

Review

# Designing Strategies of Electrolyte Additive Formula for Highly Stable Lithium Metal Batteries

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**Abstract:** For the resurgence and commercialization of lithium-metal batteries (LMBs), functional electrolytes play an important role in mitigating critical challenges, such as dendritic growth on the lithium (Li) anode, capacity degradation at the cathode, and the decomposition of the electrolyte. Modifying electrolyte additives promises a practical, accessible, and cost-competitive approach to fine control the critical electrode interface reactions including Li deposition and solid electrolyte interphase/cathode electrolyte interphase (SEI/CEI) formation. Here, we summarize the state-of-the-art electrolyte additives and their mechanism in inducing the Li deposition and SEI/CEI film formation. Based on our previous work, we prospectively propose rational designing strategies of electrolyte formula, i.e., compound electrolytes, via combining film-forming additives and leveling additives, to comprehensively and continuously tuning the film formation, film properties, and Li deposition layer throughout the long-term cycling. We hope the proposed design strategies could promote the advancement of electrolyte engineering in the commercialization of high-energy LMBs.

**Keywords:** electrolyte formula; compound additives; film-forming additive; leveling additive

## 1. Introduction

High-energy density lithium metal batteries (LMBs) are booming again due to its promising in achieving the target of 500 Wh kg<sup>-1</sup> for next generation of electric vehicle [1]. The Li metal can provide 10 times higher theoretical capacity than the graphite (372 mAh g<sup>-1</sup> with the production of LiC<sub>6</sub>), which is 3860 mAh g<sup>-1</sup> [2]. And Li metal has high compatibility with many commercial and precommercial cathode materials (such as lithium nickel manganese cobalt oxides or NMC, Li/Ni-rich NMC, LiFePO<sub>4</sub>, sulfur cathode, and oxygen cathode) considering its low electrochemical potential, which is −3.040 V versus standard hydrogen electrode (SHE) [3]. However, LMBs face practical hindrances due to inherent issues like surface corrosion, dendritic growth, and the associated electrolyte decomposition on Li metal [4,5]. What's more, cathode materials commonly experience considerable capacity degradation, such as high-voltages cathode and soluble electrode. For example, the spinel LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> (LNMO) cathode material is difficult in achieving the theoretical capacity (~148 mAh g<sup>-1</sup>) and high operating voltage cycling over 4.7 V vs. Li/Li<sup>+</sup> because of interfacial reconstruction and irreversible transition metal (TM) leaching on the electrode surface [6]. Lithium-sulfur (Li-S) batteries emerge as a transformative alternative for traditional battery systems, featuring with the sulfur's high capacity of 1672 mAh g<sup>-1</sup>, but the sulfur cathode suffers from severe shuttle effects [7].

To date, tremendous works using various additive are widely proposed for protection of either the lithium anode or the cathode [8]. The electrolyte additives can efficiently and cost-effectively tackle above issues due to the suitable additives facilitate the building of protective film covered on the electrode surface, i.e., solid-



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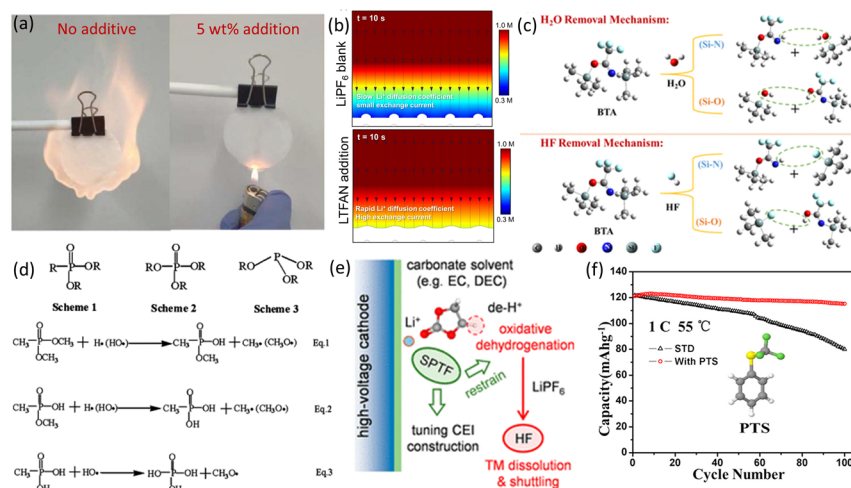
electrolyte-interphase (SEI) on the Li metal anode and cathode-electrolyte-interphase (CEI) on the cathode, via the in-situ electro(chemical) decomposition reactions [9,10]. The artificial SEI/CEI coating layer fosters stability and integrity in both the cathode and anode through suppressing the direct surface corrosive reaction or active materials dissolution between the electrolyte and electrode.

Furthermore, electrolyte additives are capable of tuning and smoothing the Li deposition/stripping process [11]. Electrolyte additives can alter the  $\text{Li}^+$  solvation structure by replacing solvent molecules, thereby facilitating the conduction of  $\text{Li}^+$  ions in the electrolyte and the nucleation process of  $\text{Li}^+$  on the electrode surface [12,13]. This alteration in the solvation structure of Li ions flattens the Li deposition/stripping process, resulting in a uniform Li deposition layer. In other cases, the additives possess the capacity to regulate the critical properties of the electrolyte-electrode interface, such as equilibrium the distribution of electrostatic and Li ions, thereby mitigating the formation of unwanted dendrites on Li metal anode surface [14–17].

Despite the extensive reports on electrolyte additives, a significant knowledge gap remains in the rational selection and optimization of additives to effectively regulate electrochemical processes at both lithium anodes and cathodes in high-energy lithium metal batteries (LMBs). In this perspective, we comprehensively summarize state-of-the-art electrolyte additives according to their key functions, including the modulation of SEI/CEI formation and lithium deposition behavior, to elucidate their structure–property relationships during battery operation. Furthermore, we highlight the critical role of compound additives (i.e., binary or multicomponent systems) in achieving enhanced cycling stability and efficiency in high-energy LMBs. We also present two of our most recent publications to validate this proposed electrolyte formulation. The underlying mechanisms of compound additives in synergistically regulating SEI/CEI chemistry and lithium deposition are systematically discussed. We anticipate that the design principles outlined herein will advance the development of high-energy LMBs.

## 2. State-of-the-Art Electrolyte Additives Focusing on SEI/CEI Film Formation

Up-to-date efforts have been put to improve the quality of SEI/CEI layer, which specifically are related with the chemical composition (i.e., organic species or the inorganic species) and physicochemical properties (i.e., mechanical resilience, ionic conductivity, and thermal stability) of the protective layer. The organic species (such as alkyl chain, oligomer, and Li-organic carbon/sulfur complex) enhance the flexibility and elasticity of SEI/CEI layers [18]. However, the SEI/CEI layers that are rich in organic species exhibit limitations in terms of unstable physicochemical properties, including the low Young's modulus (e.g.,  $\text{ROCO}_2\text{Li}/\text{ROLi} < 1$  GPa) and solubility in the electrolyte, which result in reduced protection for the electrode surface [19,20]. Meanwhile, the inorganic species (such as  $\text{LiF}$ ,  $\text{Li}_3\text{N}$ ,  $\text{Li}_3\text{P}$ , and  $\text{Li}_2\text{S}_x$ ) primarily play the role in mechanical resilience and ionic conduction, as a result boosting the reaction dynamic on the electrode surface [21–23]. The compact dual-layer structure, comprising organic components on the top and abundant inorganic components at the bottom, is considered the most critical design feature of the SEI [24]. In this context, electrolyte additives serve as an essential tool for engineering the interfacial structure and composition. Here, additives are discussed in detail based on the functional atoms/groups, including fluorine (F)-, nitrogen (N)-, silicon (Si)-, phosphorus (P)-, boron (B)-, and sulfur (S)-containing, to provide a clear overview of the diversity and functionality of these additives in SEI/CEI formation and electrolyte design (Figure 1 and Table 1).



**Figure 1.** Characteristic of electrolyte additives based on different key element: (a) F-contained additives such as ethoxy-(pentafluoro)-cyclotriphosphazene (denoted as PFN) is characterized with flame retardant property [25].

Reproduced from Ref. [25] with permission from Elsevier B.V. **(b)** N-contained additives with the example of lithium trifluoroacetate-lithium nitrate (denoted as LTFAN) facilitating the uniform  $\text{Li}^+$  flux near the Li electrode surface [26]. Reproduced from Ref. [26] with permission from John Wiley & Sons, Inc. **(c)** Si-contained additives such as N,O-bis(trimethylsilyl) trifluoro acetamide (denoted as BTA) enable to capture the trace of water and HF in the electrolyte [27]. Reproduced from Ref. [27] with permission from American Chemical Society. **(d)** P-contained additives such as dimethyl methylphosphonate (denoted as DMMP) react with radicals (such as  $\text{H}^*$  and  $\text{HO}^*$ ) to reduce the flammable risk of the electrolyte [28]. Reproduced from Ref. [28] with permission from Elsevier B.V. **(e)** B-contained additives such as potassium (4-methylsulfonylphenyl)trifluoroborate (denoted as SPTF) stabilize the surface of high-voltage cathode through formation of B-rich CEI layer [29]. Reproduced from Ref. [29] with permission from American Chemical Society. **(f)** S-contained additives such as phenyl trifluoromethyl sulfide (denoted as PTS) enable the cells cycling at 55 °C [30]. Reproduced from Ref. [30] with permission from Elsevier B.V.

Fluorine (F)-containing additives, typically are the LiF and fluoroethylene carbonate (FEC), are well-established electrolyte additives recognized for their efficacy in forming the uniform and stable LiF-rich SEI layer [31,32]. LiF is recognized as one of the most effective inorganic components of SEI due to its exceptional electrochemical stability, high surface energy ( $73.28 \text{ meV } \text{\AA}^{-2}$ ), wide band gap, and substantial modulus [33–35]. Some F-contained additives are particularly effective in passivating the cathode interface and leading the formation of metal fluoride, LiF, and C-F compounds on particle surface, which reduces the interfacial resistance and inhibit the dissolution of active mass [25,36,37]. Additionally, the F-contained additives exhibit higher flash points and greater ease of oxidation or reduction compared to solvents, which significantly enhance the thermal stability and safety of electrolyte (Figure 1a) [38,39]. The challenges of F-contained additives is its reduced products (i.e., LiF-based SEI) suffering from low intrinsic  $\text{Li}^+$  conductivity (ca.  $10^{-31} \text{ S cm}^{-1}$ ), significant overpotential, and sluggish charging in high current density. To address these issues, the LiF-based SEI layer is suggested to be modulated by incorporating inorganic lithiated species (such as  $\text{Li}_2\text{S}$ , [40]  $\text{Li}_3\text{N}$ , [41]  $\text{Li}_3\text{P}$  [42] and  $\text{Li}_2\text{CO}_3$  [21]) or doping organic species (such as P-O and P-F [43–45]).

Nitrogen (N)-containing additives, typically are  $\text{LiNO}_3$ , are reported to change the (electro)chemical properties of SEI and CEI layer. The in-situ generated N-rich SEI layer, commonly comprising the  $\text{LiN}_x\text{O}_y$ ,  $\text{Li}_3\text{N}$ , and  $\text{Li}_2\text{O}$ , can reduce the  $\text{Li}^+$  interfacial diffusion energy barrier and enhance the ionic conductivity (ca.  $10^{-3} \text{ S cm}^{-1}$ ), thereby providing a uniform  $\text{Li}^+$  flux between the electrode and electrolyte (Figure 1b) [46]. Notably,  $\text{LiNO}_3$  exhibits a unique protective effect on high-voltage cathode materials. During the charging process, the  $\text{NO}_3^-$  accumulate on the charged cathode interface and form a thermodynamically favorable electric double layer (EDL) [26]. This EDL plays a crucial role in preventing electrolyte decomposition and mitigating active capacity loss on the cathode surface. However, the challenge of the  $\text{LiNO}_3$  additives is its extremely low dissolution in the electrolyte ( $<0.01 \text{ mg mL}^{-1}$ ), thus continuous consumption of  $\text{LiNO}_3$  cause the less protection after the repeated and long cycling [47]. The strategies are replacing  $\text{LiNO}_3$  with N-containing small molecules [48] or combining with the functional additive as solubilizer (such as  $\text{LiBF}_4$  or  $\text{Mg}(\text{TFSI})_2$  salt) [49,50].

