Electrolytes for Lithium and Lithium-Ion Batteries

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In this chapter, new trends in the formulation of non-aqueous liquid electrolytes will be discussed. Novel solvents and salts used in Li-ion battery electrolytes are categorized and illustrated, and the progress in understanding the formation mechanism behind the solid-electrolyte interphase (SEI) is discussed.

1 Introduction

There has been an explosion of development in portable electronics over the last several decades. As a consequence, Li-ion battery technology has also evolved tremendously to meet the demand for higher energy density, longer cycle life, and lower cost. Now, the technology is moving into applications requiring even higher energy and power density, such as electric vehicles [10, 29, 102]. For this purpose, great advances have been made in both high-energy anode materials [49] and cathode materials [115].

On the anode side, silicon-based materials emerged as a super high-capacity anode for the Li-ion battery [111]. Other alloy anode materials [80, 137] and metal oxides [83, 112] also showed great promise. However, due to their different characteristics from the conventional carbonaceous anode, these anode materials raise new challenges for battery electrolytes. The ability to deliver higher capacity usually also means larger volume expansion during lithiation, and as a result, the SEI with conventional electrolyte is damaged/cracked due to repeated dramatic changes of the anode material morphology during cycling [37, 50].

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On the cathode side, the introduction of high-energy materials has also presented new challenges. In conventional Li-ion batteries, the cathode/electrolyte interface is rarely a problem because the cut-off potential of conventional cathode materials (lower than 4 V vs. Li^+/Li) is usually far below the oxidative decomposition potential of the state-of-the-art (SOA) electrolyte. However, many of the new-generation cathode materials set cut-off potentials around 4.3 V, with the potential reaching above 4.5 V versus Li^+/Li [44]. The high-voltage cathode materials have even higher charging potentials, some close to 5 V versus Li^+/Li [19, 56, 87], which is well above the decomposition threshold of SOA electrolytes [129].

With both the anode and cathode chemistry becoming much more challenging, the electrolyte requirements for a high-energy Li-ion cell have never been more stringent. A single electrolyte formulation could never meet the demands of so many high-energy materials, so to accommodate different cell chemistries, researchers have developed numerous electrolyte formulations consisting of both conventional and novel organic solvents and lithium salts in combination with performance-enhancing additives. Besides the requirement of high performance, batteries used in transportation applications must also be safe. Conventional organic electrolytes are highly flammable, raising concerns over the safety of batteries with such electrolytes in electric vehicles and aircraft. Consequently, flame retardant additives and electrolyte formulations with overcharge protection have been investigated [14]. Some batteries used in niche applications demand specialty electrolytes. For example, the electrolytes for batteries used in oil well drilling need to withstand temperature over 200 °C as well as strong vibrations and shocks [40], and electrolytes for batteries used in satellites and space missions need to withstand extremely low temperatures [82]. In each of these situations, the electrolyte has to be tailored to the specific needs of the application.

Obviously, the properties of the electrolyte in Li-ion batteries are of crucial importance, and a few comprehensive general review articles have already been published on the subject [116, 117, 120, 133]. In this chapter, the recent advances and new trends in electrolyte research will be overviewed from a wide angle, with a focus on novel electrolytes and electrolyte additives for high-energy electrode materials.

2 Electrolyte Solvents for Non-aqueous Electrolyte

Due to the highly reductive nature of the lithiated anode material, the lithium and lithium ion battery electrolytes usually consist of a lithium salt and either a single aprotic organic solvent or a mixture of them [116] instead of the aqueous electrolytes used in many conventional primary and secondary batteries. Even with organic, aprotic electrolytes, there are still challenges associated with the electrolyte/electrode interface. Since the redox potential of carbonaceous anode (graphite), the most common anode materials for Li-ion batteries, is slightly above the redox potential of Li^+/Li, the charging potential of the graphite anode is usually much lower than the reduction potential of most organic solvents. As a result, the thermodynamically unstable organic electrolyte can only be stabilized kinetically on the anode surface through the generation of a protective passivation layer on the anode surface. This passivating layer can be formed by the reductive decomposition of the organic electrolyte or another component in the electrolyte. The passivation layer is often referred to as the solid-electrolyte interphase (SEI). Due to the extremely important role of the SEI layer, the ability to form a robust SEI (ionically conductive, resistant to degradation during cycling) becomes a governing factor to determine the suitability of a new electrolyte for the Li-ion chemistry.

Being an organic electrolyte, the organic solvent used in the electrolyte formulations is the most influential component to consider. The most prominent electrolyte solvent for the first-generation Li-ion battery is, without a doubt, ethylene carbonate (usually abbreviated as EC in the Li-ion battery literature) (Fig. 1). This cyclic carbonate possesses several desirable properties as an electrolyte solvent, including large dipole moment, good salt solubility, low vapor pressure and above all, the ability to form a robust SEI on the surface of the graphite anode [32]. The drawback of EC is that it has high melting point (34–37 °C) and high viscosity (1.90 cP at 40 °C), so it is conventionally used in combination with linear carbonates (Fig. 1) to increase the liquid range and ion mobility of the resulting electrolyte. The EC/linear carbonate formulations laid the foundation of modern Li-ion battery electrolyte technology and usually serve as the basis of various advanced formulations used in industry. Another well-known cyclic carbonate is propylene carbonate, abbreviated as PC, a solvent that was used in Li metal batteries until carbonaceous anodes became popular. Unfortunately, PC was found to co-intercalate with Li ions into the graphene layers causing exfoliation of the graphite structure, which deemed it inappropriate for Li-ion batteries [23]. Because of its destructive effect on carbonaceous anodes, to date it has been widely used as an electrolyte for the evaluation of anode SEI formation additives, which will be discussed in detail in Chap. 9.

The other major component in a liquid organic electrolyte is the lithium salt, which is the ionic source of the electrolyte. The salt is generally the lithium conjugate base of a super acid, which makes the anion anodically stable and easily dissociates from Li^+ in organic solvents. Compared with electrolyte solvents, the

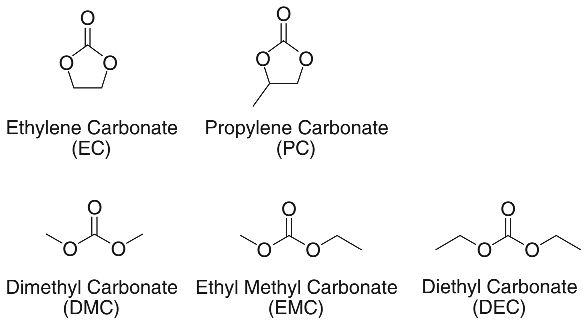


Fig. 1 Common electrolyte solvents in SOA Li-ion batteries

lithium salts generally receive less attention because the choice of salt is much more limited. The SOA lithium salt used in Li-ion batteries is lithium hexafluorophosphate, with the chemical formula $LiPF_6$. This salt has good solubility in the carbonate solvents mentioned above and good ion mobility, is resistant to reduction and oxidation, and can passivate the aluminum current collectors used in batteries [130]. It is the predominant lithium salt used in the EC-based electrolyte formulations and widely used in commercial Li-ion batteries. Other commonly used salts in the research labs include lithium perchlorate ($LiClO_4$), lithium tetrafluoroborate ($LiBF_4$), lithium hexafluoroarsenate ($LiAsF_6$), lithium trifluoromethanesulfonate ($LiSO_3CF_3$) and lithium salts based on fluorinated sulfonyl imide anions such as lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The negative charge in such anions (i.e., $TFSI^-$ or $[N(SO_2CF_3)_2]^-$) is extensively delocalized resulting in weak cation-anion interactions. Unfortunately, corrosion of aluminum current collectors occurs in liquid electrolytes containing LiTFSI.

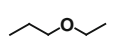
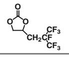
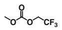
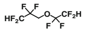
With the development of high-energy electrode materials, the design of organic electrolytes has evolved accordingly. On the anode side, electrolytes that are compatible with novel high-capacity anode materials are in great demand. On the cathode side, high-voltage electrolytes using novel solvents are being investigated because conventional carbonate solvents are anodically unstable at the elevated charging potentials required to deliver higher energy. Furthermore, development of electrolytes with enhanced safety properties is also a focus of transportation technology research. In this part of the chapter, the organic solvents used in the cutting-edge Li-ion batteries will be discussed in detail, with a focus on novel solvents.

