M LiTFSI electrolyte in adiponitrile (ADN) has been proved to have an oxidation voltage of 6.2 V by cyclic voltammetry (CV) scan.^[21] While the 1.28 M LiTFSI-FEC (fluoroethylene carbonate)/FEMC (methyl (2,2,2-trifluoroethyl) carbonate)-D2 (tetrafluoro-1-(2,2,2-trifluoroethoxy)) could improve the LiNi_{0.5}Mn_{1.5}O₄ (LNMO) | Li cell to operate at 5.0 V and showed an excellent capacity retention of 93.7% after 1000 cycles (Figure 2b). Benefiting from the stable lithium salt of LiTFSI and the large amount of F atoms in the solvent structures, the F-rich SEI was generated. The electrolyte was

demonstrated to contribute to the long cycle performance of battery at a high-voltage.^[22]

In addition to introducing composited salts, elevating the lithium salts concentration (> 3 M) is also a commonly used method to prevent the Al foil corrosion and elevate the operation voltages above 4.5 V.^[23–25] Therefore, high concentration electrolytes (HCEs) have been widely applied to improve the performance of LIBs with high-voltage property. As for high concentration electrolytes, lithium ions are highly coordinated with the solvents, resulting in the reduction of free solvent molecules in the electrolyte composition. The remaining anions participated in the film-forming reactions and increased the inorganic composition of SEI/CEI films. Because the particular structure of electrolytes and anion-derived electrodes/electrolytes films, the electrolytes were endowed with some intriguing characteristics, such as the improved oxidation resistance, wide operation voltage window, and high corrosion resistance for current collectors. As a result, the high-voltage stability of the battery can be highly improved.^[11] For example, Xu et al.^[7] reported the 3.25 M LiTFSI in a carbonate-free solvent of sulfone (SL) as an electrolyte for high-voltage LNMO/graphite full cell,

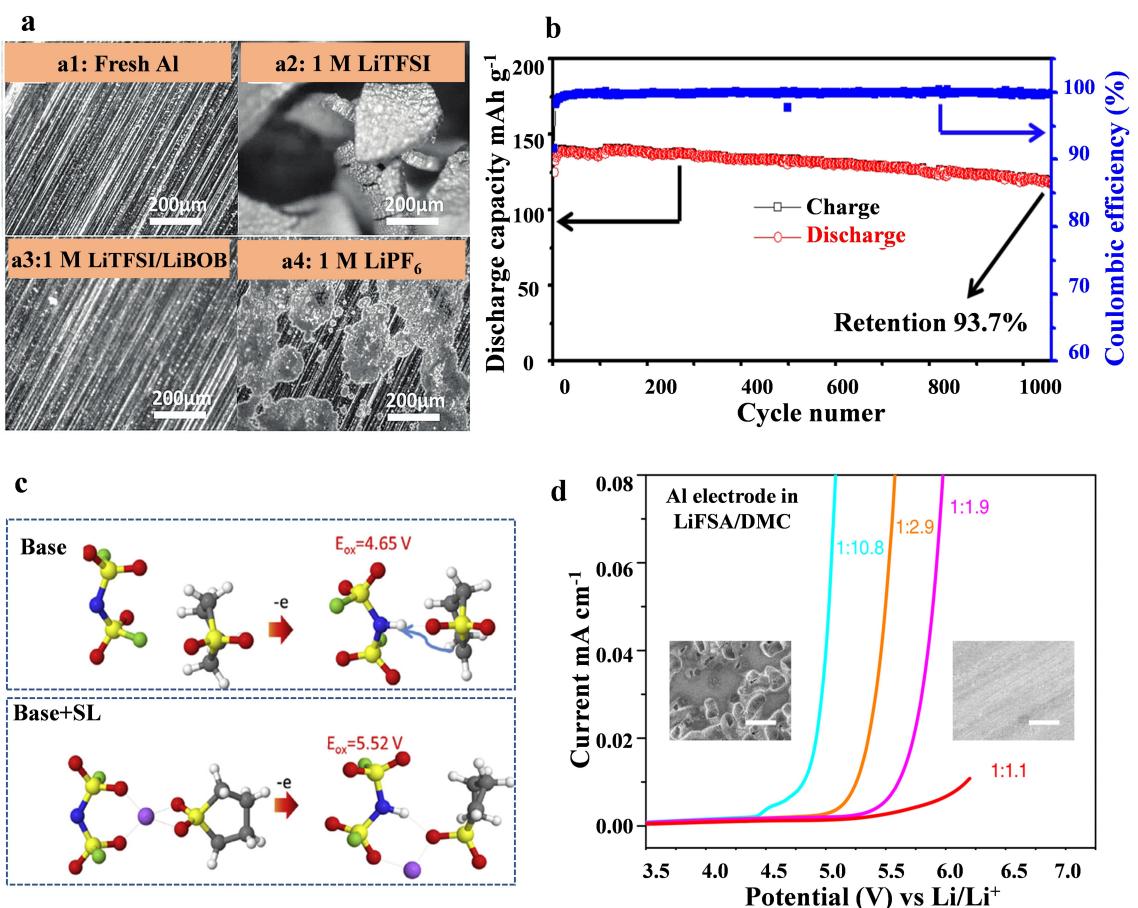


Figure 2. a) SEM of fresh Al foil (a1) and Al foils after anodic polarization tests at 3.9 V and 60°C for 5 days in three electrolytes (a2–a4). Reproduced with permission from Ref. [20]. Copyright (2019) Wiley-VCH. b) Cycling performance of LiNi_{0.5}Mn_{1.5}O₄ | Li cell in 1.28 M LiTFSI-FEC/FEMC-D2 electrolyte at room temperature. Reproduced with permission from Ref. [22]. Copyright (2020) Nature Publishing Group. c) Oxidation potential (vs. Li/Li⁺) with clusters surrounded by Base and Base + SL solvent model. Reproduced with permission from Ref. [7]. Copyright (2018) Elsevier. d) LSV of Al electrode in various concentrations of LiFSA/DMC electrolytes in a three-electrode system. The SEM of the Al surface polarized in the dilute 1:10.8 (left of panel) and super concentrated 1:1.1 (right of panel) electrolytes. Reproduced with permission from Ref. [23]. Copyright (2016) The Authors. Published by Springer Nature.

the cell could retain about 70% capacity after 1000 cycles at 4.85 V. The SL molecules participated in the formation of solvated structure with Li^+ , endowing a high working potential enhanced from 4.65 V to 5.52 V (Figure 2c). The anions in salt were demonstrated to be reduced to LiF-rich interphase film that enabled excellent reversible cycling performance and prevented the graphite from solvent co-intercalation. The smaller free solvent fraction and FSI anions adsorbed on the positively charged cathode contributed to improving the electrolyte stability at the high-voltage. Furthermore, Wang et al.^[23] proposed an electrolyte with 5.49 M $\text{LiN}(\text{SO}_2\text{F})_2$ (LiFSA) in DMC and demonstrated the electrochemical performance of LNMO/graphite cell operating at a high voltage. A smoother Al surface (Figure 2d) was obtained for the superconcentrated electrolyte (LiFSA:DMC = 1:1.1 molar ratio) compared with that of the traditional electrolyte (LiFSA:DMC = 1:10.8 molar ratio), suggesting the super concentrated electrolyte prevented the corrosion of Al current collector and protected the integrity cathode. Benefiting from these merits, the cell showed over 95 % discharge capacity retention after 100 cycles at 3.5–5.2 V.

Furthermore, Li et al.^[24] introduced F-rich electrolyte with 7 M LiFSI in FEC solvent for LNMO/Li cell and improved the Coulombic efficiency to 99.64 %. The cell in the designed electrolyte also demonstrated excellent performance even at

5 V, the reason of which was contributed to the LiF nanolayer formed in the F-rich electrolyte. The F-rich SEI prevented the growth of Li whiskers and formed ductile morphology with less residual stress, which benefiting for the uniform Li deposition (Figure 3). Doi et al.^[26] investigated nearly saturated concentration of 7.25 mol kg⁻¹ LiBF_4 as a salt in PC solvent for the spinel LNMO/Li cell. Although the highly concentrated electrolyte held a high viscosity and low ionic conductivity, the cell still showed relatively small polarization in the charge/discharge process and excellent cycling performance between 3.5–5.0 V. The free PC solvents declined with the increase of salts concentrations leading to a lower HOMO value of solvation Li^+ in PC, which was believed to facilitate the elevated oxidation of the electrolyte against high working voltage.^[27]

Although HCEs exhibited great promising in improving the performance of LIBs at high-voltages, there also exist many disadvantages including low conductivity, poor penetration and high cost. Strategies such as adjusting the formulas of lithium salts, introducing solvents with good wettability and adding dilute-solvents are demonstrated to be efficient and have received intensive investigations in recent years.^[28–30] By introducing 1,1,1,3,3-hexafluoroisopropyl methyl ether (HFP) as dilute-solvent into 3 mol L⁻¹ LiPF_6 DMC/FEC to form located high-concentration electrolyte (LHCE),^[29] the corresponding LNMO/Li cell delivered excellent discharge capacity of 122.2 mAh g⁻¹ after 400 cycles at 2.0–4.8 V. The dilute-solvent HFP could help the cathode form a dense protective film on the surface with 5–8 nm thickness. At the same time, FEC and HFP also offered F-source and promoted the formation of abundant LiF-contained SEI film, which was beneficial for suppressing the continuous electrolytes decomposition.

In order to clearly understand the advantageous effects of HCEs or LHCEs for LIBs at high-voltages. We selected some typical cycling performances of representative batteries in selected concentrated electrolytes at or above 4.8 V in Table 1, some of them have already been described in the above.

