



# A review on electrolyte additives for lithium-ion batteries

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## Abstract

This paper reviews electrolyte additives used in Li-ion batteries. According to their functions, the additives can be divided into these categories: (1) solid electrolyte interface (SEI) forming improver, (2) cathode protection agent, (3)  $\text{LiPF}_6$  salt stabilizer, (4) safety protection agent, (5) Li deposition improver, and (6) other agents such as solvation enhancer, Al corrosion inhibitor, and wetting agent. The function and mechanism of each category additives are generally described and discussed.

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*Keywords:* Electrolyte; Additive; Solid electrolyte interface; Overcharge; Li-ion battery

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## 1. Introduction

Use of electrolyte additives is one of the most economic and effective methods for the improvement of Li-ion battery

performance. Usually, the amount of an additive in the electrolyte is no more than 5% either by weight or by volume while its presence significantly improves the cycleability and cycle life of Li-ion batteries. For better battery performance, the additives are able to: (1) facilitate formation of solid electrolyte interface/interphase (SEI) on the surface of graphite, (2) reduce irreversible capacity and gas generation for the SEI formation and long-term cycling, (3) enhance thermal stability of

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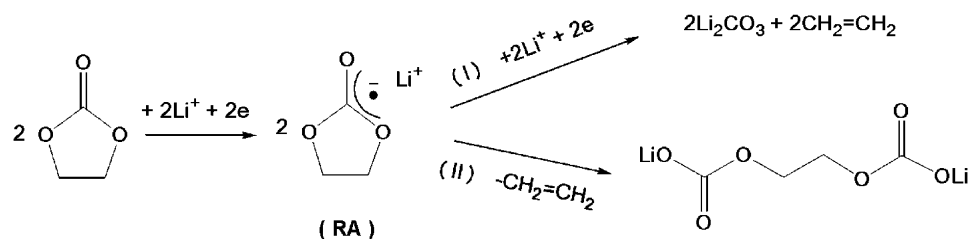
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LiPF<sub>6</sub> against the organic electrolyte solvents, (4) protect cathode material from dissolution and overcharge, and (5) improve physical properties of the electrolyte such as ionic conductivity, viscosity, wettability to the polyolefine separator, and so forth. For better battery safety, the additives are able to: (1) lower flammability of organic electrolytes, (2) provide overcharge protection or increase overcharge tolerance, and (3) terminate battery operation in abuse conditions. This paper reviews these additives and discusses their functions in improving Li-ion battery performance.

## 2. SEI forming improver

### 2.1. Understanding of SEI formation

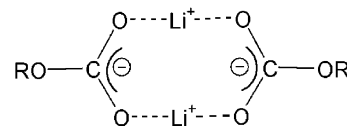
Extensive investigations using various spectroscopic techniques have identified that the main components of SEI are the decomposed products of electrolyte solvents and salts. These components include Li<sub>2</sub>CO<sub>3</sub>, lithium alkyl carbonate, lithium alkyloxide, and other salt moieties such as LiF for LiPF<sub>6</sub>-based electrolytes [1,2]. Based on this fact, two mechanisms have been proposed for the electrochemically induced reduction of carbonate-based solvents, for example ethylene carbonate (EC):



where RA is an abbreviation for “radical anion”. Both of these two mechanisms are present in the process of SEI formation and compete with each other. When mechanism (I) is predominant, the reduction of solvents generates more gaseous products, and the resulting SEI is Li<sub>2</sub>CO<sub>3</sub>-abundant and less stable. On contrary, mechanism (II) leads to less gaseous products and the resulting products are substantially insoluble in the electrolyte. As a result, the formed SEI is more compact and stable. Many researches have indicated that these two mechanisms are affected by the morphology and chemistry of graphite surface, and are associated with the catalytic activity of the fresh graphite surface. The catalytic effect has been confirmed by the strong location-dependence of SEI composition [3,4]. That is, the SEI formed in prismatic (edge) areas of a highly oriented pyrolytic graphite is enriched with inorganic compounds, while that in basal planes is enriched with organic compounds [3,4]. The catalytic phenomenon was further supported by the fact that surface modification, such as mild chemical oxidization [5–8] and physical surface coating [9–11], on graphite materials significantly facilitated SEI formation and reduced gas generation in the first intercalation of Li<sup>+</sup> ions into graphite. These modifications are considered to deactivate the catalytic activity of the fresh graphite surface.