2.1 Fluorinated Carbonates

As stated above, carbonates are the main solvents in the current SOA Li-ion batteries due to their large dipole moment, good solubility of lithium salts, and ability to form a good SEI on carbonaceous anodes. However, conventional alkyl carbonate solvents experience extensive oxidative decomposition on the cathode side at higher potential (>4.3 V vs. Li^+/Li) [61, 129], which makes them unsuitable for high-energy cathode materials. With the exception of this disadvantage, carbonates generally have better properties than any other solvents used in Li-ion batteries. As a result, modified carbonates with electron withdrawing groups that raise the oxidation potential are promising targets of electrolyte research for high voltage high energy cathodes. Fluorination is one of the most popular methods to achieve a higher oxidation potential.

Theoretical calculations using density function theory (DFT) have shown a moderate to dramatic increase in the oxidation potential of organic carbonates compared with their non-fluorinated counterparts (Table 1) [138]. The calculated oxidation potentials are much higher than those measured on actual electrodes, but the results could serve as a source of comparison between different structures in the same model. The electrolytes formulated from these fluorinated carbonates showed

Table 1 Structure, oxidation potential, and energies for highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbit (LUMO) of carbonates (EC and EMC), ethers (EPE), fluorinated carbonates (F-AEC and F-EMC), and fluorinated ethers (F-EPE)

Molecule	Structure	Pox (V Theory)	HOMO (au)	LUMO (au)
EC		6.91 (6.83 open)	−0.31005	−0.01067
EMC		6.63	−0.29905	0.00251
EPE		5.511	−0.26153	0.00596
F-AEC		6.98	−0.31780	−0.01795
F-EMC		7.01	−0.31946	−0.00363
F-EPE		7.24	−0.35426	−0.00356

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high stability on the 5-V Ni/Mn spinel cathode $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO). However, the fluorinated cyclic carbonate F-AEC shown in Table 1 was only compatible with $Li_4Ti_5O_{12}$ (LTO) used as anode due to its inability to form a functional SEI on the graphite anode surface [138].

SEI formation on the graphite anode is a major concern with fluorinated carbonate electrolytes. It is generally agreed that fluorinated compounds reductively decompose and form an insulating layer on the anode surface, and the repeated decomposition on the anode results in higher interfacial impedance and irreversible capacity loss. One of the simplest and most used fluorinated carbonate as reported in the literature is fluoroethylene carbonate (4-fluoro-1,3-dioxolan-2-one), commonly abbreviated as FEC, or F-EC (Fig. 2). FEC is a well-known co-solvent and SEI formation additive for the graphite anode [67] and silicon anode [71]. Especially for the silicon anode, FEC is the singularly necessary electrolyte additive to mitigate capacity fading during repeated charge and discharge cycling. There are different views on the SEI formation mechanism of FEC as an anode additive, and

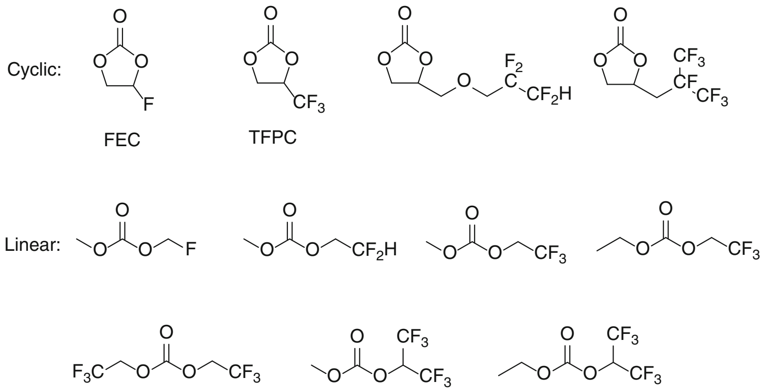


Fig. 2 A selection of fluorinated carbonates for high voltage Li-ion battery electrolytes

generally it falls into the vinylene carbonate (VC) mechanism [28] or vinyl fluoride mechanism [71]; their details will be discussed in Chap. 9. On the cathode side, FEC is reported to have better stability than EC on the LNMO cathode and enables greatly improved performance for LNMO/graphite full cells even at elevated temperature (55 °C) [45].

Other than FEC, the trifluoromethyl substituted ethylene carbonate (or fluorinated propylene carbonate) (TFPC, Fig. 2) also has received attention as a possible co-solvent and SEI formation additive. While most research suggests TFPC is not as effective as FEC in terms of capability of SEI formation on graphite anode, at least one study showed that TFPC is superior to FEC in suppressing the irreversible capacity of the graphite anode [106] (Fig. 3). While electron microscopy results indicated that TFPC is capable of forming a SEI on the graphite anode [48], TFPC has much higher production cost than FEC, so the interest in this molecule as a candidate for the commercial Li-ion battery is low.

Besides FEC and TFPC, more advanced structures of fluorinated cyclic carbonates have also been synthesized and evaluated in Li-ion batteries. Two examples of such molecules are given in Fig. 2. These molecules have traditionally been used in specialized applications such as coolants and supercapacitors, and their use in Li-ion batteries is relatively new [5, 6, 74, 78]. Regardless, these molecules have shown increased stability toward oxidation, better thermal stability, and low flammability.

Compared with fluorinated cyclic carbonates, less research has been conducted on fluorinated linear carbonates due to their limited availability. The structure variation of the fluorinated linear carbonates are much more diverse than that of

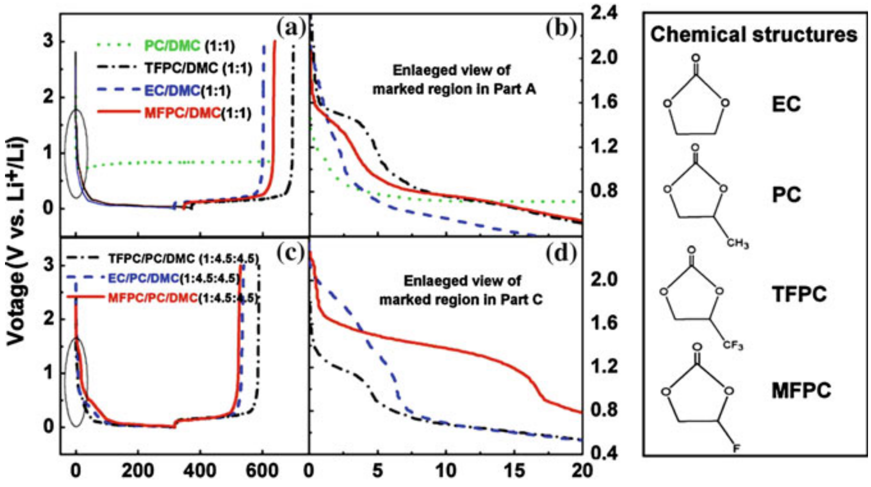


Fig. 3 Voltage profiles in the first cycle of Li/mesocarbon microbead (MCMB) half cells with 1 M $LiPF_6$ in bi-solvent and tri-solvent electrolytes containing EC, PC, FEC (labeled as MFPC in the graph), and TFPC. Reproduced with permission [106]. Copyright 2010 Elsevier

cyclic carbonates because the two groups on both side of the carbonate center can be introduced with various fluorinated alcohol precursors, and the synthesis chemistry is less complicated than that of the fluorinated cyclic carbonates. Consequently, fluorinated linear carbonates hold greater promise as electrolyte candidates for Li-ion batteries, with some examples of fluorinated linear carbonates shown in Fig. 2. Fluorination of linear carbonates is being investigated in order to improve both the oxidative stability and the melting point. Higher oxidation stability would enable use of these solvents with high-voltage cathodes. The methyl trifluoroethyl carbonate (FEMC) (asymmetric fluorinated EMC) has been shown to have much higher oxidation stability of the formulated electrolyte on the high voltage $LiNi_{0.5}Mn_{1.5}O_4$ [45, 138] than its non-fluorinated counterpart. The second purpose of fluorination is to lower both melting point and viscosity, which would enable the electrolyte for low temperature applications [93]. Fluorinated molecules behave differently than their non-fluorinated counterparts, and these different behaviors include decreased boiling and melting points and increased surface tension. Thus, fluorinated carbonates, especially linear carbonates, are excellent candidates for the low-temperature Li-ion batteries for space and deep-sea missions. Last but not least, the low-flammability to non-flammability of fluorinated compounds could potentially improve the safety of Li-ion batteries [5, 6].