Silicon (Si)-containing additives, for example 2,2,2-trifluoro-N-methyl-N-(trimethylsilyl)acetamide (MSTFA) [51], N,O-bis(trimethylsilyl)trifluoroacetamide (BTA) [27], and 3-trimethylsilyl-2-oxazolidinone (TMS-ON) [52], are designed as water/HF acid remover in the electrolyte. The Si-O, Si-N, and Si-C bonds in the Si-containing additives actively adsorb and react with the trace of water and HF acid (Figure 1c), suppressing the parasitic reaction in the electrolyte and the corrosion on the electrode surface. What's more, the adsorption of Si-containing additives on lithium metal surface can reduce the electrolyte decomposition and lithium dendrite formation due to its less reactivity on lithium metal [53]. The challenge in using the Si-containing additives is the high-volume amount addition (mostly are 20–60 Vol.%) increase the cost and viscosity of the electrolyte [54–56].

Phosphorus (P)-containing additives, often in the form of phosphate esters, enable to enhance the flame-retardant properties of the electrolyte due to the radical scavenging species (such as  $\text{PO}^*$  and  $\text{PO}_2^*$ ) can interact with the radicals (such as  $\text{H}^*$  and  $\text{HO}^*$ ) produced within the organic electrolyte (Figure 1d) [28,57,58]. The phosphate esters, such as tri(trimethylsilyl) phosphate (TMSP) [59] and triphenylphosphate (TPP) [60], function as Lewis bases capable of neutralizing the HF on the electrolyte and cathode surface. The resulting stable and dense protective film (mainly are P-O based compounds) on the electrode surface significantly boost the high temperature cycling performance of high energy NCM cathode materials [61].

Boron (B)-containing additives, such as lithium bis(oxalato)borate (LiBOB) and 3-thiopheneboronic acid (TB), are attractive as Lewis acid to accept and combine anions (e.g.,  $\text{PF}_6^-$  and  $\text{F}^-$ ). Thus, it facilitates the dissociation and migration of  $\text{Li}^+$  as well as reduction of interaction between anions and solvent [62]. Additionally, the interaction between B and  $\text{PF}_6^-$  enhances the thermodynamic stability of  $\text{PF}_6^-$ , thereby suppressing its decomposition while

facilitating the formation of a B-rich interfacial film [63]. Among them, potassium (4-methylsulfonylphenyl)trifluoroborate (denoted as SPTF) are particularly suitable for stabilizing high-voltage  $\text{LiCoO}_2$  cathode through modifying the electrolyte decomposition and tailoring the CEI formation (Figure 1e) [29].

Sulfur (S)-containing additives, such as 1,3-propane sultone (PS) [64], 3-sulfolene (3SF) [65], diethyl sulfate (DTD) [66], and acid dimethyl ester (MMDS) [67,68], have attracted significant attention because of their structural similarity to organic carbonate electrolytes and high-temperature cycling performance of LMBs up to 55 °C (Figure 1f) [30,69,70]. The S-containing additives are film forming additives which can boost the composition and structure of the SEI/CEI layer. Butylene sulfite (BS) is a representative sulfur-containing film-forming additive that enables the use of propylene carbonate (PC)-based electrolytes with graphite anodes by suppressing solvent co-intercalation and promoting the formation of a compact, stable SEI [71]. DFT calculations reveal that the lower LUMO energy of BS compared with conventional carbonate solvents makes it preferentially reduced, generating inorganic/organic sulfur-rich interphase components such as  $\text{Li}_2\text{SO}_3$  and  $\text{ROSO}_2\text{Li}$  that enhance interfacial stability. Consequently, even a small amount of BS (5 vol.%) significantly improves thermal stability, oxidation tolerance, and cycling reversibility, demonstrating the effectiveness of sulfur-containing additives in regulating SEI chemistry and electrolyte stability. But it is hard to identify the suitable composition of S-containing additive because it has different decomposition products and pathway [66]. And S-containing additives suffer from complicated side reactions, making it challenging to be used alone.



Table 1. The category of electrolyte additives based on F, N, Si, P, B, S-based key element.

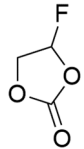
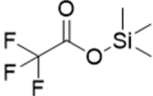
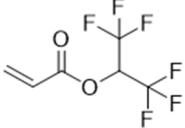
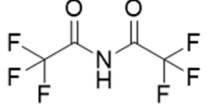
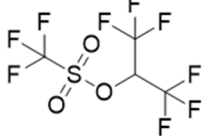
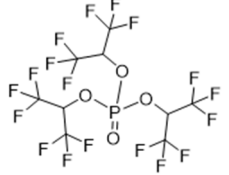
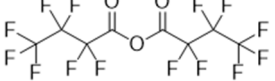
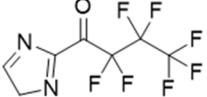
| Key Element | Additive            | Molecular Structure                                                                 | Cathode                                                                | Anode | Charge/Discharge Rate   | Cutoff Voltage | Capacity Retention | References |
|-------------|---------------------|-------------------------------------------------------------------------------------|------------------------------------------------------------------------|-------|-------------------------|----------------|--------------------|------------|
| F-based     | FEC                 |    | LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub> | Li    | 1 C/1 C                 | 4.3 V          | 65.0% @ 100cyc     | [72]       |
|             |                     |                                                                                     | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li    | 1 C/1 C                 | 4.6 V          | 87.3% @ 100cyc     | [73]       |
|             | TMSTFA              |    | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub> | Li    | 1 C/1 C                 | 4.5 V          | 80.0% @ 200 cyc    | [74]       |
|             | HFAC                |    | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li    | 1 C/1 C                 | 4.5 V          | 74.0% @ 200 cyc    | [75]       |
|             | BFA                 |    | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li    | 0.5 mA·cm <sup>-2</sup> | 4.5 V          | 78.5% @ 200 cyc    | [76]       |
|             | HFPTf               |    | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub> | Li    | 100 mA·g <sup>-1</sup>  | 4.5 V          | 70.0% @ 150 cyc    | [77]       |
|             | THFP                |   | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li    | 100 mA·g <sup>-1</sup>  | 4.3 V          | 82.0% @ 200 cyc    | [78]       |
|             | HFA                 |  | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li    | 1 C/1 C                 | 4.5 V          | 65.1% @ 250 cyc    | [79]       |
|             | HFBMZ               |  | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li    | 0.5 A·g <sup>-1</sup>   | 4.5 V          | 82.4% @ 150 cyc    | [80]       |
|             | K <sup>+</sup> PFHS |  | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li    | 0.2 A·g <sup>-1</sup>   | 4.5 V          | 77.1% @ 200 cyc    | [81]       |

Table 1. Cont.

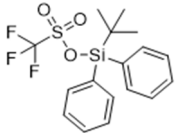
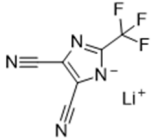
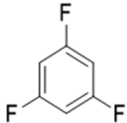
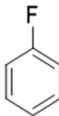
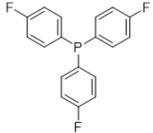
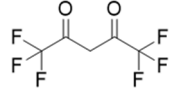
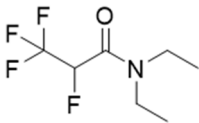
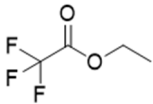
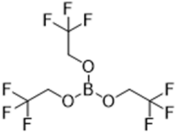
| Key Element | Additive                                       | Molecular Structure                                                                 | Cathode                                                                | Anode | Charge/Discharge Rate | Cutoff Voltage | Capacity Retention | References |
|-------------|------------------------------------------------|-------------------------------------------------------------------------------------|------------------------------------------------------------------------|-------|-----------------------|----------------|--------------------|------------|
| F-based     | TB                                             |    | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li    | 2 C/2 C               | 4.3 V          | 66.7% @ 200 cyc    | [82]       |
|             | C <sub>6</sub> F <sub>3</sub> LiN <sub>4</sub> |    | LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub> | Li    | 1 C/1 C               | 4.3 V          | 82.6% @ 400 cyc    | [83]       |
|             | 3FB                                            |    | LiCoO <sub>2</sub>                                                     | Li    | 2 C/2 C               | 4.5 V          | 80.0% @ 600 cyc    | [84]       |
|             | FB                                             |    |                                                                        |       |                       |                |                    |            |
|             | TFPP                                           |    | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li    | 0.1 A·g <sup>-1</sup> | 4.5 V          | 87.8% @ 200 cyc    | [85]       |
|             | HFAA                                           |   | LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub> | Li    | 10 C/10 C             | 4.6 V          | 60.9% @ 300 cyc    | [4]        |
|             | DETFP                                          |  | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub> | Li    | 1 C/1 C               | 4.3 V          | 98.1% @ 100 cyc    | [86]       |
|             | 2,2,2-TFTF                                     |  | LiFePO <sub>4</sub>                                                    | Li    | 5 C/5 C               | 4.2 V          | 86.0% @ 500cyc     | [87]       |
|             | TTFEB                                          |  | LiFePO <sub>4</sub>                                                    | Li    | 1 C/1 C               | 4.2 V          | 92.1% @ 500cyc     | [88]       |

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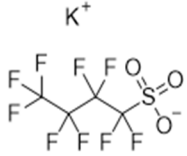
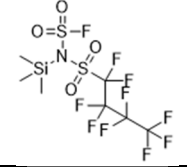
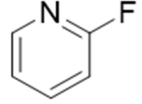
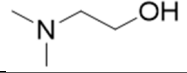
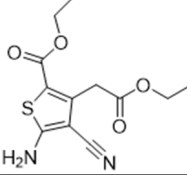
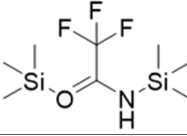
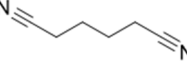
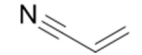
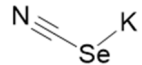
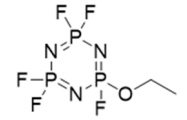
| Key Element | Additive  | Molecular Structure                                                                 | Cathode                                                                                                                                          | Anode | Charge/Discharge Rate                               | Cutoff Voltage          | Capacity Retention                                 | References   |
|-------------|-----------|-------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------|-------|-----------------------------------------------------|-------------------------|----------------------------------------------------|--------------|
| F-based     | KPBS      |    | LiFePO <sub>4</sub>                                                                                                                              | Li    | 1 mA·cm <sup>-1</sup>                               | 3.8 V                   | 80.0% @ 400cyc                                     | [89]         |
|             | TMS-FNFSI |    | LiFePO <sub>4</sub>                                                                                                                              | Li    | 0.2 C/0.2 C                                         | 3.8 V                   | 92.0% @ 100cyc                                     | [90]         |
| N-based     | 2-FP      |    | LiNi <sub>1/3</sub> Mn <sub>1/3</sub> Co <sub>1/3</sub> O <sub>2</sub><br>LiFePO <sub>4</sub>                                                    | Li    | 0.75 mA·cm <sup>-1</sup><br>1.5 mA·cm <sup>-1</sup> | 4.3 V                   | 67.6% @ 300cyc<br>68.0% @ 200cyc                   | [91]         |
|             | DMEA      |    | LiCoO <sub>2</sub>                                                                                                                               | Li    | 0.5 C/0.5 C                                         | 4.4 V                   | 84.2% @ 200cyc                                     | [92]         |
|             | TAEC      |    | LiCoO <sub>2</sub>                                                                                                                               | Li    | 1 C/1 C                                             | 4.5 V                   | 85.1% @ 100cyc                                     | [93]         |
|             | BSTFA     |   | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub><br>LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub> | Li    | 2 C/2 C<br>1 C/2 C                                  | 4.6 V<br>4.4 V          | 75.3% @ 100cyc<br>50% @ 750cyc                     | [94]<br>[27] |
|             | AND       |  | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub>                                                                           | Li    | 50 mA·g <sup>-1</sup>                               | 4.4 V<br>4.6 V<br>4.8 V | 80.7% @ 100cyc<br>70.4% @ 100cyc<br>35.3% @ 100cyc | [95]         |
|             | AN        |  | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> (pouch cells)                                                             | Li    | 1/10 C/1/3 C                                        | 3.7 V                   | 84.7% @ 120cyc                                     | [96]         |
|             | KSeCN     |  | LiCoO <sub>2</sub>                                                                                                                               | Li    | 1 C/1 C<br>2 C/5 C                                  | 4.6 V                   | 68.6% @ 750cyc<br>70.4% @ 1000cyc                  | [97]         |
|             | PFN       |  | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub> (pouch cells)                                                             | Li    | 0.33 CC/0.5 CD                                      | 4.4 V                   | 92.5% @ 50cyc                                      | [98]         |
|             |           |                                                                                     | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub>                                                                                             |       | 1.45 A                                              | 4.2 V                   | 80% @ 45cyc                                        | [99]         |
|             |           |                                                                                     | LiCoO <sub>2</sub>                                                                                                                               |       | 0.5 C/0.5 C<br>0.2 C/0.5 C                          | 4.9 V<br>4.5 V          | 90.7% @ 100cyc<br>70% @ 100cyc                     | [100]        |