From Table 1, LNMO/Li cells are popular in high-voltage LIBs systems above 4.7 V, while the operation voltages of other cathodes are often lower than LNMO. Ren et al.^[33] designed an ether-based LHCE composed of LiFSI-1.0 DME-3.0 TTE (1,1,2,2-

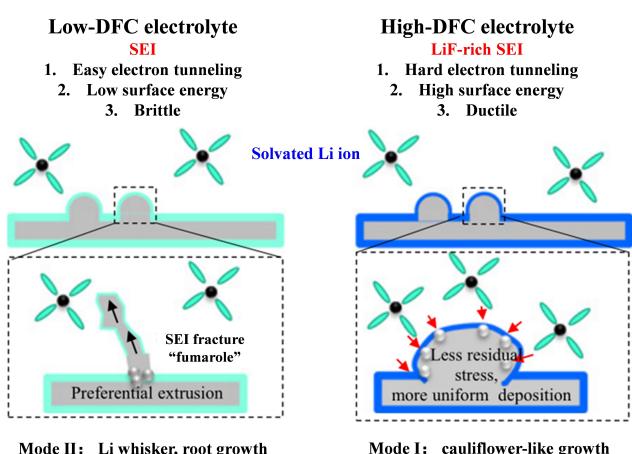


Figure 3. Schematic diagram of corresponding Li growth mechanism in two electrolytes. Reproduced with permission from Ref. [24]. Copyright (2018) Published under PNAS license.

Table 1. Cycling performance of LIBs in selected high-voltage electrolytes.

Electrolytes	Electrodes and cutoff voltage	Cycling performance	References
7 M LiFSI FEC	$\text{Li} \parallel \text{LNMO}$, 5.0 V	94.3 %@150th	[24]
7.25 M LiBF_4 PC	$\text{Li} \parallel \text{LNMO}$, 5.0 V	92.5 %@50th	[26]
4.27 M LiPF_6 PC	$\text{Li} \parallel \text{LNMO}$, 5.0 V	92.3 %@50th	[27]
5.49 M LiFSI DMC	$\text{Li} \parallel \text{LNMO}$, 5.2 V	95 %@100th	[23]
4.0 M LiTFSI + 0.5 M LiDFOB FEC/DMC	$\text{Li} \parallel \text{LNMO}$, 4.9 V	88.5 %@500th	[28]
5.3 M LiFSI TMP	Graphite $\parallel \text{LNMO}$, 4.8 V	96 %@100th	[25]
3 M LiPF_6 DMC/FEC/HFP (6:1:3 by vol)	$\text{Li} \parallel \text{LNMO}$, 5.0 V	94 %@400th	[29]
3.0 M LiPF_6 EC/EMC/DMC (1:1:1 by vol)	$\text{Li} \parallel \text{Li}_{1.2}\text{Ni}_{0.15}\text{Fe}_{0.1}\text{Mn}_{0.55}\text{O}_2$, 4.8 V	94 %@500th	[31]
5.4 M LiBF_4 PC/FEC (1:1 n/n)	Graphite $\parallel \text{Li}_2\text{CoPO}_4\text{F}$, 5.2 V	70 %@700th	[32]
2.5 M LiBF_4 PC/HFE (2:1 by vol)	$\text{Li} \parallel \text{LNMO}$, 5.0 V	96 %@45th	[30]
3.25 M LiFSI sulfolane	MCMB $\parallel \text{LNMO}$, 4.85 V	69 %@1000th	[7]

tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether) for LCO/Li cell at 4.5 V. The CEI structure in the ether-based electrolyte was 5–8 nm thick after 300 cycles, while the thickness in carbonated-base electrolytes was about 7–11 nm. Moreover, the high thickness of disordered rock salt in carbonated-base electrolytes presents the Co ion dissolution during cycling comparing with the 2 nm cation mixing signs in ether-based electrolyte, contributing to the fast transport and uniform deposition of Li⁺ manifesting that the important role of thin and uniform CEI film greatly enhancing the cycle life of LCO at high-voltages. Ingeniously, Zhao et al.^[34] developed a new LHCE system of 1.5 M LiFSI in 2-(2,2,2-trifluoroethoxy)-4-(trifluoromethyl)-1,3-dioxolane (TTD) and 1,2-dimethoxyethane (DME) (1.5 M LiFSI-8TTD-2DME) for NCM811/Li cell system. TTD with much lower HOMO energy value (-8.52 eV) than EC (-8.47 eV) contributed to its oxidation stability at a high-voltage. Consequently, high oxidation stability up to 6.0 V and high CE of 99.3% over 300 cycles at 2 mA cm^{-2} and 99.4% over 210 cycles at 3 mA cm^{-2} in Li/Cu half-cell were obtained. The electrolyte was used in NCM811 cathode and achieved 80% capacity retention after 100 cycles at 4.7 V. The excellent performance of electrolyte was attributed to the strong combination between Li⁺ with DME and FSI⁻ and the sturdy SEI film.

In conclusion, the commercial LiPF₆ is easy to decompose at high-voltages, which cause corrosion of interface films and decomposition of electrodes. Lithium imides could replace LiPF₆ for their high thermal stability and high ionic conductivity at high-voltages. However, the low concentration lithium imides have a strong corrosion for Al foil. While increasing the concentration of lithium imides and mixing with other lithium salts proposed by researchers are proved effective. On the one hand, although high concentration lithium salts could elevate the operation voltage above 4.5 V, the high cost, low conductivity and poor wettability limit the further application. On the other hand, lithium borates are demonstrated to be serviceable to prevent Al corrosion, but their low solubility in carbonate solvents determines their harsh choice for solvents. Therefore, small amounts of lithium borates salts are generally used as additives with lithium imides to improve the high-voltage electrochemical performance of LIBs.

3.2. Using high-voltage stable solvents

In view of the poor oxidation stability of EC at a high-voltage, lots of replaceable solvents include fluoride, sulfone, dinitrile solvents or ionic liquids have been proposed to improve the stability problem of the electrolyte.^[11,35,36]

Among them, fluorinated solvents have a high oxidative stability and wettability due to their high electronegativity and low polarizability of fluorine atom,^[35,37–39] which are considered as promising candidates for high-voltage electrolytes. Fluorinated carbonates and fluorinated ethers could form stable fluorine-rich CEI film on cathode and protect the cathode from oxidation at a high-voltage, which were used as stable solvents to improve the cathode stability and Coulombic efficiency of the batteries at high-voltages. The stable CEI could effectively

passivate the positive electrodes surface and inhibit the generation of high-voltage side reactions, then expanding the electrochemical stability window of electrolyte from thermodynamics.^[35,36] Im et al.^[40] designed a perfluorinated electrolyte (1 M LiPF₆ in FEC/FEMC) instead of non-fluorinated electrolyte (1 M LiPF₆ in EC/EMC) for NCM523/graphite cell system. The formed robust SEI film on the anode surface contributed to a high antioxidative voltage of 4.7 V and enhanced electrochemical performance. Chen and his group^[41] selected 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether (TTE) as electrolyte co-solvents with FEC, DMC and EMC to dissolve LiPF₆. The Li/LNMO cell in the designed electrolyte with a high operate voltage range of 3.0–4.9 V showed a higher capacity retention of 98.3% with 138 mAh g^{-1} after 200 cycles at 1 C, better than the cell without TTE (127 mAh g^{-1} after 130 cycles) (Figure 4a). The elaborately formulated TTE-containing electrolyte was also fabricated in 18650 LNMO/MCMB full-battery at the voltage of 3.2–4.8 V and obtained a capacity retention of 93% after 40 cycles at 1 C (Figure 4b). The stable performance was attributed to the robust SEI film formed on the surface of MCMB electrode by F-rich TTE. Recently, by introducing a new fluorinated ether of 2,2-dime-thoxy-4-(trifluoromethyl)-1,3-dioxolane (DTDL) into 2 M LiFSI, a high oxidation voltage of 5.5 V and high Li⁺ transference number of 0.75 were achieved in a NCM811/Li cell.^[42]

In addition to the experimental investigations, theoretical calculations are also widely used to guide the electrolytes design. By computing HOMO energy, Xiao et al.^[43] designed an ultrahigh-voltage electrolyte consisted of 1 M LiPF₆ in a mixture of FEC and bis(2,2,2-trifluoroethyl) carbonate (BTC). The fluorosubstituted solvents exhibited fewer negative charges around the O atoms, which implied the weaker binding with Li leading to the improved electrochemical kinetics of Li and enhanced cycle performance. The designed all fluorination solvents-based Li/NCM811 cell with a potential window of 4.8 V exhibited 95.1% capacity retention after 160 cycles. The relatively low LUMO energy benefited the formation of LiF-rich CEI and subsequently improved the anodic stability at high-voltage. Their work proved the possibility of achieving stable interface and molecular structure-solvation behavior by adjusting the solvent structure.

Similar to fluorinated solvents, sulfone electrolytes also have strong electron-withdrawing group and high oxidation resistance at high-voltage. Amine et al.^[44] investigated 1 M LiPF₆ in tetramethyl sulfone (TMS) and EMC for 5 V LNMO positive electrode and Li₄Ti₅O₁₂ (LTO) anode. The TMS-based electrolyte holds the highest potential (Figure 4c) and the related full battery in the electrolyte delivered a highly stable cycling performance for 1000 cycles under 2 C rate. Based on the fact that methyl sulfone has a wide electrochemical stable window of 5.5 V (vs. Li/Li⁺). Dahn et al.^[45] introduced ethyl methyl sulfone (EMS) electrolyte to explore the delithiation mechanism for Li_{2/3}[Ni_{1/3} Mn_{2/3}]O₂-based battery at 3.1–5.4 V for its high electrochemical window.