On the other hand, a dynamic study using an electrochemical impedance spectroscopy (EIS) reveals that the SEI formation

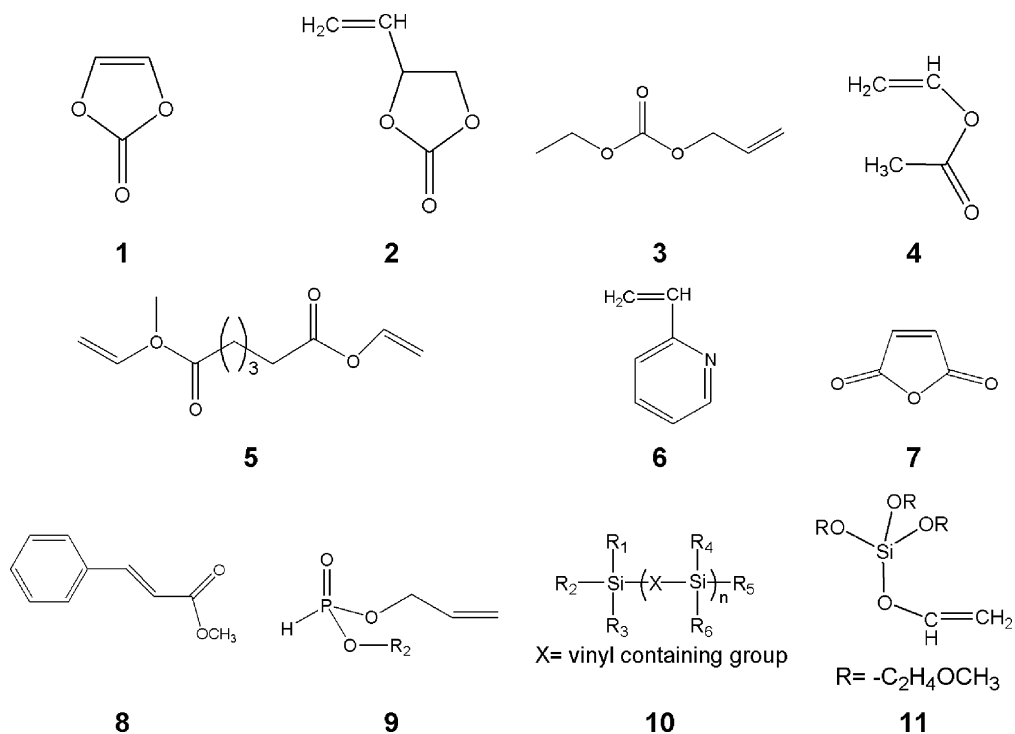
takes place in two major voltage stages [12,13]. The first stage takes place before the intercalation of Li<sup>+</sup> ions into graphite and the SEI formed in this stage is structurally porous, highly resistive, and dimensionally unstable. The second stage occurs simultaneously with the intercalation of Li<sup>+</sup> ions and the resulting SEI is more compact and highly conductive. For a specific electrolyte system of a 1.0 M LiPF<sub>6</sub> 3:7 (wt.) EC–ethyl methyl carbonate (EMC), these two stages produce nearly same irreversible capacities. The irreversible capacities suffered in the second stage are associated not only with the reduction of solvent molecules, but also with the electrochemical reduction of surface functional groups, such as carbon–hydrogen bond, carboxyl, carbonyl, and lactone, on the edge sites of graphite [5]. In the view of chemical composition, the SEI formed in the first stage is more enriched with inorganic components, while that formed in the second stage with organic components. Better stability of the latter is attributed to the formation of a network between organic compounds through the coordination of Li<sup>+</sup> ions and organic carbonate anions as below [14]:



As suggested by its chemical composition, the “dried” SEI itself is neither ionic conductive nor electronic conductive. The ionic conduction in the SEI must originate from the migration of solvated Li<sup>+</sup> through the micro-pores of SEI. Therefore, the ionic conductivity of SEI can be taken as the measure to evaluate the compactness and stability of SEI. Generally, high resistance corresponds to a compact and stable SEI [13]. Xu et al. [15] further examined the stability of the SEI formed in an EC-based electrolyte with different voltage range by changing the electrolyte into a fresh propylene carbonate (PC) electrolyte, and found that the SEI formed above 0.5 V versus Li<sup>+</sup>/Li, i.e., corresponding to the first stage, was unable to suppress the reduction of PC molecules. The information described above would be very useful to understand and develop a desirable additive.

### 2.2. Reduction-type additive

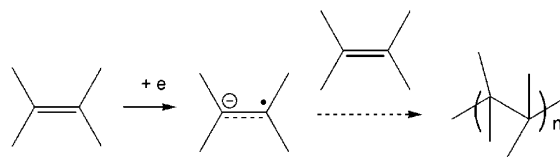
As described above, the SEI formed before the intercalation of Li<sup>+</sup> ions is unstable and abundant with inorganic compounds. Furthermore, this period produces more gaseous products, especially for PC-containing electrolytes. In the similar manner as surface modification, the SEI formation can be facilitated by chemically coating an organic film onto the surface of graphite



Scheme 1. Chemical structure of polymerizable additives.