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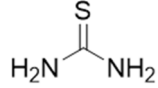
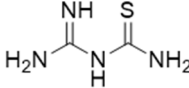
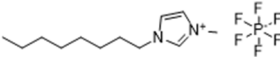
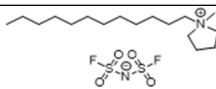
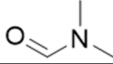
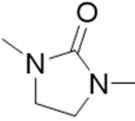
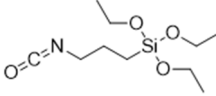
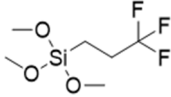
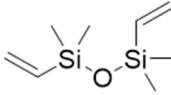
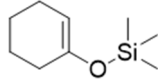
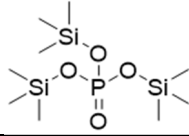
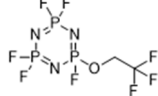
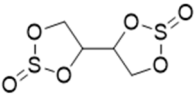
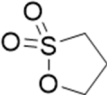
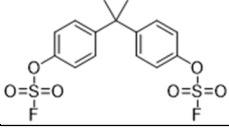
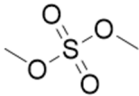
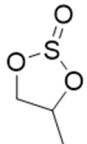
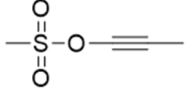
| Key Element | Additive              | Molecular Structure                                                                 | Cathode                                                                | Anode | Charge/Discharge Rate | Cutoff Voltage | Capacity Retention               | References |
|-------------|-----------------------|-------------------------------------------------------------------------------------|------------------------------------------------------------------------|-------|-----------------------|----------------|----------------------------------|------------|
| N-based     | THU                   |    | LiFePO <sub>4</sub>                                                    | Li    | 1 C/1 C<br>5 C/5 C    | 4.0 V          | 88.0% @ 800cyc<br>90.0% @ 650cyc | [101]      |
|             | ATU                   |    | LiFePO <sub>4</sub>                                                    | Li    | 2 C/2 C               | 4.0 V          | 79.2% @ 700cyc                   | [102]      |
|             | Im1(8)PF <sub>6</sub> |    | LiFePO <sub>4</sub>                                                    | Li    | 2 C/2 C               | 4.2 V          | 97.8% @ 570cyc                   | [103]      |
|             | Pyr1(12)FSI           |    | LiFePO <sub>4</sub>                                                    | Li    | 0.5 C/0.5 C           | 4.2 V          | 74.6% @ 500cyc                   | [104]      |
|             | DMF                   |    | LiFePO <sub>4</sub>                                                    | Li    | 0.2 C/0.2 C           | 4.2 V          | 85.0% @ 150cyc (60 °C)           | [105]      |
|             | DMI                   |    | LiFePO <sub>4</sub>                                                    | Li    | 5 C/5 C               | 3.65 V         | 96.5% @ 2200cyc                  | [106]      |
| Si-based    | IPTS                  |    | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub> | Li    | 0.3 C/0.3 C           | 4.5 V          | 73.1% @ 150cyc                   | [107]      |
|             | TTS                   |    | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub>                   | Li    | 0.3 C/0.3 C           | 4.5 V          | 92% @ 150cyc                     | [108]      |
|             | DTMDS                 |   | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>5</sub>                   | Li    | 0.5 C/0.5 C           | 4.95 V         | 95.3% @ 500cyc                   | [109]      |
|             | TMSCH                 |  | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub> | Li    | 1 C/1 C               | 4.3 V          | 84.9% @ 200cyc                   | [110]      |
|             | TTSP                  |  | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub> | Li    | 0.3 C/0.3 C           | 4.3 V          | 95.9% @ 80cyc                    | [111]      |
| P-based     | TFPN                  |  | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub> | Li    | 20 mA·g <sup>-1</sup> | 4.2 V          | 85.3% @ 100cyc                   | [112]      |

Table 1. Cont.

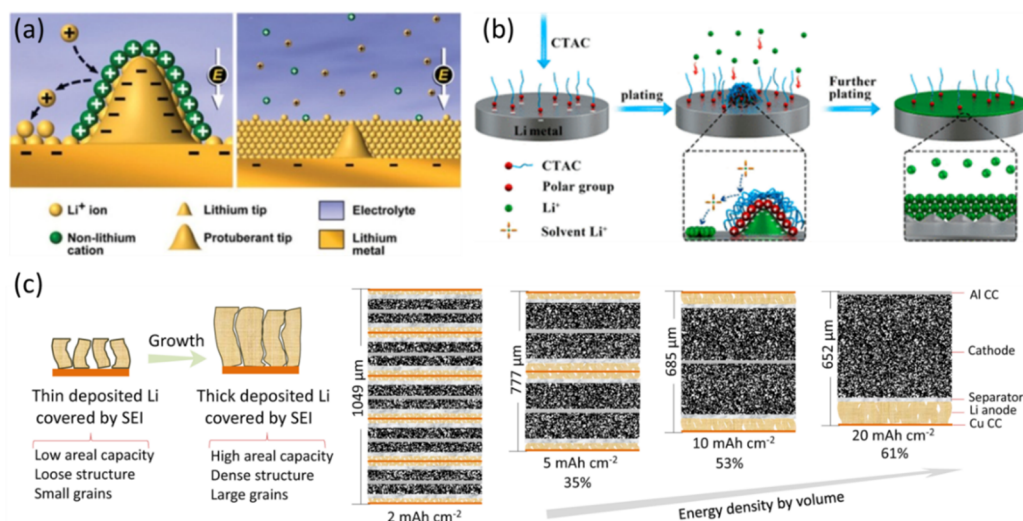
| Key Element | Additive                         | Molecular Structure                                                    | Cathode                                                                   | Anode         | Charge/Discharge Rate | Cutoff Voltage         | Capacity Retention     | References |
|-------------|----------------------------------|------------------------------------------------------------------------|---------------------------------------------------------------------------|---------------|-----------------------|------------------------|------------------------|------------|
| P-based     | DPPA                             |                                                                        | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub>    | Li            | 1 C/1 C               | 4.3 V                  | 80.8% @ 250cyc         | [113]      |
|             | LiPO <sub>2</sub> F <sub>2</sub> |                                                                        | LiCoO <sub>2</sub>                                                        | Li            | 1 C/1 C               | 4.3 V                  | 97.5% @ 160cyc         | [114]      |
|             |                                  |                                                                        | LiNi <sub>1/3</sub> Co <sub>1/3</sub> Mn <sub>1/3</sub> O <sub>2</sub>    |               | 0.5 C/0.5 C           | 4.2 V                  | 99.0% @ 100cyc         | [115]      |
|             |                                  |                                                                        | LiNi <sub>0.5</sub> Mn <sub>0.3</sub> Co <sub>0.2</sub> O <sub>2</sub>    |               | 0.5 C/0.5 C           | 4.3 V                  | 69.6% @ 300cyc (60 °C) | [116]      |
|             |                                  |                                                                        |                                                                           |               | 0.1 C/0.1 C           | 4.4 V                  | 93.7% @ 50cyc (−20 °C) |            |
|             | LiDFBP                           |                                                                        | LiNi <sub>0.8</sub> Co <sub>0.1</sub> Mn <sub>0.1</sub> O <sub>2</sub>    | Li            | 0.5 C/0.5 C           | 4.2 V                  | 94.5% @ 100cyc         | [117]      |
|             | DEPP                             |                                                                        | LiCoO <sub>2</sub>                                                        | Li            | 1 C/1 C               | 4.5 V                  | 66.8% @ 100cyc         | [118]      |
| TAP         |                                  | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub> | Li                                                                        | 1/10 C/1/10 C | 4.3 V                 | 68.1% @ 400cyc (60 °C) | [119]                  |            |
| B-based     | LCTFEB                           |                                                                        | LiNi <sub>0.5</sub> Co <sub>0.2</sub> Mn <sub>0.3</sub> O <sub>2</sub>    | Li            | 0.5 C/0.5 C           | 4.5 V                  | 91.0% @ 500cyc         | [120]      |
|             | 3-TB                             |                                                                        | LiNi <sub>0.6</sub> Co <sub>0.2</sub> Mn <sub>0.2</sub> O <sub>2</sub>    | Li            | 0.2 C/0.2 C           | 4.3 V                  | 90.1% @ 100cyc         | [121]      |
|             | TPFPB                            |                                                                        | LiNi <sub>0.5</sub> Mn <sub>1.5</sub> O <sub>4</sub>                      | Li            | 0.5 C/0.5 C           | 4.95 V                 | 90.0% @ 500cyc         | [122]      |
|             | LiBOB                            |                                                                        | LiNi <sub>0.76</sub> Mn <sub>0.14</sub> Co <sub>0.10</sub> O <sub>2</sub> | Li            | 1/3 C/1/3 C           | 4.5 V                  | 96.8% @ 200cyc         | [123]      |
|             |                                  |                                                                        |                                                                           |               | 1 C/1 C               |                        | 90.8% @ 200cyc         |            |
|             |                                  |                                                                        |                                                                           | 2 C/2 C       |                       | 92.7% @ 200cyc         |                        |            |
|             |                                  |                                                                        |                                                                           | 5 C/5 C       |                       | 82.3% @ 200cyc         |                        |            |
|             |                                  |                                                                        |                                                                           | 0.2 C/5 C     |                       | 86.1% @ 500cyc         |                        |            |

Table 1. Cont.

| Key Element | Additive        | Molecular Structure                                                                | Cathode                                                       | Anode | Charge/Discharge Rate   | Cutoff Voltage | Capacity Retention     | References |
|-------------|-----------------|------------------------------------------------------------------------------------|---------------------------------------------------------------|-------|-------------------------|----------------|------------------------|------------|
| S-based     | BDTD            |   | $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$   | Li    | 0.5 C/0.5 C             | 4.6 V          | 85.4% @ 100cyc         | [124]      |
|             | 1,3-PS          |   | $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$   | Li    | 0.5 C/0.5 C             | 4.3 V          | 80.8% @ 400cyc         | [125]      |
|             | P2PFS           |   | $\text{LiNi}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$ | Li    | 1 C/1 C                 | 4.3 V          | 94% @ 70cyc            | [126]      |
|             | SO <sub>2</sub> | $\text{O}=\text{S}=\text{O}$                                                       | $\text{LiCoO}_2$                                              | Li    | 1 C/1 C                 | 4.2 V          | 77.1% @ 180cyc         | [127]      |
|             | DMS             |   | $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$   | Li    | 0.5 C/0.5 C             | 4.2 V          | 85.0% @ 100cyc         | [128]      |
|             | 1,2-PS          |   | $\text{LiFePO}_4$                                             | Li    | 0.5 mA·cm <sup>-1</sup> | 3.6 V          | 96.0% @ 40cyc          | [129]      |
|             | DMSO            |   | $\text{LiFePO}_4$                                             | Li    | 0.2 C/0.2 C             | 3.8 V          | 88.9% @ 50cyc (−40 °C) | [130]      |
|             | PMS             |  | $\text{Li}_4\text{Ti}_5\text{O}_{12}$                         | Li    | 1 C/1 C                 | 3.0 V          | 92.1% @ 300cyc (55 °C) | [131]      |

### 3. State-of-the-Art Electrolyte Additives Influencing Li Deposition Process

The electrolyte additives have been reported to control the Li deposition during the lithium plating and stripping process. This section will review the up-to-date advances of the modulation mechanisms in Li nucleation/growth process via the addition of electrolyte additives (Figure 2).