In summary, the SOA carbonate-based electrolytes remain the most promising category of electrolyte for 4-V Li-ion batteries. However, to meet the requirements for the high-voltage high energy cells, fluorination plays a significant role in elevating the oxidation stability via F- and fluoroalkyl- substitution. Electrolyte researchers from academia, national labs and industry are actively working on this front. Widespread adoption of these fluorinated electrolytes may afford the performance, cost and safety of the high energy Li-ion cells for a wide range of applications.

2.2 Sulfone-Based Electrolytes

The research in sulfones electrolytes for Li-ion batteries dates back to the 1980s, even before the intercalation chemistry was studied [70]. However, since the emergence of the Li-ion chemistry, the interest in sulfones-based electrolytes declined due to the excellent performance of carbonate-based electrolytes for graphitic anodes. Sulfones, especially symmetric ones, have high boiling points and can be used to formulate electrolyte for batteries in high temperature applications. The pioneering studies in the sulfone-based electrolyte for Li-ion batteries were predominantly carried out by a research group led by professor Charles Austen Angell at Arizona State University [97, 98, 119], and nowadays more researchers are further exploring the potential of this group of solvents.

In recent years, the sulfone-based electrolytes have renewed interest because the new generation of cathode materials requires working potentials much higher than the oxidation stability limit of the conventional carbonate-based electrolytes.

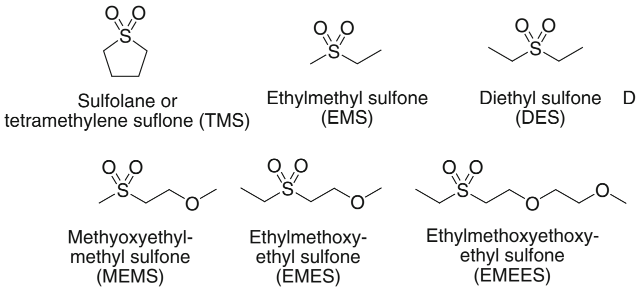


Fig. 4 Examples of commercially available and lab-synthesized sulfones

The sulfone functionality ($-SO_2-$) has the highest achievable oxidation state (+6) found in all sulfur-containing organic compounds, which makes it highly stable against oxidation. Based on quantum chemistry calculations and experimental data, sulfones generally have oxidation potentials above 5 V versus Li^+/Li (Fig. 4), even for the varieties with organic ether side chains [91]. Given proper formulation, they hold great promise as electrolyte solvents in high-voltage Li-ion batteries. However, from the earliest study of sulfone electrolytes in Li-ion batteries, it was found that many are not capable of forming an SEI on the graphite anodes [119]. The use of SEI formation additives or lithium salts that can form an SEI is common practice in many following studies [64, 99, 110].

A few commercially available sulfones and lab-synthesized sulfones that are suitable as electrolyte solvents are shown in Fig. 5. Most sulfones with simple structures suffer from high melting point and high viscosity, and consequently the formulated electrolytes generally suffer from lower ionic conductivity and subsequently low C-rate capability compared with carbonate-based electrolytes; To address this issue, in some designs, ether-type chains are incorporated into the structure [91].

One of the most widely examined sulfones is sulfolane (tetramethylene sulfone, abbreviated as TMS). Sulfolane has a melting point of 27.5 °C, and like EC it has to be mixed with a diluent to widen the liquid range and decrease the viscosity of the resulting electrolyte. Due to its high polarity, TMS can dissolve most of the common lithium salts and also dissolves less common lithium salts including lithium bis(oxalato)borate (LiBOB) [64] and lithium difluoro(oxalato)borate (LiDFOB) [110] which usually have low solubility in carbonate electrolytes. LiBOB and LiDFOB act as not only a lithium ion source in the electrolyte, but also passivate the graphite anode through the formation of a robust SEI. The utilization of such SEI-forming lithium salts eliminates the need of additional additives. TMS was reported to be stable on the high-voltage spinel cathode $LiNi_{0.5}Mn_{1.5}O_4$ when coupled with the $Li_4Ti_5O_{12}$ anode [1]. Mixed with ionic liquid, TMS can form a non-flammable electrolyte with a oxidation stability up to 4.8 V versus Li^+/Li, as examined on a $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ cathode [114]. To improve the properties of the sulfone based electrolytes, investigations of fluorinated sulfones have been initiated

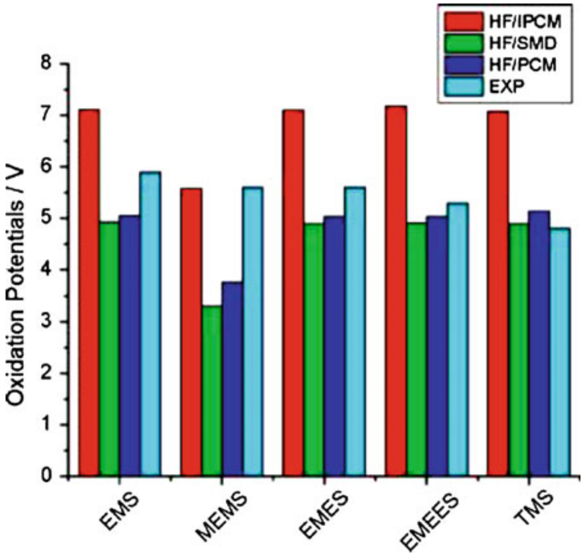


Fig. 5 Oxidation potentials calculated at the HF/6-31 + G (d, p) level for three solvation models: isodensity polarizable continuum model (IPCM), polarizable continuum model (PCM), and solvation model based on density (SMD). Experimental oxidation potentials (EXP) are from the literature. Reproduced with permission [91]. Copyright 2011 American Chemical Society

in order to further increase its voltage stability and the SEI formation capacity for high energy density lithium-ion batteries (Zhang, unpublished data).

In conclusion, sulfones show both great advantages and challenges as a new class of electrolyte solvents. The intrinsic oxidation stability makes them a good candidate for high-voltage Li-ion batteries, but the high melting point and viscosity of conventional sulfones make them inappropriate for high power applications. Future research should be focused on the functionalization of sulfones which makes them more suitable as electrolytes and/or electrolyte additives for new generation Li-ion battery.

2.3 Ether-Based Electrolytes

Due to the affinity of the oxygen atom to lithium cations, organic ethers have historically been investigated as electrolyte solvent or co-solvent to increase the ion mobility due to their low viscosity and acceptable polarity. Oligomeric linear ethers with repeating ethylene glycol units ($-CH_2CH_2O-$) such as dimethoxyethane, diglyme, triglyme, tetraglyme [26, 65, 103], and cyclic ethers such as tetrahydrofuran (THF) and 2-methyltetrahydrofuran (Me-THF) [2, 54] were investigated as the electrolyte components for Li metal batteries. However, aliphatic ethers suffer from low oxidation potentials [79], making them inappropriate for the majority of the SOA Li-ion chemistries.

Although the above-mentioned ethers may not be suitable for high-energy Li-ion batteries, they are frequently used in high-capacity batteries with relatively low operating voltage, such as lithium-sulfur (Li-S) batteries [141] and lithium-oxygen (Li-O_2) batteries [35]. Polyether with poly(ethylene oxide)(PEO) as a typical example has been widely studied as solid polymer electrolytes. Low molecular weight PEO is employed as the plasticizer of polymer electrolyte for Li-ion polymer batteries [96]. Crown ethers, due to their strong chelating effect, are used as electrolyte additives to enhance Li^+ dissociation from counterions in electrolytes [33].

To enable the compatibility of ethers in advanced Li-ion chemistry, fluorination is utilized in the molecular engineering. In contrast to the carbonates, the fluorination of ethers is usually more extensive due to the fact that the synthesis of such ethers involves highly fluorinated precursors. The high degree of fluorination sometimes completely changes the properties of the molecule. A few examples of fluorinated ethers as well as some common non-fluorinated ethers are shown in Fig. 6.