through an electrochemical reduction of additives. This type of additives usually has higher reductive potentials than the electrolyte solvents. Prior to electrochemical reduction of the electrolyte solvents, the additives are preferably reduced to form an insoluble solid product, which subsequently is covered onto the surface of graphite as a preliminary film to deactivate catalytic activity. Therefore, use of these additives not only reduces gas generation but also increases the stability of the SEI due to the participation of additive molecular moieties into the SEI. According to the characteristic of additive reactions, these additives can be divided as polymerizable monomer and reductive agent. The former as shown in Scheme 1, which is featured by one or more carbon–carbon double bonds in their molecules, includes vinylene carbonate (VC, **1**) [16–21], vinyl ethylene carbonate (**2**) [20,22], allyl ethyl carbonate (**3**) [23], vinyl acetate (**4**) [24,25], divinyl adipate (**5**) [25], acrylic acid nitrile [26], 2-vinyl pyridine (**6**) [27], maleic anhydride (**7**) [28], methyl cinnamate (**8**) [29,30], phosphonate (**9**) [31], and vinyl-containing silane-based compounds (**10**) [32] and (**11**) [33]. In addition, furan derivatives that contain two double bonds in each molecule have recently been reported as the very effective SEI forming agent by Korepp et al. [34], who described that the presence of as low as ~1% 2-cyanofuran could effectively suppress exfoliation of graphite structure in a 1 M LiClO<sub>4</sub> PC electrolyte. This merit is attributed to the highly effective reduction polymerization of the furan ring, which takes place at higher potentials than PC reduction. There was no further information available about the effect of 2-cyanofuran on the cathode although the furan derivatives are known among the excellent electrochemically polymerizable (oxidative) monomers for conducting polymers [35,36].

The mechanism of the polymerizable additives in facilitating SEI formation is based on an electrochemically induced polymerization, which can be described by a general equation:



where the radical anion can be terminated by the solvent molecules to form an insoluble and stable product as the preliminary SEI nuclei. Electrochemically, this type of additives is very effective since the electron transference is only involved in the first step. In addition to the reductive polymerization, the opposite oxidative polymerization also can occur on the positive electrode, which inevitably increases impedance and irreversibility of the cathode. Therefore, the reasonable amount of such additives in the electrolyte is not to exceed 2 wt.%. Effectiveness of such additives is affected by many factors, including: (1) efficiency of the electrochemical polymerization, (2) solubility of the resulting polymer, and (3) adhesion of the polymer to graphite surface. Since the reductive polymerization takes place at higher potentials than the solvent reduction, the improvement of such additives are mainly on the initial stage of SEI formation, which results in: (1) reduction of gas generation, (2) reduction of irreversibility capacity, and (3) stabilization of the SEI against the extended cycling.

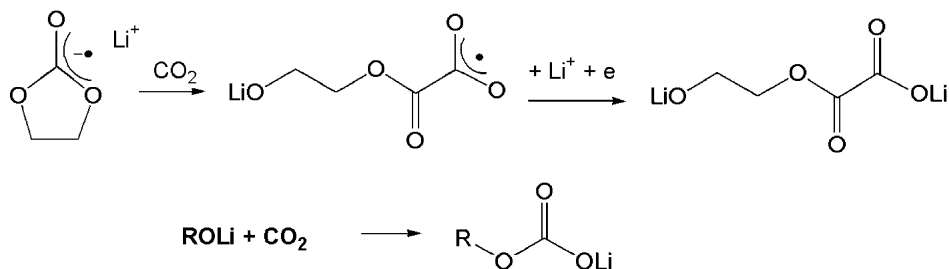
Reductive agents assist SEI formation through adsorption of their reduced products onto the catalytic active sites of graphite surface. Effectiveness of such additives in facilitating SEI formation is affected by the affinity of molecular moieties of the

reduced products to the graphite active sites. Most of this type of additives belong to sulfur-based compounds, including  $\text{SO}_2$  [37,38],  $\text{CS}_2$  [39], polysulfide ( $\text{S}_x^{2-}$ ) [40,41], cyclic alkyl sulfites (**12**) such as ethylene sulfite [42–44] and propylene sulfite [44,45], and aryl sulfites [44]. The effectiveness of these additives seems to increase with the content of sulfur in the molecule, which is in consistence with the poisoning effect of sulfur-containing compounds on many other catalysts. It should be noted that all of these sulfur compounds are soluble in the organic electrolytes and anodic unstable at high potentials, their presence may result in a high self-discharge rate as a result of the internal redox shuttle. Therefore, the amount of sulfur-based additives must be strictly limited. A favorite impact is that the SEI formed in the presence of polysulfide exhibited higher diffusion of  $\text{Li}^+$  ions, which was indicated by the reduced resistances at low frequencies [41]. Another example that is similar with the adsorption of the reduced products was demonstrated by Wu et al. [46], who described that the addition of 5 wt.%  $\text{AgPF}_6$  into 1.0 M  $\text{LiPF}_6$  3:2 (vol.) PC–DEC electrolyte could effectively

where charging at fast rate or at low temperature is required since these conditions inevitably result in lithium plating [53].