**Figure 2.** (a) Scheme of lithium deposition process based on the self-healing electrostatic shield mechanism [132]. Reproduced from Ref. [132] with permission from American Chemical Society. (b) Illustration of the lithiophobic repulsion mechanisms achieving through the addition of hexadecyl trimethylammonium chloride (CTAC) [11]. Reproduced from Ref. [11] with permission from American Chemical Society. (c) The proposed mechanism for lithium deposition on electrodes covers a range of areal capacities from low to very high. The schematic illustrates how the anode's areal capacity affects the overall energy density of Li metal full-cell batteries. When a high-capacity cathode is paired with dense lithium deposition at 20 mAh cm<sup>-2</sup>, there is a 61% increase in volumetric energy density [133]. Reproduced from Ref. [133] with permission from Springer Nature.

The initial stage of electroplating process is the nucleation of Li sites on the Li metal anode surface. The tip of the electrode is typically considered an active point for forming the Li nuclear. When assuming the whisker tip is a static hemisphere, Li ions more likely deposit on the protrusions due to the enhanced electric fields and accumulated charges near the hemispherical tip [134]. Rather than forming the uniform Li nuclear, the accumulation of Li ions on the tips will intrigue the growth of Li dendrites on the electrode surface. Regarding to addressing this issue, electrolyte additives containing the alkali metal ions, such as  $\text{Cs}^+$  and  $\text{K}^+$ , have been proposed to form a cationic electrostatic shielding layer at the tip (Figure 2a) [132]. Moreover, the repulsion between  $\text{Li}^+$  and  $\text{Cs}^+$  causes the  $\text{Li}^+$  ions to accumulate in the concave areas, thereby filling up the surface of the Li anode. Under the electrostatic shielding on electrode surface, the uniform Li ions distribution will result in the homogenous Li deposition and growth.

The lithiophobic repulsion mechanisms were further studied to achieve the spatial homogeneity of Li ions distribution on electrode surface and the dendrite-free Li deposition (Figure 2b). During the lithium plating process, cationic surfactant molecules such as hexadecyl trimethylammonium chloride (CTAC) cations [11] exhibit an electrostatic attraction to the protruding tips, owing to their interaction with outward-facing nonpolar groups. Moreover, the surface free energy at these tips experiences an elevation in comparison to a smooth electrode surface, resulting in a heightened concentration of CTAC molecules being adsorbed at the solid-liquid interface within these raised regions. As a consequence, the substantial adsorption of CTAC molecules in these protuberant areas, driven by the interplay of electrostatic interactions and surface free energy, facilitates the formation of a lithiophobic layer. As the plating process progresses, polarized solvent  $\text{Li}^+$  faces impediments when attempting to penetrate the outward lithiophobic layer, primarily due to repulsive forces. Consequently, the ensuing Li decomposition is redirected towards neighboring regions, facilitating the establishment of a smoother Li surface. Furthermore, the internally positively charged layer composed of polar groups effectively impedes the growth of Li dendrites by means of electrostatic repulsive forces.

High plating capacity such as 10–50 mAh cm<sup>-2</sup> is suggested to effectively texture the Li metal deposition accompany with the help of  $\text{LiNO}_3$  addition (Figure 2c) [133]. The (110)<sub>Li</sub> crystallographic facets are dominantly

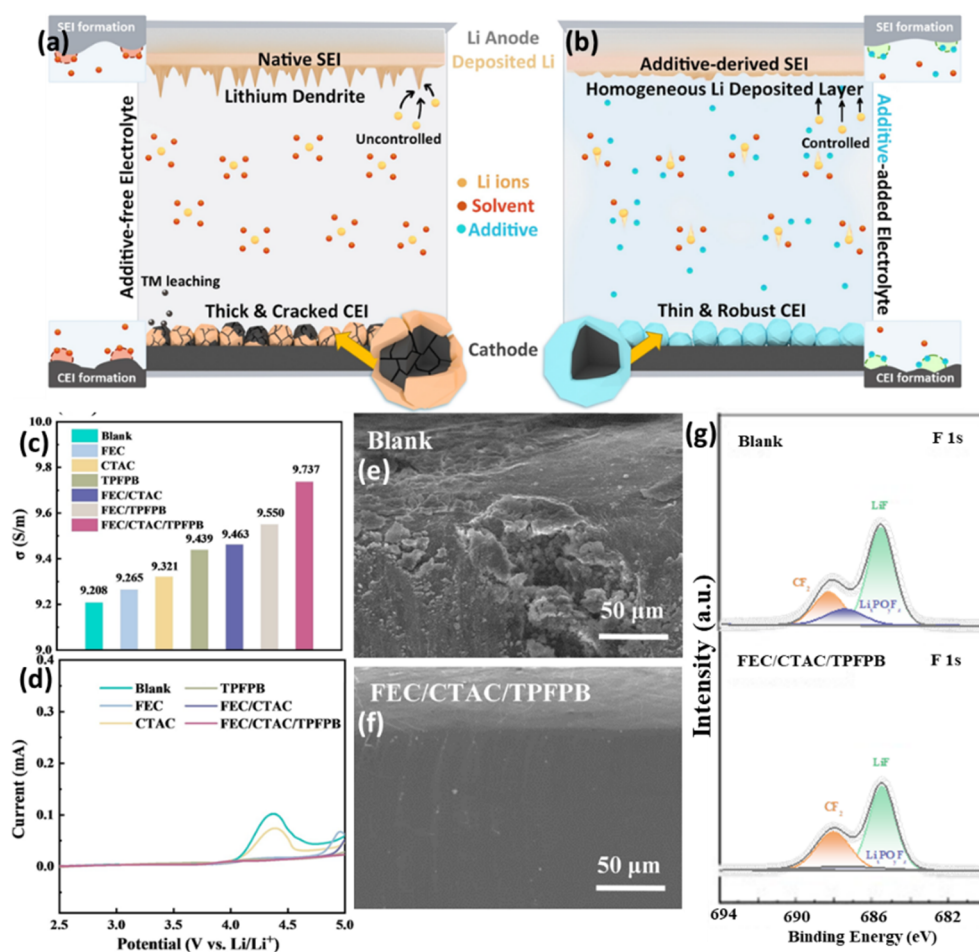


formed due to it has the lowest migration energy barrier and less likely grow into non-planar dendritic morphologies compared to other crystal facets. The decomposition of  $\text{LiNO}_3$  facilitate the formation of the robust and thin inorganic SEI layer and enhance the kinetics of lithium stripping/plating. Consequently, high areal deposition of lithium metal leads to denser structures and forming the larger grains. Both effects can slow down parasitic chemical and electrochemical reactions between the electrode and electrolyte. Simultaneously, the as-prepared battery demonstrates increased electrochemical stability with respect to the electrolyte.

#### 4. Designing Strategies of Electrolyte Additive Formula for Highly Stable Lithium Metal Batteries

As discussed above, electrolyte additives provide an efficient and cost-effective strategy to mitigate interfacial issues at both cathodes and anodes, primarily through forming functional interphases (i.e., SEI/CEI) and regulating uniform  $\text{Li}^+$  deposition. Based on our previous studies, these additives can be broadly classified into two categories: film-forming additives and leveling additives. Film-forming additives are electrochemically active at the electrode/electrolyte interface and continuously decompose to generate protective SEI/CEI layers, thereby stabilizing electrode surfaces. Incorporation of heteroatoms (e.g., N, S, Si) into these additives can enhance the structural robustness and electronic conductivity of the interphase. However, their continuous consumption during cycling compromises long-term stability, particularly under extended operation. In contrast, leveling additives exhibit higher electrochemical stability and primarily function to promote dense and uniform  $\text{Li}^+$  deposition, thereby suppressing dendrite formation.

Building on these insights, we propose the concept of compound electrolyte additives, which integrate both film-forming and leveling functionalities through the combination of two or more additive components. Such a design enables simultaneous stabilization of interfacial layers and sustained regulation of Li deposition, leading to improved cycling stability and enhanced energy density. Guided by this strategy, our previous work has successfully developed two representative systems employing compound electrolytes, demonstrating long cycle life and high energy density in lithium metal batteries (Figures 3 and 4).

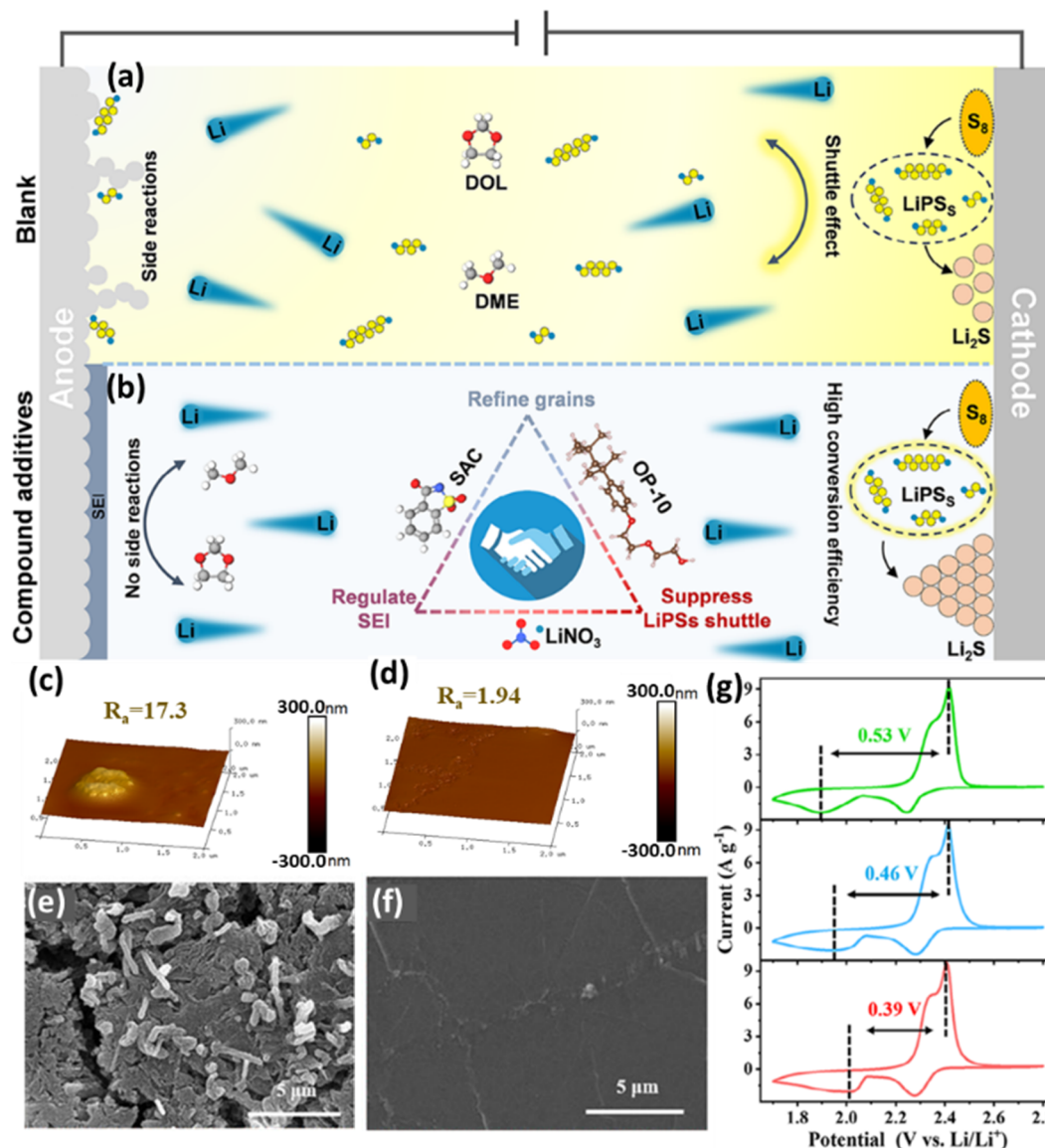


**Figure 3.** In our previous work, a compound electrolyte was developed by integrating fluoroethylene carbonate (FEC), hexadecyl trimethylammonium chloride (CTAC), and tri(pentafluorophenyl)borane (TPFPB) [135].