Additionaly, sulfonamide-based solvent was also a good choice for high-voltage batteries. Xue et al.^[46] utilized N,N-dimethyltrifluoromethanesulfonamide (DMCF₃SA) electrolyte

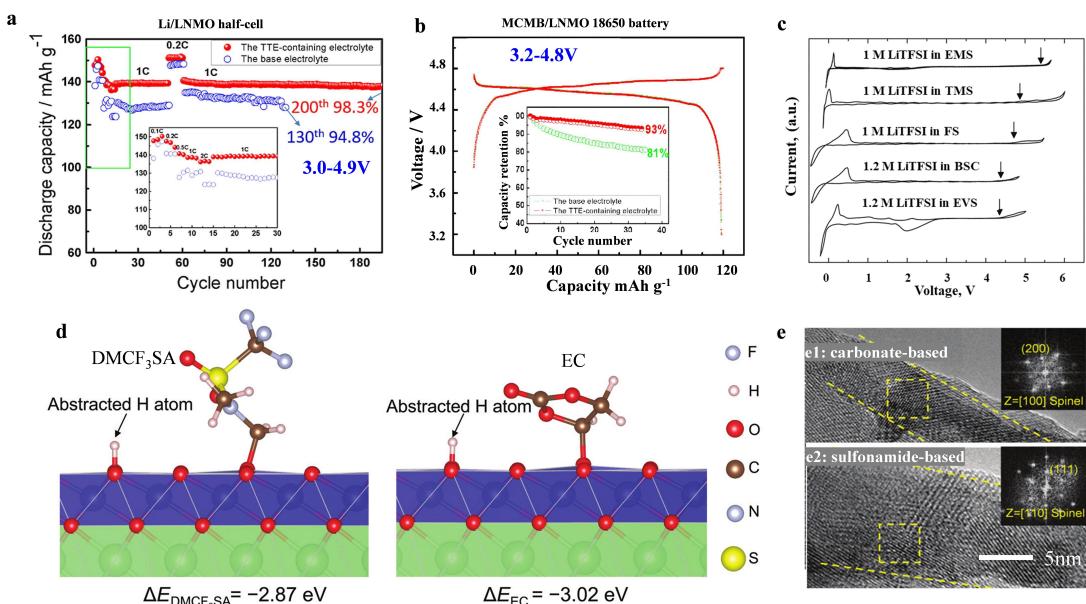


Figure 4. a) Electrochemical properties of the Li/LNMO half-cells in base and the TTE-containing electrolytes. b) The electrochemical performance of the 18650 MCMB/LiNi_{0.5}Mn_{1.5}O₄ full-cells in the base electrolyte or the TTE-containing electrolyte at 3.2–4.8 V. Reproduced with permission from Ref. [41]. Copyright (2019) Wiley-VCH. c) CV curves of cells in four kinds of sulfones electrolytes. Reproduced with permission from Ref. [44]. Copyright (2009) Elsevier. d) The reaction energy of DMCF₃SA (−2.87 eV) and EC (−3.02 eV) oxidized by the highly de-lithiated LCO surface through density functional theory (DFT) calculations. e) HRTEM images of LCO cathodes after 200 cycles in the carbonate-based (e1) and sulfonamide-based (e2) electrolytes. Yellow dot lines in (e1) and (e2) indicate the transformed spinel layers. Insets in (e1) and (e2) in the upper right corners indicating that the transformed layers were spinel structures. Reproduced with permission from Ref. [46]. Copyright (2021) Royal Society of Chemistry.

to investigate the stability of LCO/Li battery between 4.5–4.7 V. Owing to electronegative groups in molecule, DMCF₃SA displayed a higher oxidation resistance (−2.87 eV) than that of EC (−3.02 eV) (Figure 4d). As a result, the resistive layer on the surface of LCO was calculated to be about 11 nm in carbonate-based electrolyte and only about 5 nm thick in sulfonamide-based electrolyte (Figure 4e), identifying the harmful layer with spinel structure was inhibited by sulfonamide-base electrolyte. In addition, the N and S atoms induced by sulfonamide-based electrolytes could suppress Co dissolution and show a good chemical stability against oxidation even at 4.8 V. Other highly stable solvents such as nitrile electrolytes can provide high oxidation stability and thermal stability for electrolytes, which make the marketable application of 5 V-class voltage cathode materials become possible.^[47] Different from the fluorinated and sulfone electrolytes that the high-voltage stability is derived from the high entitative stability of functional groups, the stability of nitrile electrolytes at high-voltage are supposed to a −CN-TM complexes layer generated by chemisorption on the interphase between electrolyte and cathodes.^[48] At the same time, the nitrile solvents have a high polar component and big dielectric constant, which can dissolve types of lithium salts, and the rich electron-CN group in the molecule has strong nucleophilic sites with Li⁺.^[49] Benefit from the above performance, Okada et al.^[50] prepared an electrolyte by combining sebaconitrile with EC and DMC as solvents for 1 M LiBF₄, achieving an excellent potential stability beyond 6 V (vs. Li/Li⁺) in LiFePO₄ cell and 5.3 V redox voltage for Li₂NiPO₄F/Li cell during

cycling process. In addition, ionic liquids (ILs) also have many favorable properties as alternative choices to conventional carbonate-based solvents, due to their non-flammable property, low vapor pressures and wide electrochemical stability windows. Li et al.^[51] designed a new electrolyte which contained (N-propyl-N-methyl piperidinium difluoro(oxalato) borate (PP₁₃DFOB) and dimethyl carbonate (DMC) as co-solvent. The IL-based electrolyte used in Li/LNMO cell could suppress the Al corrosion and relieve the dissolution of transition metal ions in cathode at 3.0–4.9 V. Fan et al.^[52] combined the Li-Al-F phase coating and F-rich (FEC and DFEC as solvents) electrolyte to improve the LCO/Li cell to charge up to 4.6 V.

The above-mentioned strategies confirmed that introducing stable solvents can improve the performance of LIBs at high-voltage by forming stable F-rich SEI/CEI film on the surface of electrodes or producing −CN-TM layer with preventing the transition metal dissolution. These solvents all have electron-withdrawing groups and stable oxidation resistance at high-voltage. However, considering the doubtful interface chemistry and not too high cycle numbers, the failure mechanism of LIBs in these solvents at high-voltage still needs to be understood.

3.3. Introducing additives

The application of additives in electrolytes is a simple and effective method to improve the performance of LIBs. In detail, a few additives could be preferentially oxidized on the

cathodes in electrochemical process and participate the formation of CEI films at high-voltage.^[53–55] And CEI is a solid electrolyte membrane on the positive side, which prevents electron transferring from electrolyte to cathode and decreases oxidation potential of cathode with electrolyte.^[56] Jiang et al.^[57] reported that CEI on the cathode surface impeded Li⁺ transportation and raised surface impedance, but it also blocked the continuous reaction and space-charged layer between cathode and electrolyte. Therefore, it's significant to introduce suitable CEI films between electrodes and electrolyte to improve the working potential of LIBs.

To enhance the interface stability of LNMO/Li cell, Li et al.^[58] introduced 0.5% phenyl trifluoromethyl sulfide (PTS) into electrolyte. The preferentially oxidization of PTS to carbonate components in the electrolyte prevented the continuous disintegration of EC/DMC solvents and contributed to the high capacity retention of 84% after 400 cycles at 3.0–4.9 V and 0.5 C. Molecular dynamic simulations of solvent-Li⁺ for electrolytes demonstrated that PTS was easy to enrich on the surface of cathode. The proposed strategy benefited for forming stable CEI film and avoided the destruction of cathode material. In the same LNMO/Li cell system, Li and his group^[59] used trimethyl borate (TMB) and triethyl borate (TEB) as additives to improve the cycling performance of batteries at 3.0–4.9 V, respectively. the addition of 2% TMB in the base electrolyte of 1 M LiPF₆ in EC/DEC/DMC increased the discharge capacity retention from 23.4% to 85.3% after 600 cycles, and the cell with 2% TEB retained 72.6% of the capacity. The enhanced capacity retention was attributed to the denser CEI on cathode by the decomposition of borate-based additives. The catalyzation effect of TEB additive on cathode and the bigger lithium extraction resistance of TEB-containing electrolyte than that of TMB-based electrolyte, endowing the TEB-based battery with high initial Coulombic efficiency and outstanding cycling

performance. Wang et al.^[60] adopted 1% 1,3,6-Hexanetricarbonitrile (HTN) as additive in 1 mol L⁻¹ LiPF₆ dissolving in the mixture of EC and DMC for Li_{1.2}Ni_{0.13}Co_{0.13}Mn_{0.54}O₂ cathode at 4.8 V. The C≡N groups in HTN had a strong interaction with the metal ion in cathode, decreasing the oxidation decomposition of electrolyte and preventing the cathode surface from HF corrosion and phase transition. Moreover, the HTN-containing electrolytes also effectively increased the dynamic performance of Li⁺ due to the lower interfacial resistance. Recently, Chen et al.^[61] added 0.7 wt.% 3-cyano-5-fluorophenylboronic acid (CFBA) to electrolyte to modify the cycling performance of Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O₂(LMR)/Li cell using 1 M LiPF₆ in EC:EMC: DMC as the electrolyte at the voltage range from 2.0 V to 4.8 V. The investigated additive could not only remove the pernicious HF produced by LiPF₆ but also participate the CEI membrane formation on LMR surface (Figure 5a), thus keeping the cathode particle from dissolution of Mn/Ni/Co ions (Figure 5b) and the subsequent good cycle stability (Figure 5c). Similarly, to CFBA, a new scavenger additive of tris(trimethylsilyl)phosphite (TMSP)^[62] was reported to eliminate HF by Song and his group. TMSP protected Mn and Ni dissolution from LNMO cathode and suppressed the electrolyte oxidation and then formed a thinner SEI on the cathode surface (Figure 5d). The reaction products of TMSP further modified the surface chemistry of SEI film and prevented LNMO cathode from further decomposition. The cell in TMSP-added electrolyte showed high rate performance of 3 C at 3.0–5.0 V, which was far higher than that in the base electrolyte (Figure 5e).