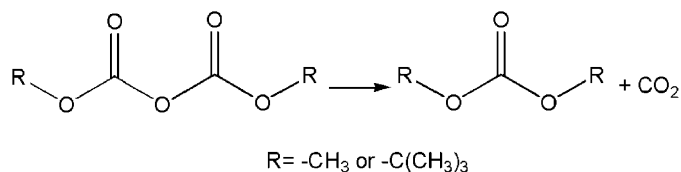
### 2.3. Reaction-type additive

This type of additives may not be reduced electrochemically in the whole potential range of  $\text{Li}^+$ -ion intercalation, however, they are able to either scavenge radical anions, an intermediate compound of the solvent reduction (see Section 2.1), or combine with the final products such as lithium alkyl dicarbonate and lithium alkyloxy to form more stable SEI components. Early report about this type of additives was that the presence of  $\text{CO}_2$  reduced the initial irreversible capacity and stabilized SEI [38,41,54–56]. A Fourier transform infrared (FTIR) spectroscopy analysis by Zhuang et al. [57] revealed that  $\text{Li}_2\text{C}_2\text{O}_4$ -like compounds were present in the SEI formed with EC and PC-based electrolytes. Therefore, two reactions below can be proposed to explain the fact of  $\text{CO}_2$  facilitating SEI formation:



which indicate that  $\text{CO}_2$  stabilizes the SEI through its direct incorporation to the SEI formation.

The similar results were obtained by using dialkyl pyrocarbonate as an in situ  $\text{CO}_2$ -provider [58,59] through the decomposing reaction:

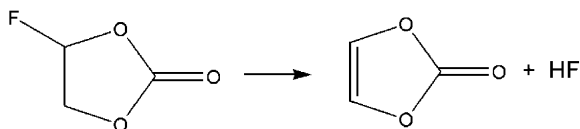


The advantage of this approach is that it solves the problem of low solubility and high vapor pressure with  $\text{CO}_2$  gas. More interestingly, the SEI thus formed shows much low resistance at low temperatures [58]. Other similar approaches are the saturation of the electrolyte solution with  $\text{Li}_2\text{CO}_3$  [60,61], which has proven to reduce gas generation, increase initial reversibility, and extend cycle life of the Li-ion battery. These improvements are attributed to the formation of a more compact and thin SEI [60].

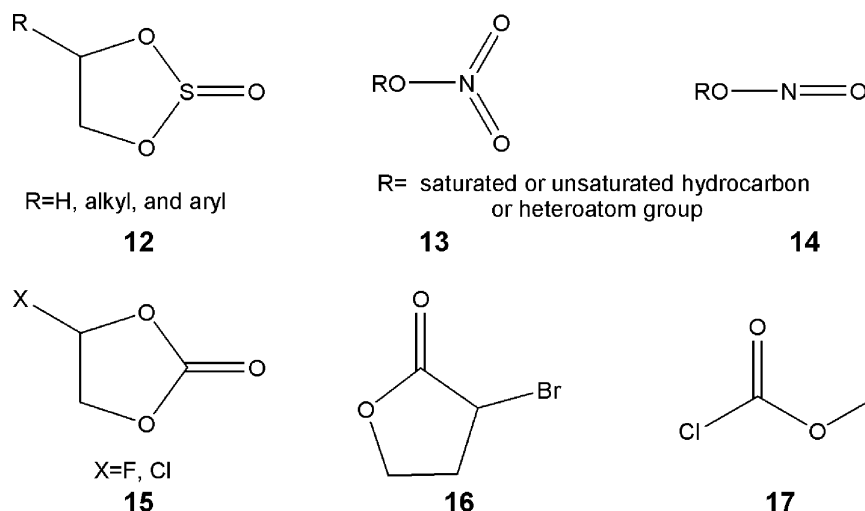
A series of carboxyl phenol (**18**) [62], aromatic esters (**19**) [62], and anhydride (**20**) [63] has been proposed to improve SEI formation (see Scheme 3). These compounds feature a well-conjugated structure, which is believed to be capable of stabilizing intermediate RAs through delocalization of the radical. For example, catechol carbonate (**20**) can capture a less stable RA to form more stable one (**21**), which further results in the formation of more stable SEI [63].

suppress PC reduction and graphite exfoliation due to the preferable deposition of Ag particles at 2.15 V versus  $\text{Li}^+/\text{Li}$ . Their conclusion was supported by XRD analysis and SEM observation.

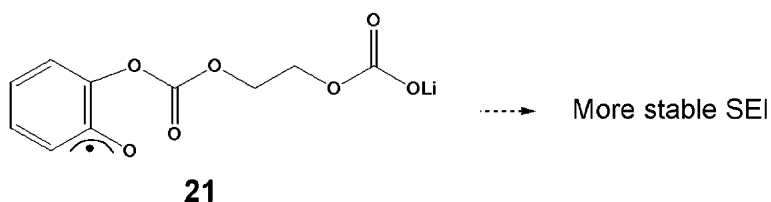
The other reductive additives include  $\text{N}_2\text{O}$  [41], nitrate (**13**) [47], nitrite (**14**) [48], halogenated ethylene carbonate (**15**) [43,49–51], halogenated lactone such as  $\alpha$ -bromo- $\gamma$ -butyrolactone (**16**), and methyl chloroformate (**17**) [52] as shown in Scheme 2. The later three compounds contain a carbonyl ( $>\text{C}=\text{O}$ ) group, which can be electrochemically reduced in the similar manner as EC. Their function in facilitating SEI formation is attributed to the possible bonds between the halogen species of the SEI consisting of the reduced products of electrolyte solvents and halogen-containing additive [52]. Fluoroethylene carbonate (FEC, **15**) [43,51] is an interesting compound, which itself does not contain vinyl group, however, it can lose a HF molecule to form a VC molecule as below:



The resulting VC in turn serves as a polymerizable additive and HF effectively improves the cycleability of metallic lithium (to be discussed in Section 6). Therefore, FEC could be of special importance for these specific operations



Scheme 2. Chemical structure of reduction-type additives.