(a,b) Schematic illustrations of  $\text{Li}^+$  solvation structures and electrode interfacial process with and without the addition of additives in the electrolytes during Li deposition/stripping. (c) Ionic conductivities of different electrolytes additive compositions. (d) Linear sweep voltammetry (LSV) curves of Li-Al cells with single or compound additives at a scan rate of  $5 \text{ mV s}^{-1}$ . (e,f) Cross-sectional scanning electron microscopy (SEM) images of Li foils after 10 cycles at  $1 \text{ mA cm}^{-2}$  and  $3 \text{ mAh cm}^{-2}$ . (g) High-resolution X-ray photoelectron spectroscopy (XPS) depth profiles of the F 1s orbital for the LNMO cathode after 10 cycles in different electrolytes. Reproduced from Ref. [135] with permission from Wiley-VCH GmbH.

In 2024, our previous work successfully implemented a compound electrolyte formulation comprising ternary components, including fluoroethylene carbonate (FEC), hexadecyl trimethylammonium chloride (CTAC), and tri(pentafluorophenyl)borane (TPFPB), in 7.3 Ah-class  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$  ( $x = 0.83$ , NCM83)|Li pouch cells [135]. In the blank electrolyte, high-voltage LMBs suffer from severe interfacial instability, including uncontrolled and massive lithium dendrite growth, fragile native SEI on the lithium anode, as well as transition metal dissolution and the formation of thick, cracked CEI layers on the high-voltage cathode (Figure 3a). In contrast, the ternary electrolyte system significantly improves electrode-electrolyte interactions by enabling uniform  $\text{Li}^+$  deposition and forming robust SEI and CEI layers (Figure 3b). Mechanistically, FEC promotes the formation of fluorine-rich interphases, suppressing electrolyte decomposition and stabilizing electrode interfaces [72]. CTAC regulates uniform and dense  $\text{Li}^+$  ions deposition, thereby preserving SEI integrity during prolonged cycling [11]. TPFPB further enhances ionic transport and improves the mechanical robustness of the interfacial films [122]. Although all electrolytes appear visually similar, their ionic conductivities differ markedly (Figure 3c). The binary FEC/CTAC system increases ionic conductivity relative to the baseline electrolyte, while incorporation of TPFPB leads to a further enhancement. Correspondingly, the TPFPB-containing electrolyte delivers higher specific capacity than electrolytes with only FEC or CTAC. Notably, at high current density (5 C), the capacity of the CTAC-containing electrolyte declines sharply, likely due to its limited oxidative stability, resulting in decomposition under high-voltage conditions, as confirmed by LSV measurements (Figure 3d). Cross-sectional SEM images (Figure 3e,f) reveal that Li deposited in the blank electrolyte exhibits uneven, fragmented morphology with pronounced cracks, whereas the compound-additive electrolyte enables a dense and intact Li structure, free of noticeable fissures or voids. To further elucidate cathode interfacial chemistry, XPS analysis of the LNMO cathode was performed (Figure 3g). The F 1s spectrum shows characteristic peaks corresponding to  $\text{CF}_2$  ( $\sim 688.0 \text{ eV}$ ),  $\text{LiF}$  ( $\sim 685.0 \text{ eV}$ ), and  $\text{Li}_x\text{PO}_y\text{F}_z$  ( $\sim 687.0 \text{ eV}$ ), originating from the decomposition of PVDF and  $\text{LiPF}_6$ . The formation of a fluorine-rich CEI is critical for stabilizing the high-voltage NCM83 cathode. As a result, the  $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_{1-x-y}]\text{O}_2$  ( $x = 0.83$ , NCM83)|Li pouch cell presents a high energy density of  $522 \text{ Wh kg}^{-1}$  and maintains stable cycling over 178 cycles with a capacity retention over 80.9%. These results highlight the superior practical potential of multi-component electrolyte additives compared to single-additive systems, particularly for high-voltage lithium metal batteries.

In 2025, our previous work further developed a compound additive system comprising lithium nitrate ( $\text{LiNO}_3$ ), sodium saccharin (SAC), and octaphenyl polyoxyethylene (OP-10) for lithium-sulfur (Li-S) batteries. Mechanistically,  $\text{LiNO}_3$  promotes SEI formation and regulates polysulfide solvation, SAC refines SEI morphology to facilitate planar Li deposition, and OP-10 increase  $\text{Li}^+$  flux uniformity while immobilizing polysulfides via polar interactions (Figure 4a,b) [136]. Atomic force microscopy (AFM) of Cu foils immersed in different electrolytes reveals obviously different interfacial adsorption behaviors. As shown in Figure 4c,d, the  $\text{LiNO}_3/\text{SAC}/\text{OP-10}$  system exhibits the lowest average surface roughness ( $R_a$ ) and a notably smooth microstructure, arising from synergistic adsorption at the electrode-electrolyte interface. This effect provides a favorable foundation for forming a stable SEI [137]. Furthermore, scanning electron microscopy (SEM) of cycled lithium anodes corroborates the enhanced interfacial stability and elucidates the performance improvement enabled by the composite additive system. After 10 cycles, the blank electrolyte exhibits massive dendritic and obvious surface cracking (Figure 4e), whereas the ternary  $\text{LiNO}_3/\text{SAC}/\text{OP-10}$  system maintains a smooth and compact Li morphology (Figure 4f). Cyclic voltammetry (CV) profiles (Figure 4g) show cathodic peaks at 2.28 and 2.04 V, corresponding to the reduction of insoluble  $\text{S}_8$  to soluble long-chain polysulfides and their subsequent conversion to  $\text{Li}_2\text{S}_2/\text{Li}_2\text{S}$ , respectively. The anodic peaks at 2.34 and 2.40 V are attributed to the reverse oxidation processes. The cell incorporating compound additives exhibits minimal peak polarization, indicating accelerated polysulfide conversion kinetics and improved sulfur utilization [138]. Consequently, the compound electrolyte effectively suppresses lithium dendrite growth, enabling Li|Li symmetric cells to operate stably for over 1400 h at  $1 \text{ mA cm}^{-2}$  with an areal capacity of  $3 \text{ mAh cm}^{-2}$ . Under quasi-practical conditions, the Li-S cell achieves an areal capacity of  $2.72 \text{ mAh cm}^{-2}$  after 150 cycles. These results demonstrate that compound additive simultaneously mitigates dendrite formation and the polysulfide shuttle effect, offering a promising strategy for high-performance Li-S batteries.



**Figure 4.** In our previous work, a compound electrolyte system was developed by integrating lithium nitrate (LiNO<sub>3</sub>), sodium saccharin (SAC), and octaphenyl polyoxyethylene (OP-10) [136]. **(a,b)** Schematic illustrations of Li-S batteries with and without compound additives. **(c,d)** Atomic force microscopy (AFM) images of Cu foil after 24 h immersion in blank and additive-containing electrolytes. **(e,f)** Scanning electron microscopy (SEM) images of Li foil after cycling in corresponding electrolytes. **(g)** Cyclic voltammetry (CV) curves of Li-S batteries with blank electrolyte (green), LiNO<sub>3</sub>/SAC (blue), and LiNO<sub>3</sub>/SAC/OP-10 (red) electrolytes. Reproduced from Ref. [136] with permission from Wiley-VCH GmbH.

Besides, the compound additive engineering has also been demonstrated in other studies on lithium metal batteries, where their complementary physicochemical functions enable the simultaneous regulation of additive solubility, electrolyte solvation chemistry, ion transport, and interphase formation, producing synergistic effects that cannot be achieved by individual additives alone. For example, a “small-sized carrier” strategy employed vinylene carbonate (VC) to promote the dissolution of the film-forming additive LiNO<sub>3</sub> in carbonate electrolytes, while Zn(BF<sub>4</sub>)<sub>2</sub> further regulated interfacial chemistry by facilitating the formation of a uniform organic-inorganic cathode electrolyte interphase (CEI) and, together with LiNO<sub>3</sub>, constructing an inorganic-rich SEI on the lithium metal anode [139]. The cooperative coordination of VC and NO<sub>3</sub><sup>−</sup> with Li<sup>+</sup> also optimized the solvation structure and accelerated ion transport, leading to enhanced interfacial stability and electrochemical performance. In another example, 1,3-dimethylimidazolium dimethyl phosphate (DIDP) and trimethylsilyl trifluoroacetate (TMSF) were designed to undergo an in-situ transesterification reaction, generating multifunctional additives that performed complementary roles [140]. The resulting products simultaneously scavenged moisture and HF, enhanced the dissolution of LiNO<sub>3</sub>, optimized the Li<sup>+</sup> solvation environment, and preferentially decomposed to form robust additive-derived interphases on both the cathode and lithium metal anode. These representative examples highlight

the broad potential of compound additive engineering as a universal strategy for developing high-performance electrolytes for lithium metal batteries.

## 5. Conclusions and Outlook

In conclusion, we have summarized the recent advances on the development of electrolyte additives according to their functions in Li deposition and SEI/CEI film formation. We have clearly discussed and analyzed the chemical composition and functions mechanism of electrolyte additives on electrode surface. The structure-property relationship of the additives molecules and related capability are also analyzed in the literature review section. Most importantly, we proposed the significance of compound electrolyte to achieve both high-energy-density and longevity for lithium metal batteries. The compound electrolyte contains two or more additives to facilitate both robust CEI/SEI layer formation via film-forming additives and uniform Li deposition via leveling additives. To verify our proposed electrolyte formula, we also presented and summarized two of our most recent publications in using the three-component compound electrolyte in both high-voltage lithium metal batteries and high-energy lithium-sulfur batteries.

Beyond binary systems that combine film-forming and leveling additives, ternary compound electrolytes offer greater adaptability for operation under complex conditions. From an application perspective, the third additive can be tailored to introduce specific functionalities, such as high ionic conductivity, robustness, wide-temperature operability (e.g., ultra-low or high temperatures), flame retardancy, high-voltage stability, overcharge protection, and corrosion resistance. For instance, in lithium–sulfur batteries, incorporating anticorrosive or polysulfide-adsorbing additives is essential, as dissolved polysulfides can induce severe corrosion of the lithium anode. Meanwhile, key physicochemical parameters-including freezing point, melting point, flash point, decomposition voltage, and ionic conductivity-should be systematically evaluated to guide the rational selection and formulation of electrolyte additives. Such integrated design and application of compound electrolytes will further advance our fundamental understanding of electrolyte systems and their interfacial chemistry.

## Author Contributions

T.T.: writing—original draft preparation; Z.W.: writing—original draft preparation, reviewing, and editing; C.S. and C.L.: supervision—reviewing and editing. All authors have read and agreed to the published version of the manuscript.