So far, the most reported fluorinated ether for Li-ion battery study is 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether [6, 45, 78, 138]. This solvent is also listed in Table 1 for the molecule F-EPE. Compared with the non-fluorinated ethyl propyl ether, the calculated oxidation potential of F-EPE increases from 5.51 to 7.24 V, which is the most dramatic change among the fluorinated compounds listed in Table 1. The source of this dramatic increase in oxidation potential lies in the oxidation mechanism of ethers shown in Scheme 1. The source of the oxidative vulnerability of non-fluorinated ethers is that the C-H bond next to the ether oxygen is subject to hydrogen extraction to form radicals, which is then stabilized by the lone pair electron on the ether oxygen atom. The resulting radical subsequently traps an oxygen molecule to form a peroxide radical. In highly fluorinated ethers, especially those with fluorinated α carbon, the strong electron-withdrawing effect of the fluoroalkyl group pulls the electron density of the lone pair electrons on the oxygen atom away from the neighboring $-CH_2$ group, and the stabilizing effect is

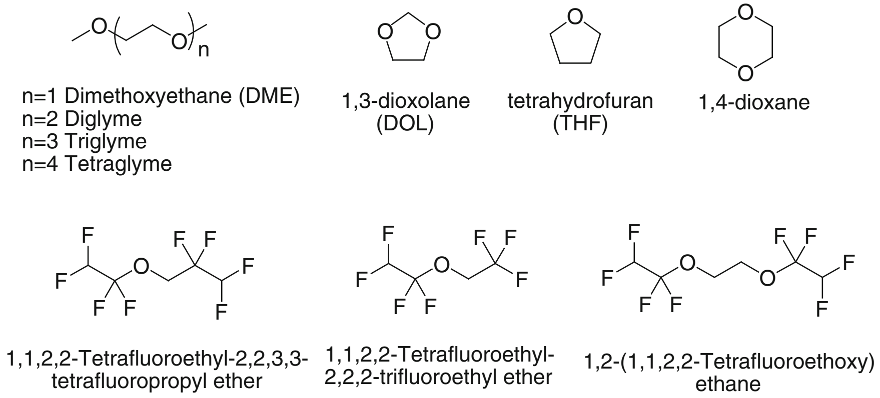
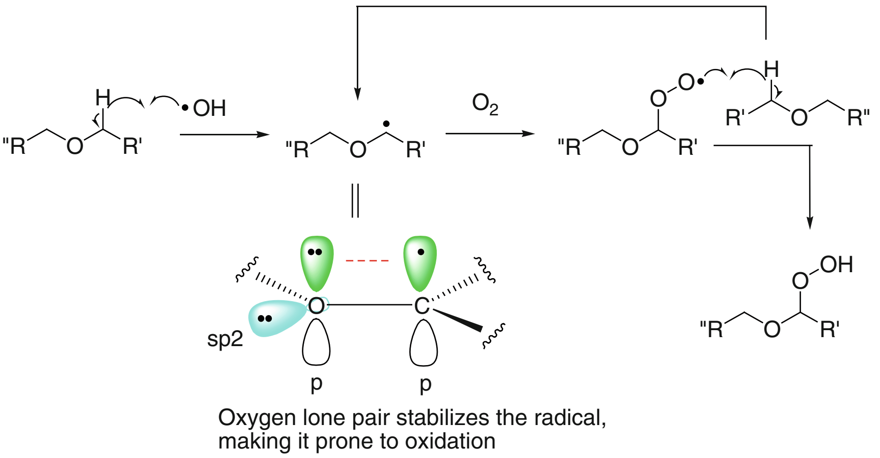


Fig. 6 Examples of non-fluorinated ethers and fluorinated ethers



Oxygen lone pair stabilizes the radical, making it prone to oxidation

Scheme 1 Oxidation and peroxide formation mechanism of ether molecules

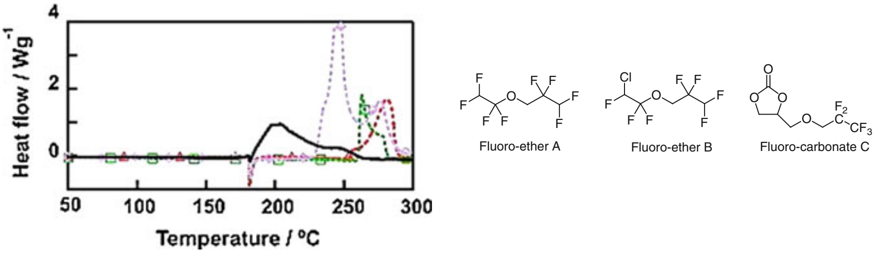


Fig. 7 Differential scanning calorimetry (DSC) curves for mixtures of metallic Li and EC/DMC (1:1 vol. ratio) or fluorine compound (**A**, **B** or **C**). *Solid black curve* EC/DMC; ---△--- fluoro-ether **A**; ---□--- fluoro-ether **B**; ---◇--- fluoro-carbonate **C**. Reproduced with permission [78]. Copyright 2013 Elsevier

greatly reduced. This effect results in the much higher oxidation potential of fluorinated ethers, making them good candidates for high-voltage Li-ion batteries. In addition to the anodic stability, fluorinated ethers also possess wide liquid range, non-flammability, and enhanced thermal stability (Fig. 7) [78], all of which are necessary properties of Li-ion batteries designed for vehicles.

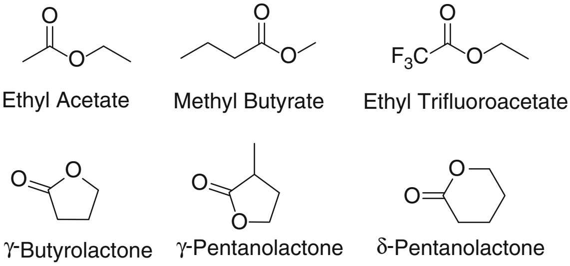
Besides F-EPE, many other fluorinated ethers are synthesized by the addition reaction of tetrafluoroethylene with fluorinated and non-fluorinated alcohols. Some of the new structures may have superior properties to F-EPE as electrolyte solvents for Li-ion batteries and beyond Li-ion batteries. Recently, F-EPE was investigated for the first time as the electrolyte solvent in the lithium-sulfur battery [12]. The new fluorinated electrolyte DOL/F-EPE-1.0 M LiTFSI suppressed the deleterious shuttling effect and improved the capacity retention and coulombic efficiency in Li-S cell tests. In addition, it was found to eliminate the self-discharge of lithium-sulfur batteries. Another fluorinated ether, bis(2,2,2-trifluoroethyl) ether (BTFE), was reported to mitigate self-discharge of Li-S cells having both low- and high-sulfur loading sulfur cathodes [13, 38]. This electrolyte significantly decreased self-discharge at elevated temperature, though differences in behavior of cells with high- and low-sulfur loading were also noted. Further investigation showed that this effect likely stems from the formation of a more robust protective film on the anode surface. New fluoroethers with unique structures are certainly worthy of exploration.

2.4 Ester and Lactone-Based Electrolytes

Esters and lactones (cyclic esters) can be considered as cousins of linear and cyclic carbonates, as their physical properties are alike. Figure 8 shows the chemical structures of some common esters and lactones. Due to the lower oxidation state of esters compared to that of carbonates, esters have generally inferior oxidation stability. For this reason, esters have not been widely studied as electrolyte solvents as the trend of Li-ion battery development is leading towards higher cell voltages. However, linear esters continue to be attractive as a diluent in electrolyte formulations due to their low viscosity and melting point which improve low temperature performance of the conventional Li-ion battery [95].

Among lactones, γ-butyrolactone (GBL) has been widely investigated as an alternative to cyclic carbonates and frequently used in many electrolyte compositions. Like EC, GBL has high dielectric constant, high solubility of lithium salts, high boiling point (b.p. 204 °C) and low melting point (−43.5 °C), making it more suitable for transportation application. Although the most compatible salt with carbonate solvents is $LiPF_6$, the optimal lithium salt for GBL is $LiBF_4$. It was first demonstrated by Japanese researchers from Toshiba that an electrolyte formulated with GBL/EC/$LiBF_4$ showed good performance in laminated thin-film Li-ion cells [100, 101]. A later paper [20] reported that among five salts ($LiBF_4$, $LiPF_6$, $LiAsF_6$, LiTFSI, and $LiClO_4$) tested with EC/GBL mixed solvents, only $LiBF_4$ offered reversible intercalation with capacity up to the theoretical value of graphite. After that, most studies involved only $LiBF_4$ as the default salt for GBL-based electrolytes. To further improve the stability and reduce the resistance of the electrolyte/anode interface, additives such as maleic anhydride [104], VC [53], FEC [52], and many others have been used to successfully enhance the performance of GBL-based electrolytes.