As a promising cathode for improving the energy density through raising the charging voltage from 4.2 V to 4.6 V, the application of LCO was impeded by the serious corrosion of HF which generated by the decomposing of traditional electrolytes under 4.5 V, as well as the crystal lattice shrinkage and phase transformation caused by the excessive Li⁺,^[63–65] leading to

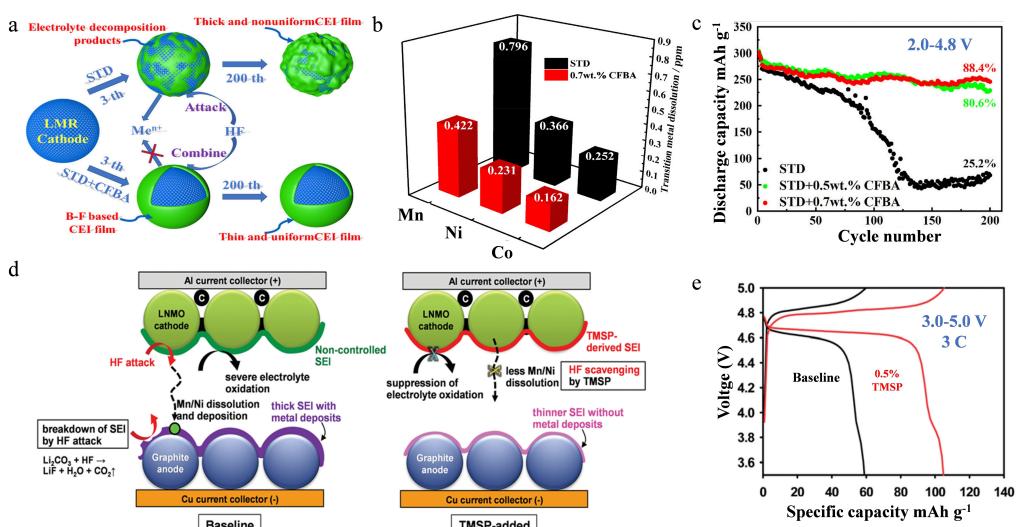


Figure 5. a) The reaction mechanism illustration of CFBA in the formation of protective CEI films. b) Contents of metal ions in stand standard (STD) electrolyte and 0.7 wt.% CFBA adding electrolyte. c) Cycle performance of the LNMO/Li cell at 2.0–4.8 V. Reproduced with permission from Ref. [61]. Copyright (2015) Elsevier. d) Schematic representation of unique functions for TMSP oxidative decomposition and scavenging HF from the electrolyte. e) Charge and discharge curves at 3.0–5.0 V and 3 C. Reproduced with permission from Ref. [62]. Copyright (2014) Royal Society of Chemistry.

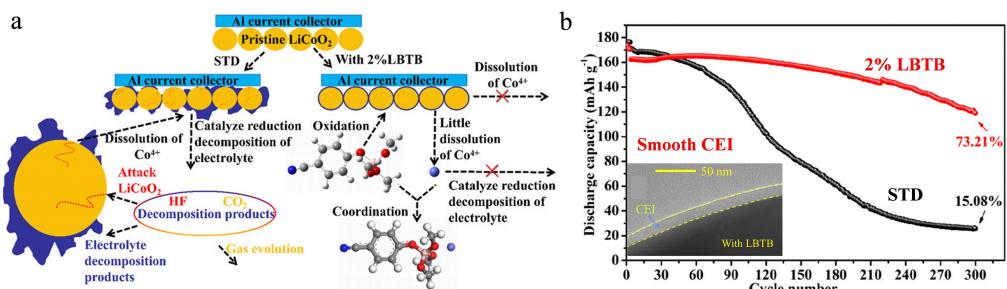


Figure 6. a) Schematic illustration of the mechanism of LBTB to stabilize LiCoO₂/electrolyte interfaces. b) Cyclic stability of Li/LiCoO₂ cells at 1 C in STD and LBTB added electrolytes, illustration in b) showed smooth and uniform CEI in LBTB added electrolyte. Reproduced with permission from Ref. [71]. Copyright (2021) Elsevier.

broken structure and decreased cycle performance. Nitrile ether contained the C=N bonds could suppress Co³⁺ dissolution and benefit the repairing and stabilization of the interface films at a high-voltage. The LCO/artificial graphite with nitrile ether electrolyte could keep excellent capacity retention more than 1000 cycles at 4.5 V and 1 C.^[66] Moreover, 1,3,5-tri-2-propenyl-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione (TAIC) was also reported to be effective for 4.5 V LCO cathode.^[67] In order to achieve higher voltage of LCO cell, Zou et al.^[5] selected 0.5% triisopropanolamine cyclic borate (TPCB) as an additive for 4.6 V LCO. The C–N, B–O/B–F bonds in CEI enabled to suppress electrolyte decomposition and maintained the structure integrity at high-voltage and long-term cycling process. The B and N elements in the additive inspired them to explore more multifunctional additives. Recently, they reported an additive 2,4,6-tris(4-fluorophenyl)boroxine (TFPB) for 4.6 V LCO. The B–O bond was demonstrated to protect the cathode-electrolyte interphase and reduce the side reactions.^[68] The same group also designed 4-methylmorpholine-2,6-dione (MMD)^[69] as an additive to improve the LCO/Li cell voltage even to 4.7 V. Thanks to the anhydride and amine functional groups in MMD, the additive could construct a stable CEI film and effectively capture harmful HF, H₂O in the electrolyte. The LCO/Li cell with MMD electrolyte retained 122 mAh g⁻¹ after 200 cycles, while the cell in base electrolyte only retained 91 mAh g⁻¹.

Moreover, some lithium salts were also proved to be effective additives for high-voltage LCO cathodes by coordination effect with transition metal ions in cathodes or forming interfacial films. 1 wt.% difluoro(oxalate)borate (LiDFOB) was used as an additive to enhance the 4.5 V high-voltage LCO/Li cell for the strong coordination between LiDFOB and Co ion.^[70] The combination action could prevent the Co deposition on the anode and inhibit the electrolyte decomposition, thus leading to the improved battery performance. Sun et al.^[71] synthesized a novel additive lithium 4-benzonitrile trimethyl borate (LBTB) for LCO/Li cell and presented the schematic illustration of the improved mechanism (Figure 6a). The additive was oxidized at low voltage, which could prevent the HF formation and Co ions decomposition. At the same time, the oxidation product from LBTB formed robust and uniform film on the surface (inset in Figure 6b), thus improving the high-voltage stability (Figure 6b).

In addition, Ni-rich cathodes are received as the most promising cathode for high energy density LIBs by the merits of its high specific capacity (180–240 mAh g⁻¹ at the voltage range from 2.7 to 4.3 V).^[72] However, Ni-rich cathode is easy to fail at high operate voltages for its unstable structure. Introducing high-voltage electrolytes matching with Ni-rich material was an effective method to improve the stability and cycle life of battery.^[43] Thus, electrolytes design for high-voltage Ni-rich materials are widely studied. Zhao et al.^[73] reported a novel F-containing electrolyte of 1 M LiPF₆ and 0.2 M LiDFOB in FEC/EMC/2,2,2-trifluoroethyl acetate (TFA). The solvents of FEC and TFA processed a high oxidation potential while LiDFOB showed film-forming passivation ability both on the surface of NCM811 and graphite. The formed electrode-electrolyte interfaces (EEI) were rich in F and B species (Figure 7), which could decrease the cracking and detrimental phase change of NCM811 particles. Therefore, the NCM811/graphite cell showed a high capacity of 247.2 mAh g⁻¹ and 83.3% capacity retention after 100 cycles at 4.6 V. The related work demonstrated that EEI dominated the main factor for electrochemical performance rather than conductivity and migration number of Li⁺. Surprisingly, Zhou et al.^[74] prepared a novel solid electrolyte for NCM811 cathode by complexing poly(ethylene oxide) (PEO), LiTFSI with decabromodiphenyl ethane (DBDPE). The DBDPE

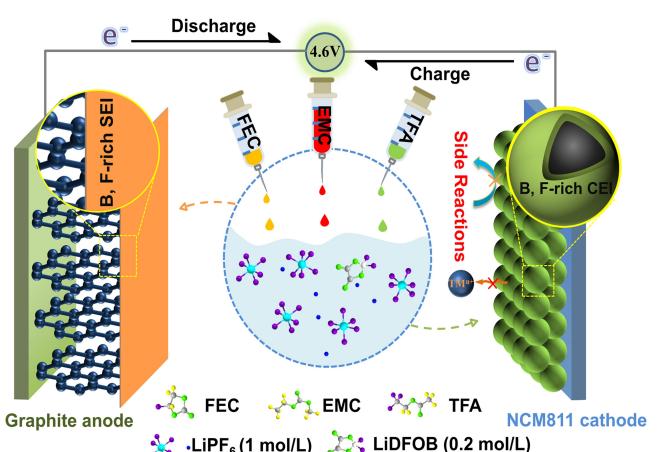


Figure 7. Schematic illustrations of EEI formation behavior in Gr/NCM811 batteries with F-electrolyte at 4.6 V. Reproduced with permission from Ref. [73]. Copyright (2022) Elsevier.

could be preferably oxidized and decomposed to LiBr at a high-voltage, which induced the formation of organic-rich CEI on the surface of cathode. The CEI improved the fast Li⁺ diffusion across the interface and prevented the PEO further oxidation. The novel electrolyte enabled the NCM811 cell to deliver perfect performance at 4.5 V (Figure 8).