Other additives having the similar functions include maleic anhydride [28], succinimide (**22**) [64] and *N*-benzyloxy carbonyloxy succinimide (**23**) [64], where “N” atom is linked by two carbonyl groups with strong RA-delocalizing ability (Scheme 3). All these additives (**18–20**, **22**, **23**) are very effective in suppressing PC reduction and stabilizing the SEI. A common characteristic of these additives is that the potential of the SEI formation during the initial Li<sup>+</sup> intercalation is very close to that of the solvent reduction [62] since the additives themselves do not involve reduction, instead capture the less stable solvent RA to form the more stable RA (see Fig. 1). In some

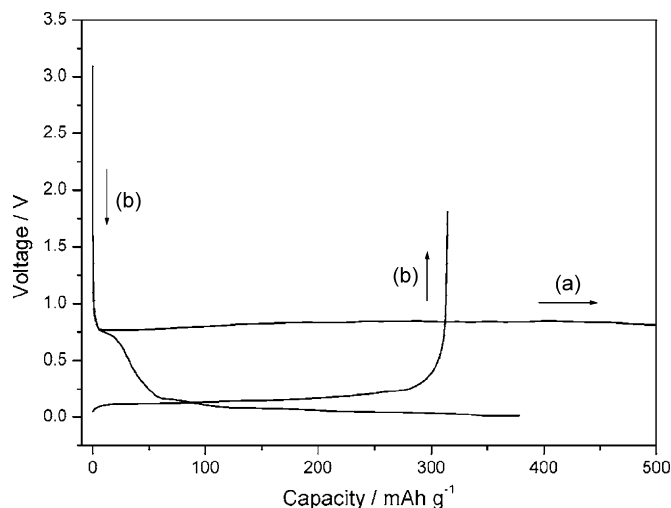
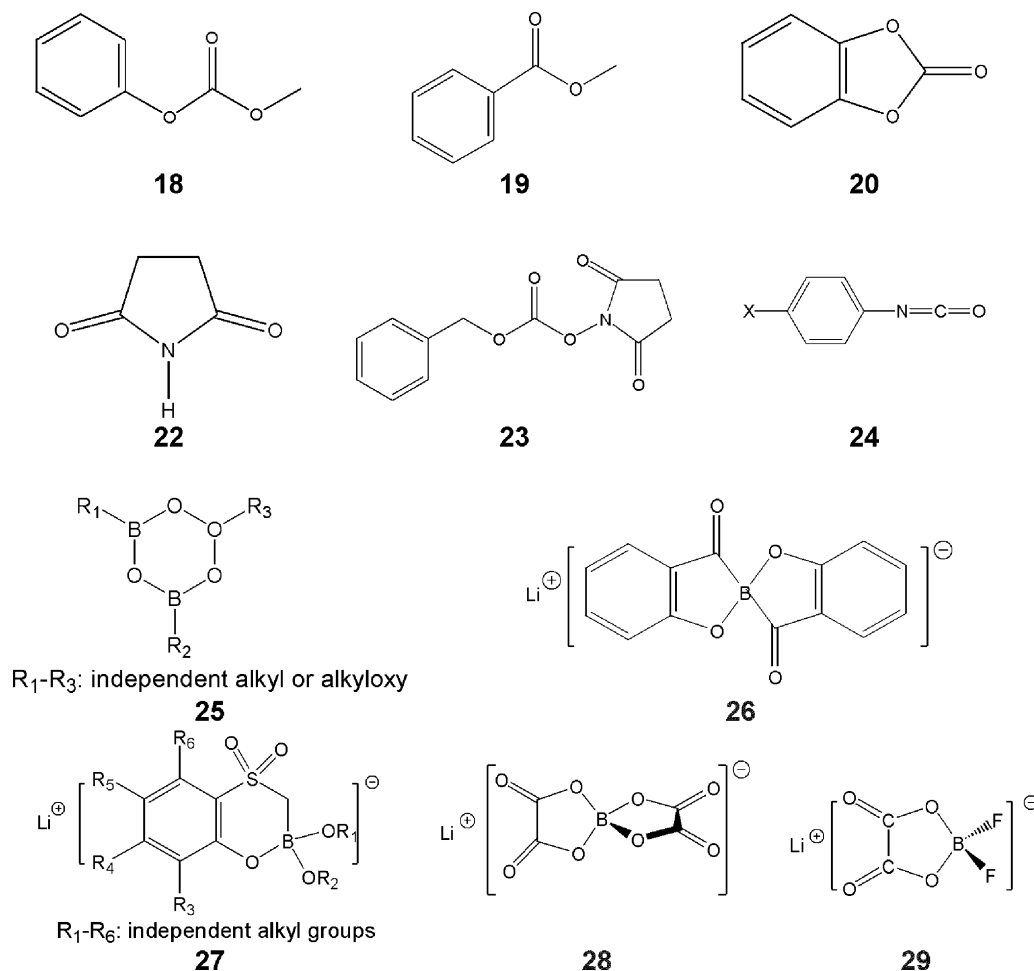