Fig. 8 Examples of esters and lactones



Another leading trend of GBL-based electrolyte research is associated with LiBOB as a lithium salt [118]. Being a fluorine-free salt, LiBOB has long been considered as a safer and greener alternative to the $LiPF_6$. However, LiBOB has low solubility in linear carbonates, so the resulting electrolyte has low conductivity compared with $LiPF_6$-based electrolytes. In contrast, LiBOB has high solubility in GBL and even linear esters such as ethyl acetate [118], which makes the LiBOB/ester system promising [11, 46]. An electrolyte consisting of solely GBL with LiBOB shows large irreversible capacity during formation [118], and additives [81] or mixing with carbonates [30] have been investigated to solve this issue. Not only a lithium ion source, LiBOB acts as a stable SEI formation additive as it is frequently used in carbonate and silicon-based electrolytes [9, 140].

While the majority study of GBL electrolyte have been focused on the 4 V electrode materials, at least one study reports that a binary mixture of GBL/Sulfolane results in an electrolyte that is more stable than the SOA carbonate electrolyte on the high-voltage spinel LNMO cathode [24]. The reported electrolyte also enables a higher discharge potential and comparable rate capability than the conventional electrolyte (Fig. 9). Beside the previously mentioned merits,

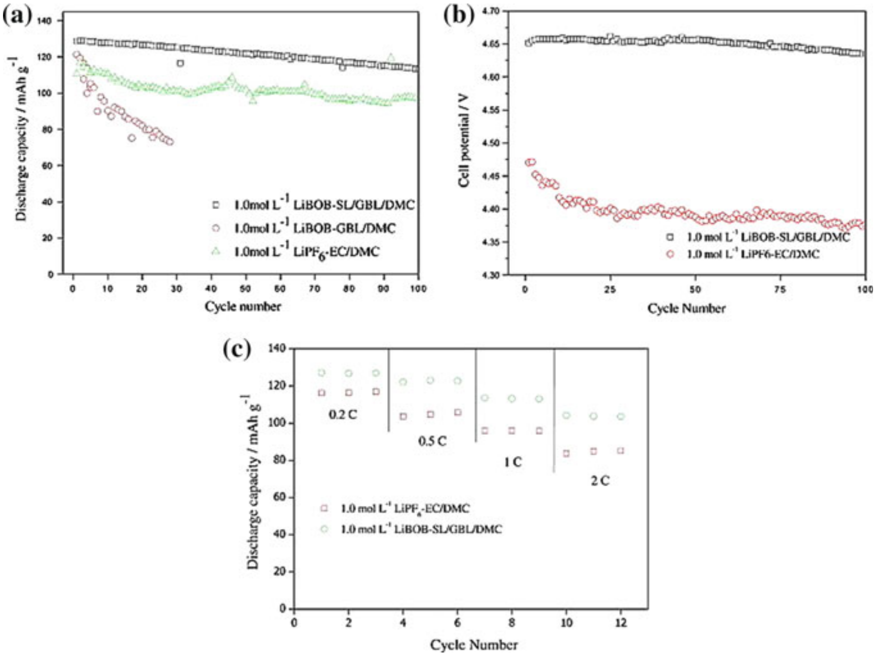


Fig. 9 **a** Cycle performance of $LiNi_{0.5}Mn_{1.5}O_4$/Li cells with different electrolytes cycled at 0.5 C discharge rate and room temperature. **b** Mean voltages of $LiNi_{0.5}Mn_{1.5}O_4$/Li cells with two electrolytes cycled at 0.5 C discharge rate and room temperature. **c** Discharge capacities of $LiNi_{0.5}Mn_{1.5}O_4$/Li cells cycled at different discharge rates and room temperature. Reproduced with permission [24]. Copyright 2013 Elsevier

GBL-based electrolyte has also shown superior thermal stability [18], especially when combined with the $LiBF_4$.

Linear esters, as mentioned above, are not widely used in Li-ion batteries due to their inferior anodic stability compared to linear carbonates. Although numerous patents for electrolyte formulations claim various ester structures as the co-solvents, literature reports on the esters are considerably fewer. Although esters oxidize much more easily than carbonates, at least one reference reported an electrolyte formulated from a mixture of sulfone and ethyl acetate showing better electrochemical properties than carbonate-based electrolyte in LNMO/Li half cells [108]. Due to their low viscosity and melting point, linear esters are considered to be candidates for low-temperature Li-ion batteries. Both non-fluorinated [94] and fluorinated esters [95] have been examined by scientists at the Jet Propulsion Laboratory as Li-ion battery electrolyte co-solvents for space missions.

In conclusion, the utilization of esters and lactones in Li-ion battery electrolytes is currently limited and is underexplored. The ease of synthesis and purification of esters should not be overlooked for potential cost reduction and more work on this group of solvents is needed.

2.5 *Nitriles-Based Electrolytes*

Due to the strong electron withdrawing ability of the cyanide functionality (−CN), organic nitriles are strongly polar solvents with high salt solubility, high oxidation potential, and low viscosity. The resulting electrolytes often have a wide electrochemical window and high conductivity. While nitriles have high stability toward oxidation, they are easily reduced on the anode. In fact, acetonitrile reacts with Li metal violently and is unable to form a stable passivation layer [86], which has led to a lack of interest in nitrile as an electrolyte solvent for Li-ion batteries. Other nitriles (Fig. 10) have shown potential as the electrolyte solvent of Li primary [39] and secondary batteries [105].

As the demand for high-voltage Li-ion batteries increased, the interest in the nitrile-based electrolyte was reignited due to its promising stability against oxidation, a similar case to the sulfone-based electrolyte described earlier. Conventional electrolyte additives [36] and novel additives tailored for the nitrile-based

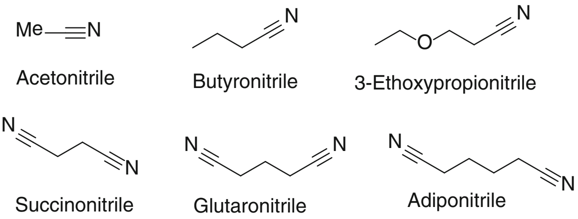


Fig. 10 Examples of organic nitriles used in Li-ion batteries

electrolytes [76, 77] were investigated to increase compatibility with the graphite anode. An electrolyte formulated with acetonitrile and LiBOB was studied for the purpose of physical properties, although no electrochemical evaluation was performed [42]. Recently, a ground-breaking discovery was reported by a Japanese group in which increasing the concentration of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) to 4.2 M suppressed the spontaneous reaction between acetonitrile and Li metal anode, and allowed for the reversible intercalation of Li ions into graphite (Fig. 11) [128]. The resulting electrolyte also demonstrated high ionic conductivity and C-rate capability. This discovery is very encouraging in terms of enabling the development of nitrile-based electrolytes, and it has also brought insight into the interaction between electrodes and electrolyte in the concentrated electrolyte solutions. More discussion on this topic will be centered on the salt LiTFSI in Sect. 3. On the cathode side, mono-functionalized nitriles [36] and di-functionalized nitriles (Fig. 10) were investigated on over-charged cathodes such as $LiCoO_2$ [3, 4] and Ni/Mn spinel LNMO [27] as high voltage electrolytes.

While nitriles may be similar to sulfones as an alternative solvent to carbonate for the high-voltage applications, nitriles are superior to sulfones due to lower viscosity and wider liquid range. More research is definitely needed to better understand and utilize the nitriles as the component in advanced Li-ion battery electrolytes.