The above mentioned reports illustrate the contribution of additives to the high-voltage LIBs system by introducing additives with low solvation energy, oxidation resistance, and by-products scavenging agent at high-voltage. Although these additives lead to stable CEI films, the internal mechanisms and original intentions are different and complex.

While with regards to practical application, several problems are existed: 1) Although sulfones or nitrile-containing solvents can keep stable at high-voltage, they are toxic, expensive, and hard for large-scale application. 2) The effective additives for high-voltage application is limited. 3) The high concentration or ionic liquid electrolytes have a poor wettability with the separator and electrodes, low ionic conductivity and high cost. 4) High-voltage electrolytes are matched with high-voltage materials systems of LNMO, LCO or NCM. However, these high-voltage materials have serious problems such as limited specific capacity, poor rate performance, low safety and short cycle life, which are not conducive to the improvement of battery energy density, power density, and life cycle. Therefore, ultra-high-voltage electrolytes for LIBs have been only studied in papers so far.

In conclusion, all the above-mentioned strategies are close to each other. Specially, the ratio of lithium salt to solvent determines the solvation structure of Li⁺ and anion, if the anion participates in the solvation reaction, they will change the composition of CEI/SEI films. Therefore, the concentration

of lithium salt in the electrolyte is very important. Generally, the high concentration electrolyte can raise the working voltage of the battery to above 4.8 V and achieve stable cycling performance. In addition, some solvents with strong electron-withdrawing group also have strong antioxidant capacity at high-voltage, which can widen the working voltage window of the electrolyte effectively. Besides, the high-voltage additives such as 3-cyano-5-fluorophenylboronic acid (CFBA) generally decomposes earlier than solvents and lithium salts, benefiting to form a CEI film rich in F/CN groups on the surface of cathode and subsequently prevent the oxidative decomposition of cathode at high-voltage. In other words, the additive serves as a sacrifice to protect the lithium salt, solvent and electrode. Therefore, the three strategies complement each other and jointly promote the high-voltage stability and lifetime of LIBs.

4. Fast-Charge Electrolytes

Generally, electrolytes for fast charging should have twice conductivity and 3–4 times lithium ionic diffusivity of common electrolytes. Based on the demands, electrolytes solvents for fast charging should have the properties of low viscous and fast diffusion. However, the solvents often have the risk of accelerating aging and easy redox effect during the electrochemical process. Thus, stable solvents and electrolytes system are the key for fast-charge cells.^[75] In order to solve the problem, Cui et al.^[9] proposed that the rate performance of the battery could be improved from the following aspects: 1) Increase the ionic conductivity in the electrolyte. 2) Increase the migration number of Li ions in the electrolyte. 3) Reduce the electrode material of curvature and quality of electrodes. In

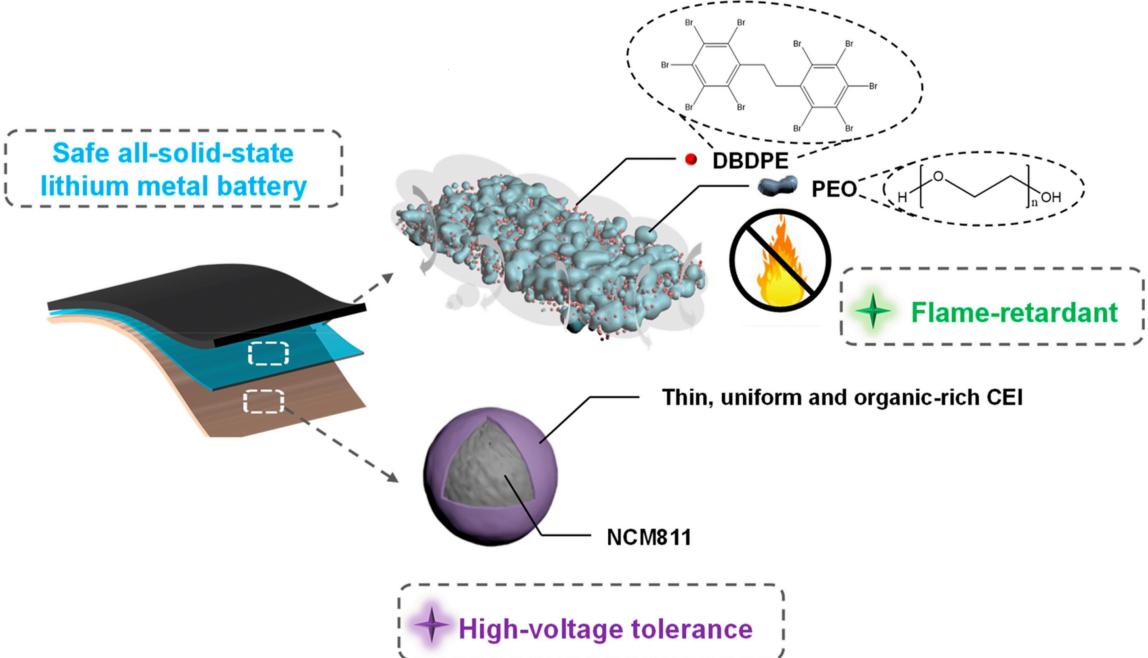


Figure 8. Design principles of the flame-retardant and high-voltage solid-state electrolyte for a safe all-solid-state lithium battery. Reproduced with permission from Ref. [74]. Copyright (2022) American Chemical Society.

this section, we mainly focus on the recent progress of electrolytes with fast-charge property achieving by modifying the ionic conductivity, migration number, SEI or CEI films, solvation and de-solvation structures etc.

4.1. Increasing ionic conductivity

The high ionic conductivity could avoid the polarization and heterogeneous distribution of Li^+ in mass transfer,^[76] while the higher bulk ion conductivity of the electrolyte, the higher conductivity of SEI or surface films.^[17] Thus, numerous efforts have been made to improve the ionic conductivity of the electrolyte. The most widely utilized method is decreasing the viscosity and freezing point of aliphatic co-solvents to ensure rate capability.^[77,78] In general, small-molecule esters as co-solvents fit the criteria above. Among them, methyl acetate (MA) has a great increase in conductivity of all esters and lower viscosity (0.4 cp) than ethyl methyl carbonate (EMC, 0.65 cp) and dimethyl carbonate (DMC, 0.59 cp) at 25 °C. Logan et al.^[78] added 20% MA as co-solvent into the based electrolyte. The NMC532/artificial graphite cells in EA-containing electrolyte showed enhanced rate performance of 2 C. However, the MA with a low molecular weight increased the polarization and impedance of the cell, which was unfavorable for the formation of SEI layers. In order to solve this problem, the same group^[76] adopted suitable additives (FEC and lithium difluorophosphate) in $\text{LiPF}_6\text{-MA}$ system enabling the excellent rate properties at 4 C rate and lower internal resistance in NMC532/graphite cell. The MA was demonstrated to be an aprotic solvent which greatly improved the ion transport and balance between the polarity and viscosity of the electrolyte.

In addition to solvents, lithium salts also have critical effects on the lithium transport for fast charging. Among the various lithium salts, LiFSI was proved to have higher ionic conductivity by comparing with other normally used salts in LIBs.^[79-81] Badwekar et al.^[82] evaluated LiFSI and LiPF_6 by physics-based electrochemical-thermal mode, confirming the former one was a more suitable electrolyte for fast-charge application to mitigate the thermal issues in cells. Moreover, lithium salts additives are also effective for improving the fast-charging ability. Wang et al.^[83] reported LiBF_4 and LiNO_3 dual-salt additives for NCM811 cell. They found the Lewis acid LiBF_4 could increase the dissolution of LiNO_3 in carbonate-based solvents. The dual-additives could release chunky lithium deposition and realize the high rate performance for NMC811. Even at 5 C, the cell delivered a specific capacity of 185.6 mAh g⁻¹. The reason of perfect rate performance was attributed to fast lithium ion conducting compound of LiN_xO_y on the CEI that was formed by BF_4^- - NO_3^- solvation chemistry. The high ion-conducting CEI film could reduce the uneven lithium deposition and lithium dendrites generation in LIBs. The uniform lithium deposition was beneficial for the fast-charge performance of LIBs. It is believed that the proposed strategy is promising for its low cost and excellent performance for commercial high-capacity material.