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## Institutional Review Board Statement

Not applicable.

## Informed Consent Statement

Not applicable.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of Interest

The authors declare no conflict of interest.

## Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

## References

1. Liu, J.; Bao, Z.; Cui, Y.; et al. Pathways for practical high-energy long-cycling lithium metal batteries. *Nat. Energy* **2019**, *4*, 180–186.
2. Wu, Z.; Tian, Y.; Chen, H.; et al. Evolving aprotic Li-air batteries. *Chem. Soc. Rev.* **2022**, *51*, 8045–8101.
3. Zhong, Y.; Huang, P.; Yan, W.; et al. Ion-Conductive Polytitanosiloxane Networks Enable a Robust Solid-Electrolyte Interface for Long-Cycling Lithium Metal Anodes. *Adv. Funct. Mater.* **2022**, *32*, 2110347.
4. Dong, J.; Dai, H.; Fan, Q.; et al. Grain refining mechanisms: Initial levelling stage during nucleation for high-stability lithium anodes. *Nano Energy* **2019**, *66*, 104128.
5. Qian, S.; Chen, H.; Zheng, M.; et al. Complementary combination of lithium protection strategies for robust and longevous lithium metal batteries. *Energy Storage Mater.* **2023**, *57*, 229–248.
6. Zhu, X.; Schulli, T.U.; Yang, X.; et al. Epitaxial growth of an atom-thin layer on a  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathode for stable Li-ion battery cycling. *Nat. Commun.* **2022**, *13*, 1565.
7. Li, G.; Zhang, J.; Wu, Z.; et al. Local structure modulations of single-atom catalysts in sulfur electrocatalysis: A comprehensive review. *Mater. Today* **2025**, *85*, 141–170.
8. Zhu, Y.; Ge, M.; Ma, F.; et al. Multifunctional Electrolyte Additives for Better Metal Batteries. *Adv. Funct. Mater.* **2024**, *34*, 2301964.
9. Wang, Y.; Wu, Z.; Azad, F.M.; et al. Fluorination in advanced battery design. *Nat. Rev. Mater.* **2024**, *9*, 119–133.
10. Dai, H.; Dong, J.; Wu, M.; et al. Cobalt-Phthalocyanine-Derived Molecular Isolation Layer for Highly Stable Lithium Anode. *Angew. Chem. Int. Ed.* **2021**, *60*, 19852–19859.
11. Dai, H.; Xi, K.; Liu, X.; et al. Cationic surfactant-based electrolyte additives for uniform lithium deposition via lithiophobic repulsion mechanisms. *J. Am. Chem. Soc.* **2018**, *140*, 17515–17521.
12. Feng, D.; Cao, F.; Hou, L.; et al. Immunizing Aqueous Zn Batteries against Dendrite Formation and Side Reactions at Various Temperatures via Electrolyte Additives. *Small* **2021**, *17*, 2103195.
13. Wu, Z.; Li, M.; Tian, Y.; et al. Cyclohexanodecyl-Assisted Interfacial Engineering for Robust and High-Performance Zinc Metal Anode. *Nano-Micro Lett.* **2022**, *14*, 110.
14. Li, L.; Dai, H.; Wang, C. Electrolyte additives: Adding the stability of lithium metal anodes. *Nano Select* **2020**, *2*, 16–36.
15. Li, D.; Liu, H.; Feng, L. A Review on Advanced FeNi-Based Catalysts for Water Splitting Reaction. *Energy Fuels* **2020**, *34*, 13491–13522.
16. Ding, F.; Xu, W.; Graff, G.L.; et al. Dendrite-Free Lithium Deposition via Self-Healing Electrostatic Shield Mechanism. *J. Am. Chem. Soc.* **2013**, *135*, 4450–4456.
17. Wu, J.; Li, X.; Rao, Z.; et al. Electrolyte with boron nitride nanosheets as leveling agent towards dendrite-free lithium metal anodes. *Nano Energy* **2020**, *72*, 104725.
18. Li, G.; Gao, Y.; He, X.; et al. Organosulfide-plasticized solid-electrolyte interphase layer enables stable lithium metal anodes for long-cycle lithium-sulfur batteries. *Nat. Commun.* **2017**, *8*, 850.
19. Cohen, Y.S.; Cohen, Y.; Aurbach, D. Micromorphological studies of lithium electrodes in alkyl carbonate solutions using in situ atomic force microscopy. *J. Phys. Chem. B* **2000**, *104*, 12282–12291.
20. Sun, H.-H.; Dolocan, A.; Weeks, J.A.; et al. In situ formation of a multicomponent inorganic-rich SEI layer provides a fast charging and high specific energy Li-metal battery. *J. Mater. Chem. A* **2019**, *7*, 17782–17789.
21. Zhang, Q.; Pan, J.; Lu, P.; et al. Synergetic effects of inorganic components in solid electrolyte interphase on high cycle efficiency of lithium ion batteries. *Nano Lett.* **2016**, *16*, 2011–2016.
22. Lu, Y.; Tu, Z.; Archer, L.A. Stable lithium electrodeposition in liquid and nanoporous solid electrolytes. *Nat. Mater.* **2014**, *13*, 961–969.
23. Li, W.; Yao, H.; Yan, K.; et al. The synergetic effect of lithium polysulfide and lithium nitrate to prevent lithium dendrite growth. *Nat. Commun.* **2015**, *6*, 7436.
24. Yan, C.; Cheng, X.B.; Tian, Y.; et al. Dual-layered film protected lithium metal anode to enable dendrite-free lithium deposition. *Adv. Mater.* **2018**, *30*, 1707629.
25. Liu, J.; Song, X.; Zhou, L.; et al. Fluorinated phosphazene derivative—A promising electrolyte additive for high voltage lithium ion batteries: From electrochemical performance to corrosion mechanism. *Nano Energy* **2018**, *46*, 404–414.
26. Wen, Z.; Fang, W.; Wang, F.; et al. Dual-Salt Electrolyte Additive Enables High Moisture Tolerance and Favorable Electric Double Layer for Lithium Metal Battery. *Angew. Chem. Int. Ed.* **2024**, *63*, e202314876.
27. Liu, Y.; Hong, L.; Jiang, R.; et al. Multifunctional electrolyte additive stabilizes electrode–electrolyte interface layers for high-voltage lithium metal batteries. *ACS Appl. Mater. Interfaces* **2021**, *13*, 57430–57441.

28. Xiang, H.; Xu, H.; Wang, Z.; et al. Dimethyl methylphosphonate (DMMP) as an efficient flame retardant additive for the lithium-ion battery electrolytes. *J. Power Sources* **2007**, *173*, 562–564.
29. Yan, Y.; Weng, S.; Fu, A.; et al. Tailoring electrolyte dehydrogenation with trace additives: Stabilizing the LiCoO<sub>2</sub> cathode beyond 4.6 V. *ACS Energy Lett.* **2022**, *7*, 2677–2684.
30. Huang, W.; Xing, L.; Zhang, R.; et al. A novel electrolyte additive for improving the interfacial stability of high voltage lithium nickel manganese oxide cathode. *J. Power Sources* **2015**, *293*, 71–77.
31. Von Aspern, N.; Rösenthaller, G.V.; Winter, M.; et al. Fluorine and lithium: Ideal partners for high-performance rechargeable battery electrolytes. *Angew. Chem. Int. Ed.* **2019**, *58*, 15978–16000.
32. Zhao, J.; Liao, L.; Shi, F.; et al. Surface fluorination of reactive battery anode materials for enhanced stability. *J. Am. Chem. Soc.* **2017**, *139*, 11550–11558.
33. Zheng, J.; Lochala, J.A.; Kwok, A.; et al. Research progress towards understanding the unique interfaces between concentrated electrolytes and electrodes for energy storage applications. *Adv. Sci.* **2017**, *4*, 1700032.
34. Yamada, Y.; Yamada, A. Superconcentrated electrolytes for lithium batteries. *J. Electrochem. Soc.* **2015**, *162*, A2406.
35. Fan, X.; Chen, L.; Borodin, O.; et al. Non-flammable electrolyte enables Li-metal batteries with aggressive cathode chemistries. *Nat. Nanotechnol.* **2018**, *13*, 715–722.
36. Lee, Y.-M.; Nam, K.-M.; Hwang, E.-H.; et al. Interfacial origin of performance improvement and fade for 4.6 V LiNi<sub>0.5</sub>Co<sub>0.2</sub>Mn<sub>0.3</sub>O<sub>2</sub> battery cathodes. *J. Phys. Chem. C* **2014**, *118*, 10631–10639.
37. Zheng, X.; Huang, T.; Pan, Y.; et al. Enhancing the high-voltage cycling performance of LiNi<sub>1/3</sub>Co<sub>1/3</sub>Mn<sub>1/3</sub>O<sub>2</sub>/graphite batteries using alkyl 3, 3, 3-trifluoropropanoate as an electrolyte additive. *ACS Appl. Mater. Interfaces* **2017**, *9*, 18758–18765.
38. Liu, Y.; Wang, K.; Lin, Y.; et al. Tetrafluoroterephthalonitrile: A novel electrolyte additive for high-voltage lithium cobalt oxide/graphite battery. *Electrochim. Acta* **2017**, *256*, 307–315.
39. Xia, L.; Xia, Y.; Liu, Z. A novel fluorocyclophosphazene as bifunctional additive for safer lithium-ion batteries. *J. Power Sources* **2015**, *278*, 190–196.
40. Cheng, X.-B.; Yan, C.; Peng, H.-J.; et al. Sulfurized solid electrolyte interphases with a rapid Li<sup>+</sup> diffusion on dendrite-free Li metal anodes. *Energy Storage Mater.* **2018**, *10*, 199–205.
41. Kim, M.S.; Zhang, Z.; Wang, J.; et al. Revealing the multifunctions of Li<sub>3</sub>N in the suspension electrolyte for lithium metal batteries. *ACS Nano* **2023**, *17*, 3168–3180.
42. Tan, Y.H.; Liu, Z.; Zheng, J.H.; et al. Inorganic Composition Modulation of Solid Electrolyte Interphase for Fast Charging Lithium Metal Batteries. *Adv. Mater.* **2024**, *36*, 2404815.
43. Zheng, H.; Xiang, H.; Jiang, F.; et al. Lithium difluorophosphate-based dual-salt low concentration electrolytes for lithium metal batteries. *Adv. Energy Mater.* **2020**, *10*, 2001440.
44. Kim, K.-E.; Jang, J.Y.; Park, I.; et al. A combination of lithium difluorophosphate and vinylene carbonate as reducible additives to improve cycling performance of graphite electrodes at high rates. *Electrochem. Commun.* **2015**, *61*, 121–124.
45. Zheng, X.; Fang, G.; Pan, Y.; et al. Synergistic effect of fluoroethylene carbonate and lithium difluorophosphate on electrochemical performance of SiC-based lithium-ion battery. *J. Power Sources* **2019**, *439*, 227081.
46. Dinh Nguyen, H.; Duong Pham, T.; Bin Faheem, A.; et al. Marrying a Non-Flammable Phosphate Solvent with Lithium Nitrate: Novel Electrolyte for Intrinsically Safe and High Performance Lithium Metal Batteries. *Batter. Supercaps* **2023**, *6*, e202200453.
47. Piao, N.; Liu, S.; Zhang, B.; et al. Lithium metal batteries enabled by synergetic additives in commercial carbonate electrolytes. *ACS Energy Lett.* **2021**, *6*, 1839–1848.
48. Baloch, M.; Shanmukaraj, D.; Bondarchuk, O.; et al. Variations on Li<sub>3</sub>N protective coating using ex-situ and in-situ techniques for Li<sup>0</sup> in sulphur batteries. *Energy Storage Mater.* **2017**, *9*, 141–149.
49. Wang, X.; Li, S.; Zhang, W.; et al. Dual-salt-additive electrolyte enables high-voltage lithium metal full batteries capable of fast-charging ability. *Nano Energy* **2021**, *89*, 106353.
50. Liu, S.; Xia, J.; Zhang, W.; et al. Salt-in-salt reinforced carbonate electrolyte for Li metal batteries. *Angew. Chem.* **2022**, *134*, e202210522.
51. Peng, Q.; Liu, Z.; Chen, S.; et al. Developing multifunctional amide additive by rational molecular design for high-performance Li metal batteries. *Nano Energy* **2023**, *113*, 108547.
52. Kim, K.; Hwang, D.; Kim, S.; et al. Cyclic aminosilane-based additive ensuring stable electrode–electrolyte interfaces in Li-ion batteries. *Adv. Energy Mater.* **2020**, *10*, 2000012.
53. Yanagisawa, R.; Endo, H.; Unno, M.; et al. Effects of organic silicon compounds as additives on charge–discharge cycling efficiencies of lithium in nonaqueous electrolytes for rechargeable lithium cells. *J. Power Sources* **2014**, *266*, 232–240.
54. Inose, T.; Tada, S.; Morimoto, H.; et al. Poly-ether modified siloxanes as electrolyte additives for rechargeable lithium cells. *J. Power Sources* **2006**, *161*, 550–559.