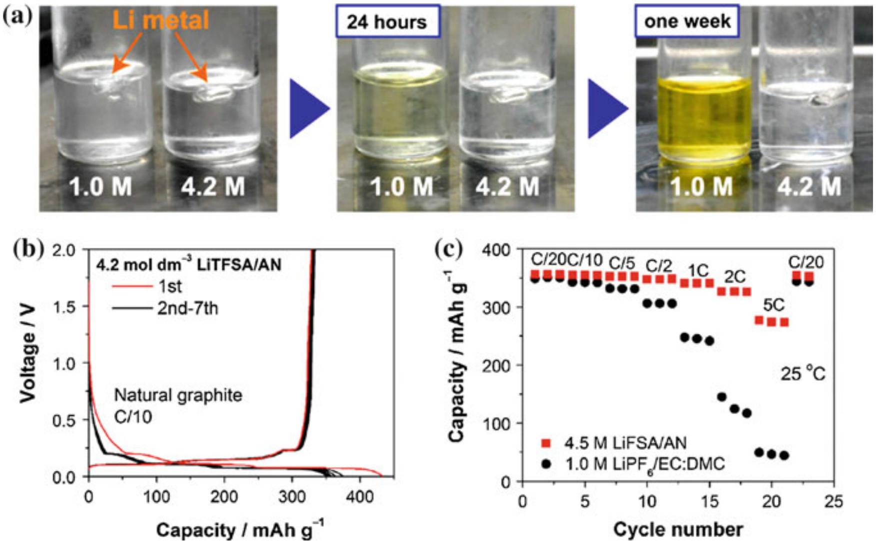


Fig. 11 **a** Reactivity of lithium metal foil and LiTFSI/acetonitrile solutions at 1.0 and 4.2 M concentrations at room temperature. **b** Charge-discharge curves of natural graphite/lithium metal cell with 4.2 M LiTFSI/acetonitrile electrolyte at C/10 rate. **c** Reversible capacity of natural graphite in the two electrolytes at various C-rates and 25 °C. Charge and discharge were conducted at the same C-rate without using a constant-voltage mode at both ends of charge and discharge, and the charge (lithium deintercalation) capacity was plotted. Reproduced with permission [128]. Copyright 2014 American Chemical Society

2.6 Organosilicon Compounds-Based Electrolytes

The application of organosilicon compounds in lithium batteries dates back to 1980s when polysiloxanes were studied as the matrix for the polymer electrolyte in Li metal batteries [31, 107]. However, the application of liquid organosilicon compounds as solvents for the Li-ion battery electrolyte is fairly recent, initiated by collaboration between Argonne National Laboratory and University of Wisconsin-Madison [7]. In this work, silanes and silyl ethers with ethylene glycol repeating units (Fig. 12) were used as the only solvent for LiBOB-based electrolyte. Such electrolytes showed tremendous improvement in the cycling performance over the $LiPF_6$ in EC/DEC electrolyte for the $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)/mesocarbon microbeads (MCMB) electrochemical couple. The cell showed no impedance rise over storage for one year at 80 % state of charge (SOC) at 55 °C (Fig. 13). Since then, this category of electrolytes have been widely applied to various Li-ion battery systems [57, 131, 132], and even to the emerging Li-O_2 battery [139].

Other groups also performed studies on this kind of solvent, but reports have been sporadic. Vinyl tris(2-methoxy)ethoxy silane [89] and ethyl tris(2-methoxy)

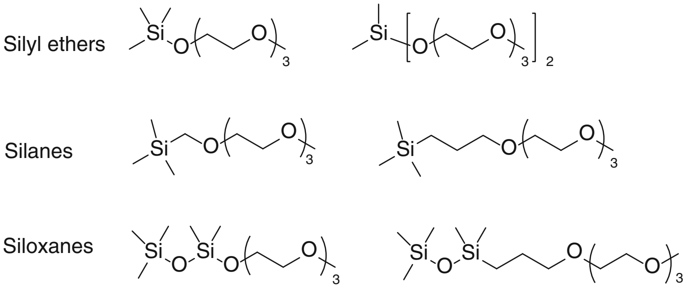


Fig. 12 Examples of organosilicon solvents for Li-ion battery applications

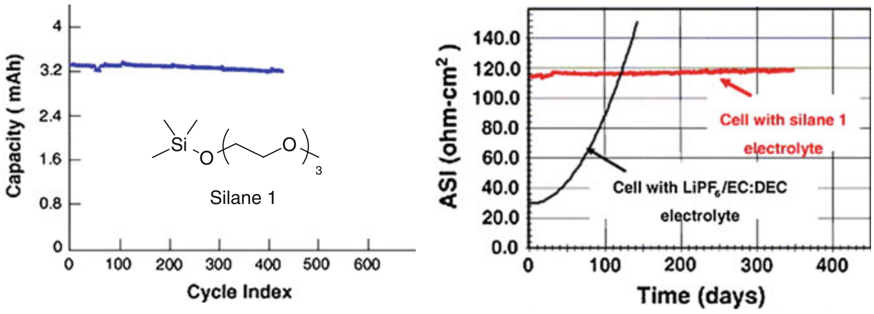


Fig. 13 Cycling performance and area specific impedance (ASI) of MCMB/$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cells with a 0.8 M LiBOB/silane or 1.0 M $LiPF_6$/EC:DEC (1:1) electrolyte. Reproduced with permission [7]. Copyright 2006 Elsevier

ethoxy silane [90] were investigated as an SEI formation additive and co-solvent for PC-based electrolyte and were shown to enable the intercalation of Li^+ ions into graphite anodes. Silanes were also shown to passivate the Li metal anode in Li-O_2 and Li-S batteries [72, 73].

Compared with other electrolyte solvents, organosilicon solvents are relatively new for battery applications. These solvents, especially those with short polyethylene glycol chains, have low toxicity and excellent biocompatibility compared to other solvents, which make them more suitable for medical applications [85]. Even with the electron-withdrawing effect of the terminal silyl group by back donating of 2p-orbital electrons of oxygen on the ether chain into the empty 3D-orbital of silicon, however, these solvents still have limited oxidation stability (usually less than 4.5 V) which restricts their applications in high-voltage Li-ion batteries.

2.7 Other Solvents

In addition to the organic solvents described above, there are quite a few more organic compounds considered as solvent candidates for Li-ion battery electrolytes. In many cases, these molecules are more appropriate as additives instead of solvents due to the inferior physical and electrochemical properties of the resulting electrolyte if such molecules are used in high concentration. These molecules include the non-fluorinated and fluorinated varieties of alkyl sulfates [113], alkyl sulfites [21, 59, 63], alkyl phosphates [66], and phosphazenes [84]. Some of them have been employed as SEI formation additives or flame retardant additives and will be discussed in the respective sections of Chap. 9.

3 Electrolyte Salts for Non-aqueous Electrolyte

While solvents certainly attract major attention, the role of salts has been often overlooked even though many cases showed that changing lithium salt vastly changes electrolyte performance. As mentioned in the introduction, the majority of lithium salts used in the SOA Li-ion battery is the lithium conjugate base of super acids such as HPF_6, HBF_4, and HSO_3CF_3. These counter-ions are non-coordinative and have high oxidation stability, which makes the respective lithium salts suitable as battery electrolyte solutes with high conductivities and wide electrochemical windows. However, most of these salts are corrosive to the cathode current collector materials, and each has its own drawbacks. For example, the most widely used salt, $LiPF_6$, has poor thermal stability and decomposes at temperatures as low as 70 °C in the presence of electrolyte solvents [92, 116]. Furthermore, it is very moisture sensitive. Other salts also have their drawbacks: $LiBF_4$ suffers from mediocre conductivity, $LiAsF_6$ is highly toxic, $LiClO_4$ is explosive, and LiTFSI is highly corrosive to aluminum, the standard material of the cathode current collector.

It seems that finding a “perfect” salt is much more difficult than finding a “perfect” solvent because the choices are very limited. Regardless, effort has been made to find less hazardous, more stable salts with better electrochemical properties and possibly the capability to form an SEI on the anode without needing the participation of solvent or additive molecules. The following discussion will address these characteristics individually in various lithium salts developed in the past decade.