4.2. Increasing migration number of Li^+

Traditionally, the migration number of nonaqueous electrolyte is usually lower than 0.5, due to the presence of a large number of solvation sheaths around Li^+ compared with typical anions.^[17] Low Li^+ migration electrolytes have adverse impacts on the performance of lifetime, charging and discharging rates, energy and power density. Therefore, improved lithium migration number holds great promise for fast-charge process of LIBs. Generally, the transportation of Li^+ in liquid electrolytes systems is complex and impacted by multi-factors including the solvation effect of Li^+ , the dissociation of lithium salt, and the viscosity of solvents. Thus, numerous routes have been proposed to increase the migration number of $\text{Li}^+.$ ^[84]

In order to achieve a high migration number of Li^+ , Videa et al.^[85] designed a giant anion with 24 fluorine atoms in lithium bis(perfluoropinacolato) borate (LiBPFPB). Benefit from the highly dissociation of lithium salt in PC, a Li^+ migration number of 0.55 was obtained at 50 °C. Furthermore, Popovic et al.^[86] presented a "salt-in-solvent" electrolyte which contained 0.45 M lithiated version of tetratriflylpropene (LiTTP) in diglyme. The electrolyte showed a high transference number of about 0.7 and higher ionic conductivity than conventional lithium triflate in diglyme solvents. The beneficial performance of LiTTP was ascribed to the strong interaction between lithium transport and the reduced mobilities of huge solvated anions. Suo and his group^[87] used the concept of "water-in-salt" and got a high Li^+ migration number of 0.73 by adding LiTFSI in DME/DOL (1,3-dioxolane) solvents. The high migration value is benefit for enhancing cycling and safety performance of LIBs by effectively suppressing the lithium dendrite growth and shape change in lithium anode. Wu et al.^[88] added five co-solvents including ethyl formate (EF), methyl acetate (MA), ethyl acetate (EA), dimethyl carbonate (DMC) into EC/EMC based electrolyte to improve the immigration number of Li^+ . By comparing the lithium plating conditions on graphite anode surface and the crystal structural changes in NCM622 cathode, DMC in the base electrolyte was confirmed to be the best solvent for fast-charge performance (6 C) in LIBs. Diederichsen et al.^[89] demonstrated that the electrolyte with relatively higher Li^+ migration numbers would enable higher power densities and allow faster charging (>2C) by drawing the state of charge (SOC) versus charge rate. The result showed the battery in high Li^+ migration numbers of electrolytes would have higher SOC at same rate and higher rate at the same SOC, which means that electrolytes with higher migration numbers are benefit for enhancing the capacity and rate performance.

As mentioned above, Li^+ transport can be adjusted by modulating lithium salts, solvents and the interaction between them. Besides, the Li^+ migration number also can be increased by controlling the formation of SEI film, which could influence the Li nucleation and growth behavior.^[90] Yang et al.^[14] investigated the decomposition products in NCM532/graphite cell at different charging rates of 1 C, 2 C, 4 C, and 8 C, through analyzing the amounts of lithium and LiF in SEI at different charging rates, they proposed the high correlation between them. With the decrease of full-charge time, the amount of LiF

on the surface of electrode increased and the surface was covered by thick layer of LiF.

Different from liquid electrolytes, solid electrolytes can raise the lithium migration number by varying the ionic migration behavior, thus, considerable effort has been made to develop effective solid electrolyte with high immigration number for fast-charge applications.^[9,91] Zhou et al.^[92] prepared α -LiAlO₂@ γ -Al₂O₃ (LAO) to anchor anions in electrolytes and get a high conductivity of 0.85 mS cm^{-1} and remarkable Li⁺ migration number of 0.92 at room temperature. They calculated the anchoring energy γ -Al₂O₃ (111), α -LiAlO₂ (101), LAO and anions respectively by density functional theory (DFT) (Figure 9a). The presence of α -LiAlO₂@ γ -Al₂O₃ (LAO) with highest adsorption energies for PF₆⁻, which was benefit for achieving high migration number and subsequently decreasing the polarization of cell as well as improved the uniform Li⁺ deposition and lithium dendrite-free growth. The LiFePO₄/Li battery with the electrolyte achieved 88% capacity retention after 2000 cycles at 2 C. The symmetric Li/Li battery realized dendrite-free ability for 1000 h at 0.5 mA cm^{-2} (Figure 9b). Han et al.^[93] synthesized a new MOF-based succinonitrile (SN) electrolyte for Li/LiFePO₄ battery (Figure 9c). The electrolytes enabled the dendrite-free lithium deposition and fast Li⁺ transport. The -CN groups on the MOF framework and SN accelerated the Li⁺ transport. As a result, a high ionic conductivity of $7.04 \times 10^{-4} \text{ S cm}^{-1}$ and high Li⁺ transport number of 0.68 were achieved. As a result, the battery in the MOF-SN-FEC system showed stable cycle performance (Figure 9d).

Buss et al.^[94] bound all the anions in lithium salt and afforded precise control of the molecular weight of polymer and charge density of the polymer backbone. The polymer was dissolved in dimethyl sulfoxide (DMSO) and got solubility of polyelectrolyte to about 1.0 M Li⁺ concentrations. The huge anions in solution provide big degree of freedom for Li⁺. The electrolyte showed high ionic conductivity of 1.2 mS cm^{-1} and transference number of 0.98 at 25 °C. Through replacing the small anions (such as TFSI⁻, PF₆⁻) used in traditional electrolyte by polyanion, the self-diffusion coefficient of anions decreased by a magnitude while the self-diffusion of Li⁺ was not affected. Moreover, Schaefer et al.^[95] reported a high t_{Li^+} electrolyte based on the anchoring organic ligands and tethered lithium salts on the metal oxide nanoparticles. Their experiments showed the electrolyte with a high t_{Li^+} about 1 and available ion-pair dissociation which delayed the lithium dendrite nucleation and improved the rechargeable performance of the battery.

4.3. Constructing stable SEI or CEI films

In addition, the properties of the SEI or CEI films are also important for ionic transport of LIBs, especially at the fast-charge condition. The chemical components and impedances of the films influence the Li⁺ transport behavior in the battery, then impacted the rate capability.^[96] Zheng and his co-workers^[97] utilized 0.05 M LiPF₆ as an additive in LiTFSI-LiBOB dual-salt/carbonate-solvent-based electrolytes for Li/NMC battery. The as-formed SEI by the electrolyte was rich in

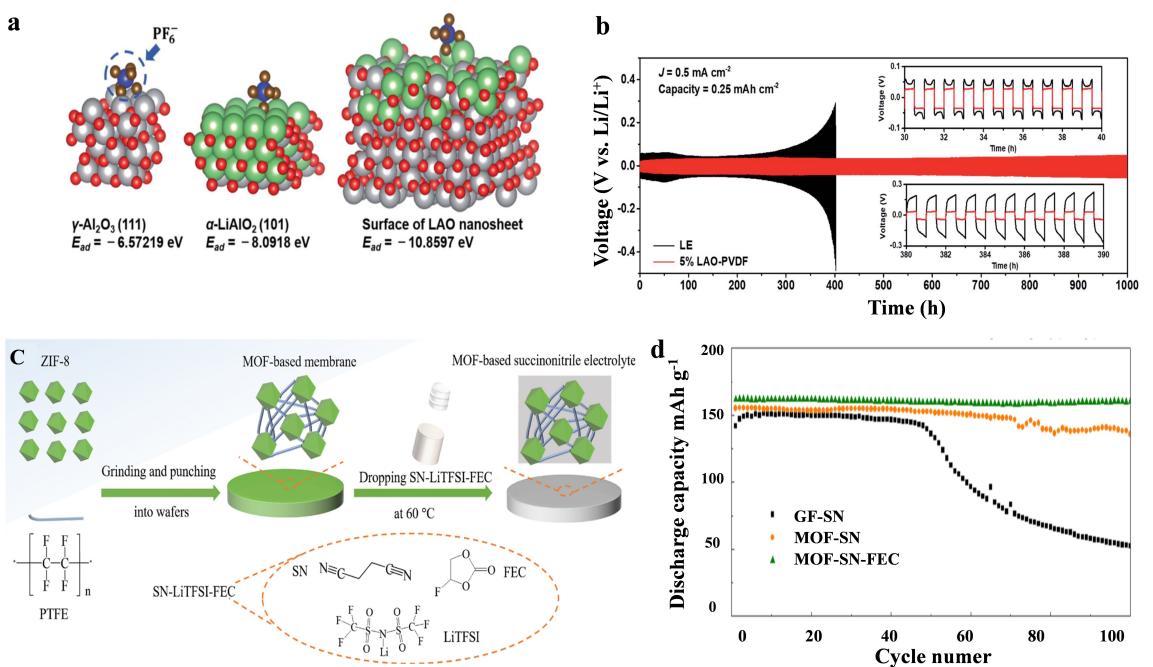


Figure 9. a) The adsorption energies on three kinds of materials by DFT calculations. (blue: phosphorus; brown: fluorine; gray: aluminum; red: oxygen; green: lithium). b) Long-term cycling of Li/Li cells with liquid electrolyte and 5% LAO-PVDF electrolyte. Reproduced with permission from Ref. [92]. Copyright (2022) Royal Society of Chemistry. c) Illustrate of the fabrication of the MOF-SN-FEC electrolyte. d) Cycling performance of the batteries in all as-prepared electrolytes. Reproduced with permission from Ref. [93]. Copyright (2022) American Chemical Society.

polycarbonate constituents, which could bond the isolated or dead Li with the Li metal anode and improved the interfacial stability of battery. The stable interface allowed the battery to operate at high charge current densities. The strategy could decrease impedance of the interface and avoid the risk of short circuit in the fast-charge process.

While in the side of cathodes, the electrolyte could prevent the Al corrosion (Figure 10a). When tested at a charge/discharge current density of 1.75 mA cm^{-2} for 500 cycles, 97.1% discharge capacity retention was retained in $\text{Li} \parallel \text{NMC}$ battery (Figure 10b). The fast-charge performance and stable lifetime were attributed to the formation of uniform and conductive SEI on the surface of lithium metal. Dong et al.^[98] added 2,2,2-trifluoroethyl-1,1,2,3,3-hexafluoropropyl ether (THE) as additive in LiTFSI/DOL+DME for $\text{Li}/\text{LiFePO}_4$ battery. Owing to the electron-withdrawing fluoroalkyl groups adjacent to oxygen atoms of THE, the interaction and solvation of Li^+ with solvents were reduced. With large amounts of fluoroalkyl groups in the molecule, THE showed ultrahigh polarity and enabled ten times elevation of lithium transference at the surface of electrolyte and anodes, enabling the formation of robust and compact SEI rich in LiF on the anode. These superiorities from THE-containing electrolyte demonstrated an unprecedented lifetime for LiFePO_4 cathode, which displayed only 0.0012% capacity decrease per cycle after 5000 cycles at 10 C (Figure 10c). Such electrolyte was also suitable for LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ cathodes-based batteries. However, some additives such as heptafluorobutyric anhydride (HFA)^[99] could optimize the component and construction of both SEI and CEI, and improve

the Li^+ de-solvation effect in electrochemical process, contributing to a high capacity retention of 65.1% after 250 cycles (corresponding the 28.8% capacity retention in reference electrolyte) and advantageous rate performance at 15 C. Obviously, realizing the importance of LiF-containing SEI, Han et al.^[100] designed an electrolyte with 3 wt.% FEC in 4.5 M lithium bis(fluorosulfonyl) imide-DME for Li/P battery. Owing to the formation of LiF-rich SEI which effectively alleviated the huge volumetric expansion of P and stabilize the P/electrolyte at 8 Ag^{-1} (about 3 minutes in an entire charging process). In conclusion, the ether, acid anhydride or esters additives can be used to build a thin and stable interfacial film, causing the low intercalation resistance and enhanced electrochemical performance.