55. Takeuchi, T.; Noguchi, S.; Morimoto, H.; et al. Carbonate-modified siloxanes as solvents of electrolyte solutions for rechargeable lithium cells. *J. Power Sources* **2010**, *195*, 580–587.
56. Takei, Y.; Takeno, K.; Morimoto, H.; et al. Effects of nonaqueous electrolyte solutions mixed with carbonate-modified siloxane on charge–discharge performance of negative electrodes for secondary lithium batteries. *J. Power Sources* **2013**, *228*, 32–38.
57. Feng, J.; Ma, P.; Yang, H.; et al. Understanding the interactions of phosphonate-based flame-retarding additives with graphitic anode for lithium ion batteries. *Electrochim. Acta* **2013**, *114*, 688–692.
58. Dunn, R.P.; Kafle, J.; Krause, F.C.; et al. Electrochemical analysis of Li-ion cells containing triphenyl phosphate. *J. Electrochem. Soc.* **2012**, *159*, A2100.
59. Zhang, J.; Wang, J.; Yang, J.; et al. Artificial interface deriving from sacrificial tris (trimethylsilyl) phosphate additive for lithium rich cathode materials. *Electrochim. Acta* **2014**, *117*, 99–104.
60. Zhao, W.; Zheng, B.; Liu, H.; et al. Toward a durable solid electrolyte film on the electrodes for Li-ion batteries with high performance. *Nano Energy* **2019**, *63*, 103815.
61. Song, Y.-M.; Kim, C.-K.; Kim, K.-E.; et al. Exploiting chemically and electrochemically reactive phosphite derivatives for high-voltage spinel  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  cathodes. *J. Power Sources* **2016**, *302*, 22–30.
62. Chen, J.; Chen, H.; Mei, Y.; et al. Polarly modulated solvent strategy for high-voltage cathode materials. *Chem. Eng. J.* **2022**, *450*, 138318.
63. Liu, Y.; Tan, L.; Li, L. Tris (trimethylsilyl) borate as an electrolyte additive to improve the cyclability of  $\text{LiMn}_2\text{O}_4$  cathode for lithium-ion battery. *J. Power Sources* **2013**, *221*, 90–96.
64. Zuo, X.; Xu, M.; Li, W.; et al. Electrochemical reduction of 1, 3-propane sultone on graphite electrodes and its application in Li-ion batteries. *Electrochem. Solid-State Lett.* **2006**, *9*, A196.
65. Wang, K.; Xing, L.; Zhi, H.; et al. High stability graphite/electrolyte interface created by a novel electrolyte additive: A theoretical and experimental study. *Electrochim. Acta* **2018**, *262*, 226–232.
66. Wu, Z.; Li, S.; Zheng, Y.; et al. The roles of sulfur-containing additives and their working mechanism on the temperature-dependent performances of li-ion batteries. *J. Electrochem. Soc.* **2018**, *165*, A2792.
67. Huang, T.; Wu, M.; Wang, W.; et al. Effect of methylene methanedisulfonate as an additive on the cycling performance of  $\text{LiMn}_2\text{O}_4$  cathode at elevated temperature. *J. Power Sources* **2014**, *262*, 303–309.
68. Bian, F.; Zhang, Z.; Yang, Y. Enhanced high temperature cycling performance of  $\text{LiMn}_2\text{O}_4$ /graphite cells with methylene methanedisulfonate (MMDS) as electrolyte additive and its acting mechanism. *J. Energy Chem.* **2014**, *23*, 383–390.
69. Ping, P.; Wang, Q.; Kong, D.; et al. Dimethyl sulfite as an additive for lithium bis (oxalate) borate/ $\gamma$ -Butyrolacton electrolyte to improve the performance of Li-ion battery. *J. Electroanal. Chem.* **2014**, *731*, 119–127.
70. Xia, J.; Harlow, J.; Petibon, R.; et al. Comparative study on methylene methyl disulfonate (MMDS) and 1, 3-propane sultone (PS) as electrolyte additives for Li-ion batteries. *J. Electrochem. Soc.* **2014**, *161*, A547.
71. Chen, R.; Wu, F.; Li, L.; et al. Butylene sulfite as a film-forming additive to propylene carbonate-based electrolytes for lithium ion batteries. *J. Power Sources* **2007**, *172*, 395–403.
72. Zhang, X.-Q.; Cheng, X.-B.; Chen, X.; et al. Fluoroethylene Carbonate Additives to Render Uniform Li Deposits in Lithium Metal Batteries. *Adv. Funct. Mater.* **2017**, *27*, 1605989.
73. Liu, L.; Wang, S.; Zhang, Z.; et al. Fluoroethylene carbonate as an electrolyte additive for improving interfacial stability of high-voltage  $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$  cathode. *Ionics* **2019**, *25*, 1035–1043.
74. Jiang, S.; Xu, X.; Yin, J.; et al. Multifunctional Electrolyte Additive for Bi-electrode Interphase Regulation and Electrolyte Stabilization in  $\text{Li/LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$  Batteries. *ACS Appl. Mater. Interfaces* **2022**, *14*, 38758–38768.
75. Li, F.; Liu, J.; He, J.; et al. Additive-Assisted Hydrophobic  $\text{Li}^+$ -Solvated Structure for Stabilizing Dual Electrode Electrolyte Interphases through Suppressing  $\text{LiPF}_6$  Hydrolysis. *Angew. Chem. Int. Ed.* **2022**, *61*, 134.
76. Li, F.; He, J.; Liu, J.; et al. Gradient Solid Electrolyte Interphase and Lithium-Ion Solvation Regulated by Bisfluoroacetamide for Stable Lithium Metal Batteries. *Angew. Chem. Int. Ed.* **2021**, *60*, 6600–6608.
77. Li, X.; Liu, J.; He, J.; et al. Hexafluoroisopropyl Trifluoromethanesulfonate-Driven Easily  $\text{Li}^+$  Desolvated Electrolyte to Afford  $\text{Li}||\text{NCM811}$  Cells with Efficient Anode/Cathode Electrolyte Interphases. *Adv. Funct. Mater.* **2021**, *31*, 2104395.
78. Sun, H.; Liu, J.; He, J.; et al. Stabilizing the cycling stability of rechargeable lithium metal batteries with tris(hexafluoroisopropyl)phosphate additive. *Sci. Bull.* **2022**, *67*, 725–732.
79. Wang, Y. Separator Wettability Enhanced by Electrolyte Additive to Boost the Electrochemical Performance of Lithium Metal Batteries. *Nanomicro Lett.* **2021**, *13*, 210.
80. Li, X.; Liu, J.; He, J.; et al. Separator-Wetted, Acid- and Water-Scavenged Electrolyte with Optimized Li-Ion Solvation to Form Dual Efficient Electrode Electrolyte Interphases via Hexa-Functional Additive. *Adv. Sci.* **2022**, *9*, e2201297.
81. Qi, S.; Wang, H.; He, J.; et al. Electrolytes enriched by potassium perfluorinated sulfonates for lithium metal batteries. *Sci. Bull.* **2021**, *66*, 685–693.



82. Zhou, H.; Li, T.; Liu, W.; et al. [tert-Butyl(diphenyl)silyl] trifluoromethanesulfonate acts as an effective additive for high-voltage lithium metal batteries. *Mater. Chem. Front.* **2022**, *6*, 2274–2283.
83. Wen, Z.; Li, H.; Li, H.; et al. Highly stable and robust bi-electrodes interfacial protective films for practical lithium metal batteries. *J. Power Sources* **2021**, *509*, 230370.
84. Zhang, H.; Zeng, Z.; He, R.; et al. 1,3,5-Trifluorobenzene and fluorobenzene co-assisted electrolyte with thermodynamic and interfacial stabilities for high-voltage lithium metal battery. *Energy Storage Mater.* **2022**, *48*, 393–402.
85. Wu, D.; He, J.; Liu, J.; et al. Li<sub>2</sub>CO<sub>3</sub>/LiF-Rich Heterostructured Solid Electrolyte Interphase with Superior Lithiophilic and Li<sup>+</sup>-Transferred Characteristics via Adjusting Electrolyte Additives. *Adv. Energy Mater.* **2022**, *12*, 2200337.
86. Zhou, P.; Xia, Y.; Hou, W.H.; et al. Rationally Designed Fluorinated Amide Additive Enables the Stable Operation of Lithium Metal Batteries by Regulating the Interfacial Chemistry. *Nano Lett.* **2022**, *22*, 5936–5943.
87. Yang, S.; Hao, M.; Wang, Z.; et al. 2,2,2-Trifluoroethyl trifluoroacetate as effective electrolyte additive for uniform Li deposition in lithium metal batteries. *Chem. Eng. J.* **2022**, *435*, 134897.
88. Ma, Y.; Zhou, Z.; Li, C.; et al. Enabling reliable lithium metal batteries by a bifunctional anionic electrolyte additive. *Energy Storage Mater.* **2018**, *11*, 197–204.
89. Wang, D.; Liu, H.; Li, M.; et al. A long-lasting dual-function electrolyte additive for stable lithium metal batteries. *Nano Energy* **2020**, *75*, 104889.
90. Tong, B.; Wang, J.; Liu, Z.; et al. (CH<sub>3</sub>)<sub>3</sub>Si-N[(FSO<sub>2</sub>)(n-C<sub>4</sub>F<sub>9</sub>SO<sub>2</sub>)]: An additive for dendrite-free lithium metal anode. *J. Power Sources* **2018**, *400*, 225–231.
91. Xie, Z.; Wu, Z.; An, X.; et al. 2-Fluoropyridine: A novel electrolyte additive for lithium metal batteries with high areal capacity as well as high cycling stability. *Chem. Eng. J.* **2020**, *393*, 124789.
92. Fan, X.; Xing, A.; Sun, W.; et al. Smart short-chain bifunctional N,N-dimethylethanolamine for high-performance lithium batteries. *Electrochim. Acta* **2018**, *282*, 711–718.
93. Zheng, Y.; Fang, W.; Zheng, H.; et al. A Multifunctional Thiophene-Based Electrolyte Additive for Lithium Metal Batteries Using High-Voltage LiCoO<sub>2</sub> Cathode. *J. Electrochem. Soc.* **2019**, *166*, A3222–A3227.
94. Zhou, H.; Shang, H.; Li, T.; et al. N,O-Bis(trimethylsilyl)trifluoroacetamide as an Effective Interface Film Additive on Lithium Anodes. *ACS Appl. Mater. Interfaces* **2022**, *14*, 5447–5458.
95. Zhao, L.; Bian, S.; Ju, Z.; et al. Lithium-Ion Batteries. *Int. J. Electrochem. Sci.* **2019**, *14*, 9755–9773.
96. Zhang, J.; Zhou, M.; Shi, J.; et al. Regulating lithium deposition via electropolymerization of acrylonitrile in rechargeable lithium metal batteries. *Nano Energy* **2021**, *88*, 106298.
97. Fu, A.; Lin, J.; Zhang, Z.; et al. Synergistical Stabilization of Li Metal Anodes and LiCoO<sub>2</sub> Cathodes in High-Voltage Li // LiCoO<sub>2</sub> Batteries by Potassium Selenocyanate (KSeCN) Additive. *ACS Energy Lett.* **2022**, *7*, 1364–1373.
98. Zhang, L.; Min, F.; Luo, Y.; et al. Practical 4.4 V Li||NCM811 batteries enabled by a thermal stable and HF free carbonate-based electrolyte. *Nano Energy* **2022**, *96*, 107122.
99. Li, H.; Wen, Z.; Wu, D.; et al. Achieving a Stable Solid Electrolyte Interphase and Enhanced Thermal Stability by a Dual-Functional Electrolyte Additive toward a High-Loading LiNi<sub>(0.8)</sub>Mn<sub>(0.1)</sub>Co<sub>(0.1)</sub>O<sub>(2)</sub> /Lithium Pouch Battery. *ACS Appl. Mater. Interfaces* **2021**, *13*, 57142–57152.
100. Liu, Q.; Chen, Z.; Liu, Y.; et al. Cooperative stabilization of bi-electrodes with robust interphases for high-voltage lithium-metal batteries. *Energy Storage Mater.* **2021**, *37*, 521–529.
101. Wang, Q.; Yang, C.; Yang, J.; et al. Dendrite-Free Lithium Deposition via a Superfilling Mechanism for High-Performance Li-Metal Batteries. *Adv. Mater.* **2019**, *31*, e1903248.
102. Lei, Y.; Xie, Y.; Huang, Y.; et al. Amidinothiourea as a new deposition-regulating additive for dendrite-free lithium metal anodes. *Chem. Commun.* **2021**, *57*, 10055–10058.
103. Wang, W.; Ma, W.; Yang, Q.; et al. Imidazolium-Based Ionic Liquid as a Solid Electrolyte Interphase-Forming Additive for Lithium Metal Anodes. *Ind. Eng. Chem. Res.* **2022**, *61*, 10883–10890.
104. Yoo, D.J.; Kim, K.J.; Choi, J.W. The Synergistic Effect of Cation and Anion of an Ionic Liquid Additive for Lithium Metal Anodes. *Adv. Energy Mater.* **2018**, *8*, 1702744.
105. You, L.; Duan, K.; Zhang, G.; et al. N,N-Dimethylformamide Electrolyte Additive Via a Blocking Strategy Enables High-Performance Lithium-Ion Battery under High Temperature. *J. Physic. Chem. C* **2019**, *123*, 5942–5950.
106. Zhou, P.; Xia, Y.; Wu, Y.; et al. Novel Urea-Based Molecule Functioning as a Solid Electrolyte Interphase Enabler and LiPF<sub>6</sub> Decomposition Inhibitor for Fast-Charging Lithium Metal Batteries. *ACS Appl. Mater. Interfaces* **2022**, *14*, 38921–38930.
107. Wang, S.; Chen, S.; Gao, W.; et al. A new additive 3-Isocyanatopropyltriethoxysilane to improve electrochemical performance of Li/NCM622 half-cell at high voltage. *J. Power Sources* **2019**, *423*, 90–97.
108. Chen, H.; Chen, J.; Zhang, W.; et al. Enhanced cycling stability of high-voltage lithium metal batteries with a trifunctional electrolyte additive. *J. Mater. Chem. A* **2020**, *8*, 22054–22064.