Fig. 1. Voltage curves of the first cycle of Li/graphite cells in a 1.0 M LiPF<sub>6</sub> (3:2 vol.) PC–DEC electrolyte without (a) and with (b) the addition of 2 wt.% phenyl acetate. (Reproduced from Fig. 1 of ref. [62] by permission of the Electrochemical Society, Inc.)

cases, such additives may not reduce the irreversible capacity of the first cycle, but significantly increase cycle life of the cell [63]. On the other hand, aromatic isocyanate compounds (**24**, where X is hydrogen or halogen) were claimed as a new multifunctional additive for the improved Li-ion battery performance [65]. First, the isocyanate stabilizes SEI through the reactions with the chemisorbed oxygen groups such as phenol and carboxyl on the surface of graphite particles based on the speculation that the resulting products have much stronger affinity to the subsequently formed SEI components. Second, the isocyanate scavenges water and acidic HF from the electrolyte based on its extremely high reactivity to these impurities. Third, the lone-pair electrons in nitrogen of isocyanate molecule serves as a weak Lewis base to deactivate the reactivity of electron-deficient PF<sub>5</sub> with the electrolyte solvents. It was shown that the addition of 5 wt.% of phenyl isocyanate or 4-fluorophenyl isocyanate enabled graphite to be cycled reversibly in a 1.0 M LiPF<sub>6</sub> 1:1 (wt.) PC–EC electrolyte without any adverse impact on the cell performance [65].

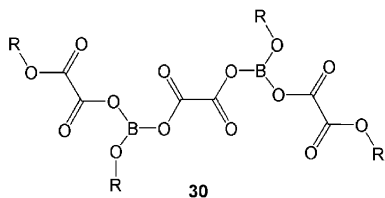
Boron-based compounds have been extensively studied as the electrolyte additive to increase the cycle life of Li-ion batteries, in which their function is believed to stabilize the resulting SEI. These compounds include inorganic B<sub>2</sub>O<sub>3</sub> [66], organic borates with undisclosed structure [18], boroxine family compounds (**25**) such as trimethoxyboroxine and trimethylboroxin [67], and lithium salt-based boron compounds (**26**) [19] and (**27**) [68]. They were found not only to reduce capacity fading rate but also to increase rate capability and low temperature performance of the Li-ion batteries [18]. Spectroscopic analyses on the electrode surface by FTIR and XPS revealed that the effect of these additives on the electrodes' performance was attributed



Scheme 3. Schematic structure of reaction-type additives.

to their incorporation to the surface chemistry of electrode [19].

Lithium bis(oxalato) borate (LiBOB, **28**) was initially studied as an alternative salt to improve the high temperature performance of Li-ion batteries [69]. It is shown that this salt not only is capable of suppressing PC irreversible reduction, but also significantly stabilizes the SEI against the extended cycling [70]. Analyses of IFTR [71] and XPS [72] verify that B–O-based molecular moieties are clearly present in the SEI formed in LiBOB-based electrolytes. Based on this fact, it was proposed that LiBOB reacts with the major SEI components such as lithium alkyl dicarbonate and lithium alkoxide to form a more stable oligomer (**30**), where R presents the molecular moieties of the reduced products of the electrolyte solvents [72,73].



According to the chemistry of LiBOB and the final product, the formation of compound (**30**) may not involve any elec-

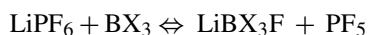
tronic transference, instead of a series of complicated exchange reactions between B–O and R–O bonds [73–75]. Further study revealed that LiBOB still retained its strong ability to facilitate SEI formation even its content in the electrolyte was reduced to an additive level [74–77]. For example, the addition of 1 mol.% LiBOB is high enough to enable graphite cycling reversibly in a 1 M LiPF<sub>6</sub> 1:1 (wt.) PC–EC electrolyte [76,77] and a 1 M LiBF<sub>4</sub> electrolyte with the same solvent [74], respectively. Another salt is lithium oxaltodifluoroborate (LiODFB, **29**) [75,76], which has the similar function to stabilize the SEI as LiBOB does, but it is superior to LiBOB in many other properties such as the solubility in carbonate solvents and the ability to provide better rate capability and low temperature performance of Li-ion batteries [75].

On the other hand, absorption-type additive also was studied to improve SEI formation [9,52,78]. This type of additives generally has strong affinity to the graphite surface, and they are physically adsorbed on the active sites of graphite to suppress PC reduction. Since the adsorption is a simple physical process, such an additive can be applied either by adding it into the electrolyte [52,78], or by pretreating graphite with the additive [9,52,78]. This type of additives was exemplified by halogenated organic compounds [52], polydimethylsiloxane [9], and silane [78].