4.4. Constructing weak solvation structures

The de-solvation process of Li^+ is the pivotal factor for the performance of LIBs.^[10] It is reported that Li^+ were mostly present as solvated Li^+ clusters and dissolution into naked Li^+ on the surface of electrodes. The fast dissolution process of solvated Li^+ into Li^+ was benefit for fast charging. As a result, it is important to develop electrolytes with low activation energy for solvation and de-solvation of Li^+ .^[101] Different from the general recognition of SEI, Zou et al.^[102] reported an electrolyte made up of 1.2 M LiPF_6 in ethyl methyl carbonate (EMC) and methyl acetate (MA) solvents without additive for LIBs at a high-voltage of 4.5 V and fast-charging rate of 3 C. The lower

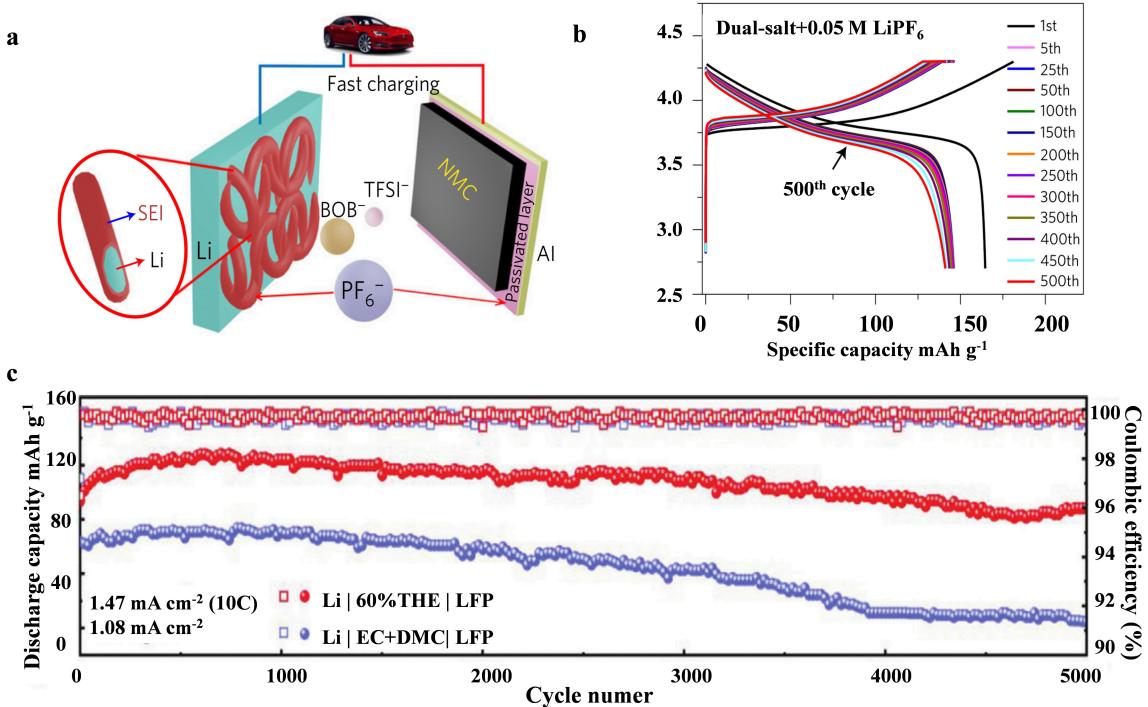


Figure 10. a) Schematic illustration demonstrating that designed electrolyte prevents the Al corrosion and improves the stability of Li metal. b) Voltage curves as a function of cycle number of $\text{Li} \parallel \text{NMC}$ batteries using the designed electrolyte. Reproduced with permission from Ref. [97]. Copyright (2017) Nature Publishing Group. c) Cycling performances of the Li/LFP cells with EC+DMC and 60%THE electrolytes at 10 C. Reproduced with permission from Ref. [98]. Copyright (2021) Wiley-VCH.

interaction strength of Li^+ -MA benefited for reducing the shielding effect on Li^+ . Therefore, the assembled NCM/Li battery exhibited long lifespan and dendrite-free properties at a large charging rate. The related work built a molecular-scale interfacial model of Li^+ -solvent-anion interactions, enabling a new viewpoint into the electrode performance and serving as the supplement to conventional understanding of the SEI or CEI effects on cell performance at the fast-charge process, the investigated battery could deliver a high reversible capacity of 450 mAh g^{-1} after 450 cycles.

The conventional wisdom holds that combining various solvents with lithium salts is an effective strategy to increase the ionic conductivity of the electrolyte so that the process of Li^+ solvation and de-solvation was ignored. In fact, through introducing different solvents and lithium salts into the electrolytes, the structure and stability of Li^+ solvation shell could be changed instead of enhancing ionic conductivity. Therefore, some low or non-polar solvents, alkali metal ions, alkaline earth metal ions would be suitable additives for ameliorating the structure of the Li^+ solvation shells. Although MA has a good solvation ability, a low viscosity, and a high ionic conductivity of 25 mScm^{-1} as solvent, the de-solvation energy barrier

between Li^+ and MA was up to 50–70 kJ mol^{-1} , which limited the achievement of high electrochemical performance.^[76,103] Some researchers proposed that the energy barrier for forming SEI and bulk electrolytes were far less than de-solvation process. Consequently, reducing de-solvation energy was regarded as a more important aspect for the fast-charge process.^[104,105] Lei et al.^[106] revealed the process of Li^+ intercalation graphite layer in LiFSI: acetonitrile (AN): fluorobenzene (FB)=1: 2.4: 3 (by molar ratio) (AN-DHCE) electrolyte. The Li^+ transport process was divided by 5 procedures in LIBs (Figure 11a). Because of the low donor number ($\text{DN}=14$), high dielectric constant ($\epsilon=39.8$) and low viscosity (0.3 cP) of AN, the solvents presented weak solvation ability and sufficient ionic conductivity. The as-formed solvation structure benefited for forming F-rich SEI and improving Li^+ transport ability. The graphite half-cell with the designed electrolyte showed 302.7 mAh g^{-1} at 8 C and 91% capacity retention after 1000 cycles at 5 C. The NCM811/graphite full cell exhibited 80% capacity retention after 50 cycles at 5 C. The weak solvation structure of Li^+ is conducive to the desolvation process, which also benefit for reducing the charge transfer resistance and heat generation in fast-charge condition.