109. Dong, Z.; Wei, J.; Yue, H.; et al. Multifunctional organosilicon compound contributes to stable operation of high-voltage lithium metal batteries. *J. Colloid Interface Sci.* **2021**, *595*, 35–42.
110. Jiang, S.; Xu, X.; Yin, J.; et al. Regulating electrode-electrolyte interphases and eliminating hydrogen fluoride to boost electrochemical performances of Li/NCM811 batteries. *Chem. Eng. J.* **2023**, *451*, 138359.
111. Ma, Q.; Zhang, X.; Wang, A.; et al. Stabilizing Solid Electrolyte Interphases on Both Anode and Cathode for High Areal Capacity, High-Voltage Lithium Metal Batteries with High Li Utilization and Lean Electrolyte. *Adv. Funct. Mater.* **2020**, *30*, 2002824.
112. Li, Y.; An, Y.; Tian, Y.; et al. Stable and Safe Lithium Metal Batteries with Ni-Rich Cathodes Enabled by a High Efficiency Flame Retardant Additive. *J. Electrochem. Soc.* **2019**, *166*, A2736–A2740.
113. Jiang, F.; Zheng, H.; Hong, L.; et al. Diphenyl Azidophosphate as a Functional Electrolyte Additive for High-Conductivity Film Construction over Lithium Metal Battery. *J. Electrochem. Soc.* **2021**, *168*, 090530.
114. Yang, G.; Shi, J.; Shen, C.; et al. Improving the cyclability performance of lithium-ion batteries by introducing lithium difluorophosphate (LiPO<sub>2</sub>F<sub>2</sub>) additive. *RSC Adv.* **2017**, *7*, 26052–26059.
115. Shi, P.; Zhang, L.; Xiang, H.; et al. Lithium Difluorophosphate as a Dendrite-Suppressing Additive for Lithium Metal Batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 22201–22209.
116. Shangguan, X.; Xu, G.; Cui, Z.; et al. Additive-Assisted Novel Dual-Salt Electrolyte Addresses Wide Temperature Operation of Lithium-Metal Batteries. *Small* **2019**, *15*, e1900269.
117. Ma, H.; Hwang, D.; Ahn, Y.J.; et al. In Situ Interfacial Tuning To Obtain High-Performance Nickel-Rich Cathodes in Lithium Metal Batteries. *ACS Appl. Mater. Interfaces* **2020**, *12*, 29365–29375.
118. Miao, C.; Qi, S.; Liang, K.; et al. Diethyl phenylphosphonite contributing to solid electrolyte interphase and cathode electrolyte interphase for lithium metal batteries. *J. Energy Chem.* **2021**, *63*, 566–573.
119. Leng, Y.; Ge, S.; Longchamps, R.S.; et al. High Voltage Stable Li Metal Batteries Enabled by Ether-Based Highly Concentrated Electrolytes at Elevated Temperatures. *J. Electrochem. Soc.* **2020**, *167*, 110543.
120. Chae, O.B.; Adiraju, V.A.K.; Lucht, B.L. Lithium Cyano Tris(2,2,2-trifluoroethyl) Borate as a Multifunctional Electrolyte Additive for High-Performance Lithium Metal Batteries. *ACS Energy Lett.* **2021**, *6*, 3851–3857.
121. Ren, W.; Huang, Y.; Li, S.; et al. 3-Thiopheneboronic acid: An effective additive for regulation on electrode/electrolyte interphase of lithium metal battery with high-loading cathode. *Electrochim. Acta* **2021**, *386*, 138485.
122. Yue, H.; Yang, Y.; Xiao, Y.; et al. Boron additive passivated carbonate electrolytes for stable cycling of 5 V lithium-metal batteries. *J. Mater. Chem. A* **2019**, *7*, 594–602.
123. Zhao, W.; Zou, L.; Zheng, J.; et al. Simultaneous Stabilization of LiNi<sub>(0.76)</sub>Mn<sub>(0.14)</sub>Co<sub>(0.10)</sub>O<sub>(2)</sub> Cathode and Lithium Metal Anode by Lithium Bis(oxalato)borate as Additive. *ChemSusChem* **2018**, *11*, 2211–2220.
124. Im, J.; Ahn, J.; Choi, H.; et al. A dual-function sulfite-type additive for long cycle life in high-voltage lithium metal batteries. *J. Alloys Compound.* **2021**, *872*, 159662.
125. Zheng, W.-C.; Shi, C.-G.; Dai, P.; et al. A functional electrolyte additive enabling robust interphases in high-voltage Li<sub>1</sub>LiNi<sub>0.8</sub>Co<sub>0.1</sub>Mn<sub>0.1</sub>O<sub>2</sub> batteries at elevated temperatures. *J. Mater. Chem. A* **2022**, *10*, 21912–21922.
126. Oh, J.; Lee, H.S.; Kim, M.P.; et al. A trade-off-free fluorosulfate-based flame-retardant electrolyte additive for high-energy lithium batteries. *J. Mater. Chem. A* **2022**, *10*, 21933–21940.
127. Moon, S.; Park, H.; Yoon, G.; et al. Simple and Effective Gas-Phase Doping for Lithium Metal Protection in Lithium Metal Batteries. *Chem. Mater.* **2017**, *29*, 9182–9191.
128. Wan, G.; Guo, F.; Li, H.; et al. Suppression of Dendritic Lithium Growth by in Situ Formation of a Chemically Stable and Mechanically Strong Solid Electrolyte Interphase. *ACS Appl. Mater. Interfaces* **2018**, *10*, 593–601.
129. Xu, J.; Tian, H.-K.; Qi, J.; et al. Mechanical and Electronic Stabilization of Solid Electrolyte Interphase with Sulfite Additive for Lithium Metal Batteries. *J. Electrochem. Soc.* **2019**, *166*, A3201–A3206.
130. Zhang, Y.; Luo, J.; Wang, C.; et al. Electrolyte additive enabled low temperature lithium metal batteries. *Mater. Chem. Front.* **2022**, *6*, 1405–1413.
131. Wang, R.; Wang, Z.; Li, X.; et al. Electrochemical Analysis the influence of Propargyl Methanesulfonate as Electrolyte Additive for Spinel LTO Interface Layer. *Electrochim. Acta* **2017**, *241*, 208–219.
132. Zhang, S.; Zhuang, X.; Du, X.; et al. A Novel Potassium Salt Regulated Solvation Chemistry Enabling Excellent Li-Anode Protection in Carbonate Electrolytes. *Adv. Mater.* **2023**, *35*, 2301312.
133. Zhao, Q.; Deng, Y.; Utomo, N.W.; et al. On the crystallography and reversibility of lithium electrodeposits at ultrahigh capacity. *Nat. Commun.* **2021**, *12*, 6034.
134. Cheng, X.-B.; Zhang, R.; Zhao, C.-Z.; et al. Toward Safe Lithium Metal Anode in Rechargeable Batteries: A Review. *Chem. Rev.* **2017**, *117*, 10403–10473.
135. Tang, T.; Sun, C.; Li, Y.; et al. Long-lifespan 522 Wh kg<sup>-1</sup> lithium metal pouch cell enabled by compound additives engineering. *Angew. Chem. Int. Ed.* **2025**, *137*, e202417471.

136. Sun, C.; Tang, T.; Zheng, M.; et al. Synergistic Compound Additives for High-Performance Lithium–Sulfur Batteries. *Adv. Mater.* **2025**, *37*, 2507006.
137. Jia, R.; Dai, H.; Tu, X.; et al. Hexabutylcyclohexane-1,2,3,4,5,6-hexamine Additive-Assisted Commercial Ester Electrolyte for 4.7 V Highly-Stable Li-Metal Batteries. *Adv. Energy Mater.* **2023**, *13*, 2302747.
138. Shi, M.; Han, X.; Qu, W.; et al. Nanocellulose-derived hierarchical carbon framework-supported P-Doped MoO<sub>2</sub> nanoparticles for optimizing redox kinetics in lithium–sulfur batteries. *Adv. Mater.* **2025**, *37*, 2419918.
139. Xu, C.; Liu, S.; Che, S.; et al. Intermolecular interaction adjustment for LiNO<sub>3</sub> solubility promotion toward high-performance Li||NCM811 Batteries. *ACS Nano* **2025**, *19*, 27754–27767.
140. Gao, Y.; Wu, G.; Fang, W.; et al. Transesterification induced multifunctional additives enable high-performance lithium metal batteries. *Angew. Chemie.* **2024**, *136*, e202403668.