3.1 Salts with SEI Formation Capability

The stabilization of the anode/electrolyte interface is one of the most pressing challenges in Li-ion batteries. Now, with the use of high voltage cathode materials, the oxidation stability of the electrolyte and the cathode/electrolyte interface are crucial to the long term cycling performance. While additives offer a solution by forming the passivation layer on electrode surface, lithium salts that can form SEI on both the anode and cathode are even more attractive. So far, some salts are already known to have such capability, independent of the solvents used. A few examples are shown in Fig. 14.

The most widely known film-forming salt is lithium bis(oxalato)borate, commonly abbreviated as LiBOB (Fig. 14). The fluorine free, non-corrosive, non-toxic (and thus environmentally friendly) features make this salt very appealing. The synthesis and solution properties of LiBOB were first reported by Prof. Angell’s lab from Arizona State University in 2001, followed by the discovery of its unique capability in stabilizing the cycling performance of Li-ion battery [127]. LiBOB contains a very weakly coordinating anion because the negative charge on the anion is delocalized by eight oxygen atoms in the two oxalate groups. The solution of LiBOB in acetonitrile has a conductivity of 25.2 mScm^{-1} at 25 °C, approaching that of aqueous solutions, and a LiBOB/PC electrolyte is anodically stable up to 4.5 V versus Li$^{+/}$Li [127]. The following year, the same group discovered that in a LiBOB/PC solution, Li^{+} can reversibly intercalate into and deintercalate out of graphite, which had not been observed with other salts (Fig. 15) [121]. This groundbreaking discovery led to the immense popularity of the salt and the interest in finding other SEI forming salts. Since then, LiBOB has been frequently used as an SEI formation additive for LiPF$_6$-based electrolyte, as well as the single salt in many novel electrolyte formulations [7, 9, 64]. Other than the ability to protect the

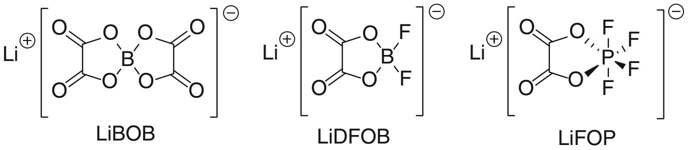


Fig. 14 Structures of LiBOB, LiDFOB, and LiFOP

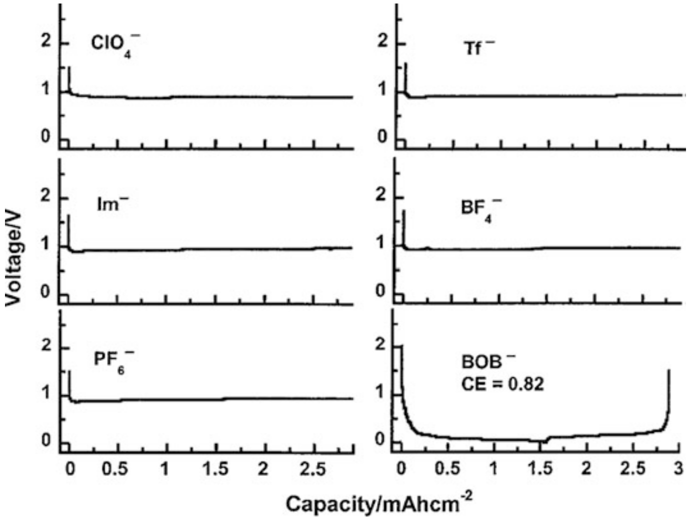


Fig. 15 The voltage profiles of the first discharge of Li/graphite half-cells employing an electrolyte with 1.0 M LiBOB dissolved in PC. For LiBOB/PC electrolyte, the first cycle is shown, with CE indicated in the graph. Reproduced with permission [121]. Copyright 2002 The Electrochemical Society

anode, LiBOB was also reported to be capable of forming a passivation film on the surface of the cathode, which mitigates the oxidative decomposition of electrolyte solvents on the high voltage cathodes [143, 122] and reduces the dissolution of transition metal ions from the cathode into the electrolyte [126]. Besides these desirable properties, both LiBOB and the SEI formed from it show excellent thermal stability [144].

One of the disadvantages of LiBOB is poor solubility in organic carbonates, especially in linear carbonates [118]. In order to increase the solubility, a structural analog of LiBOB, lithium difluoro(oxalato)borate, commonly abbreviated as LiDFOB, with a chemical structure consisting of half LiBOB and half $LiBF_4$, was developed in the U.S. Army Research Lab [22, 60, 134–136]. This salt has better solubility in linear carbonates than LiBOB while retaining similar SEI formation capability as LiBOB. Due to the similarities in chemical structure and properties, in many publications and patents LiDFOB and LiBOB are simultaneously studied/claimed as the independent lithium salt or electrolyte additive. Both LiBOB and LiDFOB seem to have become one of the “standard” additives for electrolyte formulation that have SEI formation issues. The current trend, as mentioned in Sect. 2, is to employ LiDFOB or LiBOB as the only salt for novel solvents that are not capable of forming SEI on their own [21, 59, 109, 131].

An analogue of LiDFOB is lithium tetrafluoro(oxalato)phosphate ($LiPF_4C_2O_4$, or LiFOP), in which phosphorous is the coordination center. This salt was initially synthesized by Prof. Brett Lucht’s group at the University of Rhode Island. It has been demonstrated that the electrolyte prepared from this salt has comparable conductivity (9 $mScm^{-1}$ at 25 °C) with conventional $LiPF_6$-based electrolyte while its cell performance is also similar to the $LiPF_6$ [123, 125]. Moreover, LiFOP has much improved thermal stability than $LiPF_6$ [124]. The initial concern with this salt is whether it can form SEI on the graphite anode. This concern was ruled out by the same group, showing that LiFOP enables reversible intercalation of Li^+ ions with graphite electrode even with the problematic solvent PC, firm proof that LiFOP can form SEI by itself [142].

At present, it is quite evident that the oxalate-containing salts are able to form SEI on their own, because the oxalate moiety participates in the reduction reaction (1.5–1.7 V vs. Li^+/Li) during the charging of graphite anode. Other lithium salts with oxalate functional groups might have the same SEI-forming property.

While many novel lithium salts have been developed, many of them employed EC as a co-solvent so their stand-alone ability to form SEI is unknown. As mentioned earlier, the choice of lithium salts is very limited due to the bulky molecular size and/or less structural varieties, therefore the development of a new salt with SEI formation capability is much more challenging than the development of a new solvent with such capability.

3.2 Salts with Enhanced Thermal Stability

Among the available lithium salts, $LiPF_6$ is most commonly preferred for the Li-ion battery because it holds the best comprehensive properties compared with other salts, especially with respect to solubility, resultant ionic conductivity, and passivation of the Al current collector. However, $LiPF_6$ suffers from poor thermal stability especially in the solution state. When exposed to elevated temperatures, $LiPF_6$ decomposes and reacts with the organic solvents in the electrolyte generating HF gas, which causes rapid degradation of the cell chemistry [34, 62]. Although other salts mentioned earlier have better thermal stability than $LiPF_6$, alternative salts with higher thermal stability are in demand for safety reasons.

In addition to the exceptional SEI formation ability, LiBOB and LiDFOB have excellent thermal stability compared to $LiPF_6$. Other chelating boron-based salts with good thermal stability have also been reported. Similar in structure to LiDFOB, lithium difluoro(sulfato)borate ($LiBF_2SO_4$) (Fig. 16) has been tested at 80 °C in MCMB/Li and $LiFePO_4$/Li half-cells with improved performance [58]. Boron-based chelating salts such as lithium bis[1,2-benzenediolato(2)-O,O′]borate (LBBB) (Fig. 16), lithium bis[2,3-naphthalenediolato(2)-O,O′]borate (LBNB), and lithium bis[2,2′-biphenyldiolato(2)-O,O′]borate (LBBPB) also have good thermal stability, but the electrolyte solutions containing these salts showed much inferior conductivity due to their large anion size and narrow electrochemical window [15–17]. Besides the salts mentioned above, a multivalent salt with fluorinated

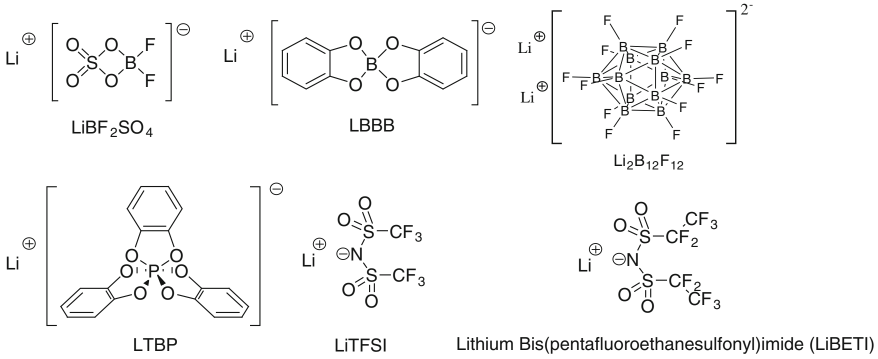


Fig. 16 A selection of thermally stable lithium salts with various structures

boron clusters, dilithium dodecafluorododecaborate ($Li_2B_{12}F_{12}$, where boron atoms occupy 12 vertices of a regular icosahedron, and each boron atom is connected to one fluorine atom) (Fig. 16) has shown enhanced storage and cycle life compared with $LiPF_6$ at 60 °C [8].