#### 2.4. SEI morphology modifier

As described in Section 2.1, the stability of SEI is affected by the content of inorganic components. In the SEI formed with  $\text{LiPF}_6$ -carbonate electrolyte, the main inorganic components are known to be  $\text{Li}_2\text{CO}_3$  and  $\text{LiF}$ , in which the presence of isolated  $\text{LiF}$  crystals has been identified as the important factor to result in SEI unstable [79]. For this reason, many boron-based anion receptors have been developed to dissolve  $\text{LiF}$  [80–83]. Among these anion receptors, the most representative compound is tris(pentafluorophenyl) borane (TPFPB), in which boron atom is extremely electron-deficient due to the strong electron-withdrawing and excellent conjugated properties of the perfluorinated phenyl groups. Theoretically, TPFPB can coordinate  $\text{LiF}$  to form a 1:1 complex and easily dissolves more than 1 M of  $\text{LiF}$  in many organic solvents [84,85]. It has been reported that the addition of 0.1–0.2 M TPFPB is sufficient to improve the cycleability and capacity retention of Li-ion cell for both  $\text{LiPF}_6$  [80,81,83] and  $\text{LiBF}_4$  [82] electrolytes. The improvement is attributed to the dissolution of  $\text{LiF}$  out of the SEI. A negative impact of TPFPB is that it captures  $\text{LiF}$  from  $\text{LiPF}_6$  to release highly reactive  $\text{PF}_5$ , which accelerates deterioration of the electrolyte solvents, i.e.,



where X represents tris(pentafluorophenyl) group [83,86]. Therefore, the amount of TPFPB added to the electrolytes should be strictly controlled so that the adverse effect can be minimized.

Alkali metal salts also have been attempted to improve SEI formation. Komaba et al. [87] first reported that the addition of 0.22 M  $\text{NaClO}_4$  into a 1 M  $\text{LiClO}_4$  1:1 (vol.) EC–diethyl carbonate (DEC) electrolyte obviously reduced the initial irreversible capacity and resulted in the better capacity retention. The SEI formed in the presence of sodium ions is more uniform and has much smaller resistance compared with that obtained in the absence of sodium ions. Alternatively, a pretreatment of graphite materials using sodium salts that are insoluble in organic electrolytes such as  $\text{Na}_2\text{CO}_3$  and  $\text{LiCl}$  has been attempted to improve SEI formation [88]. In addition to increasing reversible capacity and enhancing capacity retention, such a pretreatment led to a small elevation in the potentials of intercalation and de-intercalation of  $\text{Li}^+$  ions with graphite, as indicated in Fig. 2. This feature is very important for the development of high power Li-ion battery. One can adopt this feature to eliminate lithium plating on the graphite anode when the Li-ion batteries are charged at high rate or low temperatures.

Opposite impacts of potassium ions on the SEI formation have been observed from different electrolytes [89,90]. Zheng et al. [90] attributed this phenomenon to the high selectivity of  $\text{K}^+$  ions to the electrolyte composition. A very obvious improvement by  $\text{K}^+$  ions was obtained from 1 M  $\text{LiClO}_4$  EC–DEC system [90], which showed that the addition of small amount of  $\text{K}_2\text{CO}_3$  significantly increased graphite's reversible capacity and improved cell's rate capability. Based on Raman spectroscopic analysis, Zheng et al. [90] concluded that the presence of

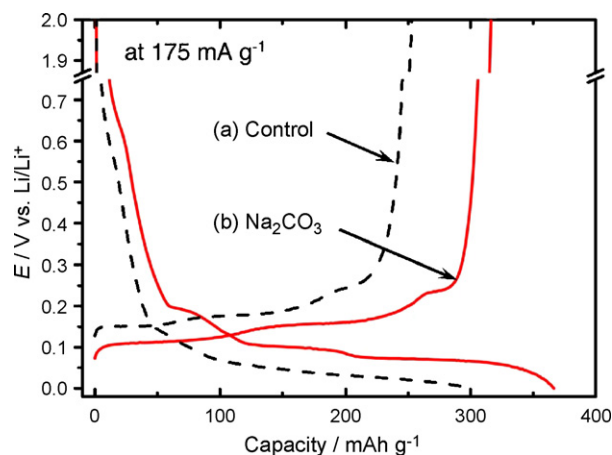


Fig. 2. Voltage profiles of the first cycle of the graphite electrodes without (a) and with (b) pretreatment using a 5.0 wt.%  $\text{Na}_2\text{CO}_3$  aqueous solution in a 1 M  $\text{LiClO}_4$  1:1 EC–DEC electrolyte. (Reproduced from Fig. 2 of ref. [88] by permission of the Electrochemical Society, Inc.)