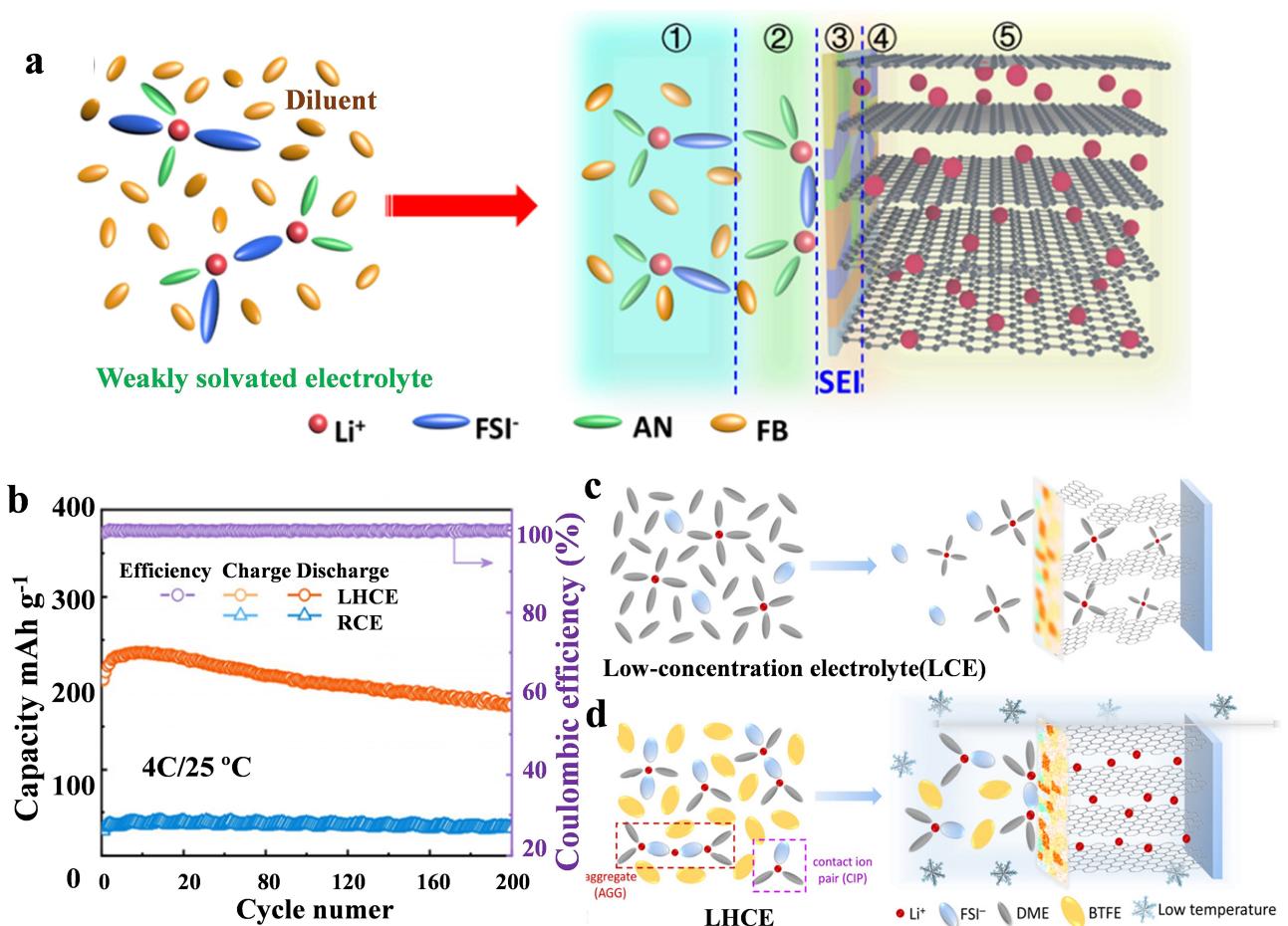


Figure 11. a) Schematic illustrations of the solution structures and the process of Li^+ intercalation graphite layer in AN-DHCE (LiFSI:AN:FB = 1:2.4:3 (by molar ratio)). Reproduced with permission.^[106] Copyright 2022 Elsevier. b) Cycling performance and Coulombic efficiency of graphite/Li cells using LHCE, HCE, and RCE after activation. c-d) Schematic illustrations of the solution structures and the process of Li^+ intercalation graphite layer in (c) LCE and (d) LHCE based on LiFSI in DME without/with BTFE. Reproduced with permission.^[108] Copyright 2020, Wiley-VCH

Furthermore, high-concentration electrolytes (HCEs) were also commonly adopted to adjust the solvation structure of Li⁺ and solvents. Because of the squeezing of anions into Li⁺ solvation sheath in HCEs and participate the generation of SEI layer, the SEI layer is dominated by inorganic components by anion-derived. Although high concentrated (> 4 M) electrolytes have been proved to be effective for reductive stability and fast charging,^[96,107] HCEs have some drawbacks that need to introduce a low-polarity diluent (insoluble for lithium salts) to achieve localized high-concentration electrolyte (LHCE). Jiang et al.^[108] designed a LHCE composed of 1.5 M LiFSI in dimethoxyethane (DME) and the diluent of bis(2,2,2-trifluoroethyl) ether for fast-charge operating battery of Li/graphite. The battery could deliver a specific capacity of 220 mAh g⁻¹ and better cycling performance at 4 C, which were higher than that of its reference sample (4.5 M LiFSI in DME and 1.5 M LiFSI in DME, Figure 11b). Owing to the special solvation structure between LHCE and Li⁺(Figure 11c and d), the structure effectively suppressed co-intercalation of ether solvent into the layers of graphite and provided fast-charge ability for LIBs.

However, Gao et al.^[75] combined theoretical and experimental characterizations to create a method to identify electrolyte formulations. The low-molecular weight solvents were demonstrated to be suitable candidates for fast-charge electrolytes and electrolyte transport was considered to be more important than the lithium de-solvation behavior in fast-charge process. Besides, by investigating the influence of electrode aging and electrolyte consumption to the high-rate charging capability of pouch cells, Sieg et al.^[6] proved the main factor that influence the fast-charging process was the electrolyte consumption but not the electrodes aging.

For electrolytes, the influence factors for fast-charge are multiple and complex. It's worth noting that one electrolyte is hard to own the all advantages for fast-charge. Meeting one of them could achieve the fast-charge property. For some solid-state electrolytes, although they have high Li⁺ migration number, they show lower rate performance than most of liquid electrolytes because of the low ionic conductivities. Therefore, the commercial progress for solid batteries develops slowly. The high ionic conductivity and Li⁺ migration number produce low impedance and low temperature rise at fast-charge condition. The stable and thin SEI or CEI films formed in fast-charge electrolytes could avoid heat accumulation, while the weak solvation structures could enhance the Li⁺ transport and promote the uniform lithium deposition. In fact, the ionic conductivity, migration number or solvent structure are relevant to SEI or CEI film formation. Thus, the four factors have effects on one another.

Therefore, referring to the examples above mentioned, we believe that the combination of high-conductivity lithium salts, weak solvating solvents and additives is a wise scheme to solve the negative effects in the fast-charge process.

5. Summary and Outlook

In this review, we focus on the current research progress of electrolytes from two typical extreme-condition application scenarios, emphasizing the operation principles and opportunities of electrolytes under these conditions. The recent progress of high-voltage electrolytes with the strategies refereeing to lithium salts, solvents, ionic liquids, and additives to provide ideas for designing high-voltage electrolytes of LIBs are discussed in detail. Additionally, the influence factors of electrolytes for fast-charge process, which covers the ionic conductivity, migration number of Li⁺, SEI or CEI films, solvation and de-solvation structures and other different views for fast-charge were also provided.

Although much efforts have been made and demonstrated to be effective to design electrolytes with appealing high-voltage and fast-charge performance, to meet the practical applications there are still many opportunities in this field.

- 1) Although the energy density of the batteries can be enhanced by increasing the specific discharge capacity of cathodes or anodes materials, designing appropriate high-voltage battery systems are also important methods to solve the plight. In recent years, the high-voltage electrode materials have been fully developed, but a large number of problems still exist in the electrolytes working at high-voltages, that hinder the satisfied performance achievement of LIBs operating at a high-voltage. The previous reported high-voltage-resistant (above 4.5 V) electrolytes can suppress side reactions and protect cathodes under high-voltages to some extent, but their chemical properties (such as toxicity, flammability, corrosion) or costs limit their commercial application.
- 2) During the process of fast charging and discharging, the parameters such as composition change in electrolyte (multiple salts and mixed solvents), heat transfer (thermodynamic, dielectric), ion concentration distribution (lithium de-solvation, charge transfer impedance) and interface characteristics (SEI or CEI, impedance, stability) should be fully considered. Meanwhile, it is necessary to combine advanced characterizations and detection methods to fundamentally understand the dynamic process and failure mechanism of the batteries during the fast-charge process. Moreover, fast-charge also induces heat growth and further increases the potential risks of LIBs. As a result, the safety problems are the bottleneck of fast-charge technology in practical application. Although solid electrolytes are regarded as the next-generation safe electrolytes instead of liquid electrolytes, the commercialization process of solid electrolytes is still a big challenge.
- 3) Except for the analysis of antioxidant potential, the in-situ characterization and failure analysis techniques should be combined to explore the specific mechanism of the film-forming and the interface interactions between the electrolytes and the corresponding electrodes.
- 4) For application, due to the development of commercial LiFSI and its excellent electrochemical performance in high-voltage and fast-charge system, lithium borates play an

important role in preventing Al foil form corrosion. Additionally, F-containing solvents have the advantages of lower cost, pollution and toxicity than sulfone or nitrile solvents. Based on the reasons above, we believe that the mixed lithium salts of LiFSI and lithium borates in F-containing solvents can realize commercial application in high-voltage electrolytes. In addition, weak solvation solvents could decrease the desolvation barrier of Li^+ and enhance the fast-charge ability, which are easy to prepare and have good compatibility with electrodes. And a small amount of additive has been proved effective in film formation for fast-charge. Therefore, matching LiFSI with weak solvation solvents and additives is regarded as suitable choice for commercial fast-charge electrolytes.

In conclusion, the improvement of electrolytes operating with high-voltage and fast-charge properties can be fulfilled by multi-strategies. Actually, the operation condition of LIBs in practical applications is complex and close to external environment. With the change of temperature and external current, the interface film will also change accordingly, which is enough to affect the performance of LIBs. In addition, the interfacial product is complex and sensitive, which is influenced by the interfacial reaction of electrolyte and electrode. What's more, in real fabrication process of electrode, some factors such as surface coating, areal density, compaction density, active material content, conductive agent, properties of the binder etc. are closely rated to the infiltration and connection situation with electrolytes. These factors can also influence the film formation behavior and components of high-voltage and fast-charge electrolytes, further affect the migration behavior of Li^+ . In the future, more attention should be paid to the following aspects:

- 1) The film forming conditions should cover the values of temperature and current. The all-sided understanding between electrolyte films and external conditions should be studied, thus helping us get better electrochemical performance of LIBs in real application.
- 2) The interfacial properties of the electrode, such as coating layer or element doping of the electrode material should be further investigated. In addition, the morphology, grain size, specific surface area and manufacturing technique of electrode materials should be also noted. As a result, only connecting the physical and chemical characterization of electrode materials with the electrochemical performance of LIBs, can we understand the reaction process more clearly.
- 3) More efforts should be made to combine all the factors that interacting with the electrolyte and the manufacturing cost to realize the commercialization of the investigated electrolytes.

For functional electrolyte design, in addition to meeting the high-voltage and fast-charge, the electrolyte also needs to be of better temperature applicability and safety. With the gradual deepening of the understanding of electrolytes, the invention and application of new electrolytes and electrode materials, combining with various advanced characterization methods and theoretical calculations, the problems can be solved.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

All data generated or analysed during this study are included in this published article (and its supplementary information files).

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