Although having P-F bonds in the structure, lithium tetrafluoro(oxalato)phosphate (LiFOP, Fig. 14) has much better thermal stability than $LiPF_6$. Another thermally stable phosphorous-based salt is a tri-chelated salt, lithium tris [1,2-benzenediolato(2)-O,O′]phosphate (LTBP, Fig. 16) [43], but it cannot be used in the Li-ion battery because of its insufficient electrochemical window related to the less stable phenol ligands.

The nitrogen-centered imide salts are good candidates for thermally stable lithium salts. The best known salt is LiTFSI (Fig. 16), which was found to be indefinitely stable at temperatures as high as 100 °C [25]. Unfortunately, this salt leads to corrosion of the aluminum current collector on the cathode [55], making it unsuitable for SOA Li-ion batteries. The larger imide analogue, lithium bis (perfluoroethanesulfonyl)imide (LiBETI, Fig. 16), exhibits much better passivation of aluminum, leading to improved stability [69, 75]. Recent progress in the understanding of the solvation properties of electrolyte solutions has brought new insight to LiTFSI salt. EC-based electrolytes with high LiTFSI concentrations, for example a 3:1 or 2:1 (molar ratio), did not corrode aluminum [68] (Fig. 17a). Moreover, the highly solvated solvent molecules makes the electrolyte solvent anodically and thermally stable (Fig. 17b). This finding suggests that it is feasible for researchers to reconsider utilizing thermally stable salts such as LiTFSI in a new way and this endeavor should be pursued for the safety benefits.

In addition to highly concentrated electrolytes, anions with longer perfluorinated chains also passivate aluminum while still providing good thermal stability to the resulting electrolyte [41, 47, 51, 55].

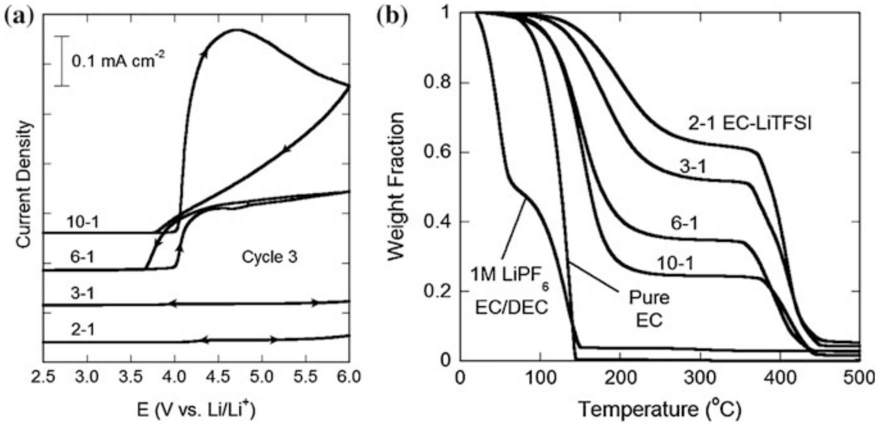


Fig. 17 **a** The 3rd cycle cyclic voltammetry scan of coin cells with Al foil as working electrodes, Li metal as counter/reference electrodes, and EC-LiTFSI (from 10:1 to 2:1) as electrolyte. **b** Thermal gravimetric analysis (5 °C min^{-1}) of 1.0 M $LiPF_6$ in EC/DEC (3:7 volume ratio), pure EC, and various EC-LiTFSI (from 10:1 to 2:1) electrolyte. Reproduced with permission [68]. Copyright 2014 Royal Society of Chemistry

3.3 Emerging Salts

There is new focus on developing lithium salts with fewer corrosion issues and less environmental impact. Most of the conventional lithium salts contain fluorine because it is among the smallest yet strongest electron withdrawing groups, and anions with fluorine substitution generally have high anodic stability. However, many fluorinated salts are corrosive and hazardous to the environment. Thermal runaway in batteries containing fluorinated salts may result in the release of toxic fumes containing HF, which is extremely dangerous as well as harmful to the atmosphere. As a result, developing fluorine-free salts marks the first step toward environmentally friendly batteries.

An alternative to fluorine as the electron-withdrawing group is the cyanide (CN) group. Recently synthesized cyanide salts include lithium dicyanamide (LDCA), lithium 4,5-dicyano-1,2,3-triazolate (LDCTA), and lithium tetracyanoborate ($LiB(CN)_4$) (Fig. 18) [88]. Although CN fits the goal of fluorine free, the oxidation potential of these anions is lower than that of fluorine-based salts, so the application of lithium cyanide salts is limited to low voltage cathodes such as $LiFePO_4$.

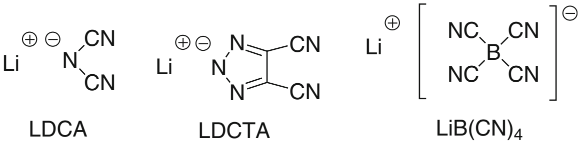


Fig. 18 Lithium salts based on cyanide functionality

4 Conclusion and Future Outlook

Li-ion battery chemistry is a mature technology that has been commercialized over the decades, although it is still far from reaching its limit. Lithium metal, which is considered as the "holy grail" of lithium battery anodes, is still unable to deliver the desired cell performance despite new progress made for effective suppression of the dendrite formation. Lithium transition metal oxide-based inorganic cathodes have been constantly achieving new levels of performance in terms of the capacity and voltage, while organic cathode materials have also started to show great promise. The development of new anode and cathode materials goes hand in hand with electrolyte development, as each new material with new challenges necessitates a compatible electrolyte. The number of patent application and journal publication on Li-ion battery electrolytes has increased exponentially in the past decade (Fig. 19), which is evidence of the burst of interest in this field. Novel electrolytes and electrolyte additives that are tailored to the various lithium-ion chemistries will be the main focus of future research and development. It is of vital importance that mechanistic studies using in situ characterization techniques and computational efforts should be carried out to support electrolyte development.

For emerging battery technologies such as Li-S, Li-O_2, Na-ion and magnesium-ion batteries, the knowledge achieved in the course of Li-ion battery electrolyte research will be able to provide insight and support for the development of new electrolytes for various electrochemical energy storage chemistries.

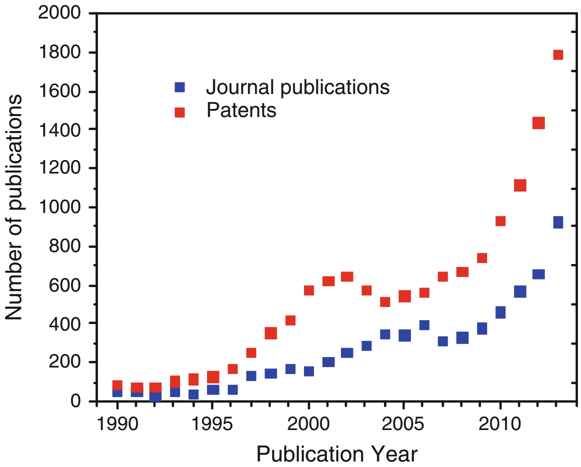


Fig. 19 Total numbers of journal publications and patents on the topic of Li-ion battery electrolyte by year searched by SciFinder. Copyright 2014 American Chemical Society

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