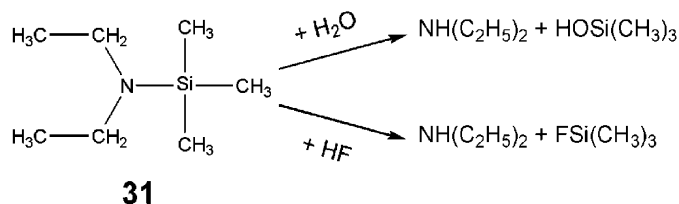
a K salt decreased solvation of  $\text{Li}^+$  ions by EC molecules, which mitigates solvent decomposition and results in the formation of more porous and thinner SEI. The latter has been confirmed by much lower surface resistance and charge-transfer resistance.

On the other hand, it was reported that 12-crown-4 and 15-crown-5 could effectively suppress PC reduction during the initial SEI formation [91,92], which is attributed to their extremely strong solvating ability to  $\text{Li}^+$  ion [93]. In the presence of these crown ethers, solvation of  $\text{Li}^+$  ions by PC molecules is greatly weakened so that PC has less chance to co-intercalate with the solvated  $\text{Li}^+$  ion into graphite, which as a result reduces PC reduction. However, their high toxicity makes it impossible to use crown ethers as the electrolyte additive in Li-ion batteries.

### 3. Cathode protection agent

In the view of electrolyte, performance deterioration of the cathodes origins from two factors: (1) water and acidic impurities, and (2) irreversible oxidization of the electrolyte solvents. Since the contents of water and acidic impurities (HF) in the electrolyte have been strictly controlled before use, these impurities are mainly generated during charging, especially during occasionally overcharging. A possible mechanism proposed by Wang et al. [94] shows that the solvents are chemically oxidized by the oxygen released from the cathode to generate  $\text{H}_2\text{O}$  and  $\text{CO}_2$ , and that the resulting  $\text{H}_2\text{O}$  further hydrolyzes  $\text{LiPF}_6$  to form acidic products such as HF and  $\text{POF}_3$ . Since HF is the main source for the dissolution of the cathode materials, especially spinel  $\text{LiMn}_2\text{O}_4$ , most of the current efforts have been focused on these additives capable of scavenging water and acids. Aiming at reducing the dissolution of spinel  $\text{LiMn}_2\text{O}_4$ , Saidi et al. [95] proposed amine-based organic base such as butylamine to scavenge acidic impurities, while Takechi et al. [96] used carbodiimide-based compounds such as *N,N'*-dicyclohexylcarbodiimide to react with water to prevent acid generation. Both approaches showed in different degree improvement on the capacity retention of  $\text{LiMn}_2\text{O}_4$  cathode. In their further efforts, Takechi and

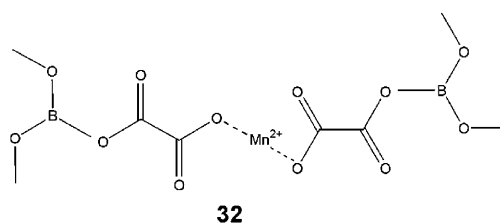
Shiga [97] proposed a bifunctional additive based on a series of “N–Si”-based compounds, such as *N,N*-diethylamino trimethylsilane (31), which are capable of scavenging both H<sub>2</sub>O and HF via breaking “N–Si” bond as below:



Deactivation of PF<sub>5</sub> would be the other reason for amines to reduce the dissolution of the cathode materials, which has been less recognized. Chemically, the equilibrium of “LiPF<sub>6</sub> ⇌ LiF + PF<sub>5</sub>” is always present in the electrolyte, and the reaction (here using MnO as an example) of “PF<sub>5</sub> + MnO → POF<sub>3</sub> + MnF<sub>2</sub>” is possible. Due to their electron-donating property, the amine molecules can complex PF<sub>5</sub> to reduce the reactivity and acidity of PF<sub>5</sub> and as a result suppress the dissolution of the cathode materials.

The other approach was to form a protective film on the cathode surface to prevent further dissolution. The idea is that the additive molecules combine with the dissolved metal ions to form substantially insoluble products, which are subsequently covered onto the cathode surface to prevent further dissolution. In the effort to search for such an additive, Amine et al. [98] added LiMn<sub>2</sub>O<sub>4</sub> powder into a 0.7 M LiBOB 1:1:3 EC–PC–DMC electrolyte and stored the mixture at 55 °C for 4 weeks. After this, they found almost no Mn ions in the electrolyte. In their further effort [99], they used LiBOB as the additive at the concentration of no more than 0.1 M to examine the power and capacity performance of graphite/LiMn<sub>1/3</sub>Ni<sub>1/3</sub>Co<sub>1/3</sub>O<sub>2</sub> cells in LiPF<sub>6</sub>-based electrolyte. The results showed that such cells exhibited excellent capacity retention at 55 °C and their impedance met the requirement set by the FreedomCar Partnership. Although the mechanism for the role of LiBOB in suppressing the Mn<sup>2+</sup> dissolution has not been understood well, a possible one is that the dissolved Mn<sup>2+</sup> and BOB anion are combined with each other to form an insol-

uble and stable surface layer with a network structure (32) like below:



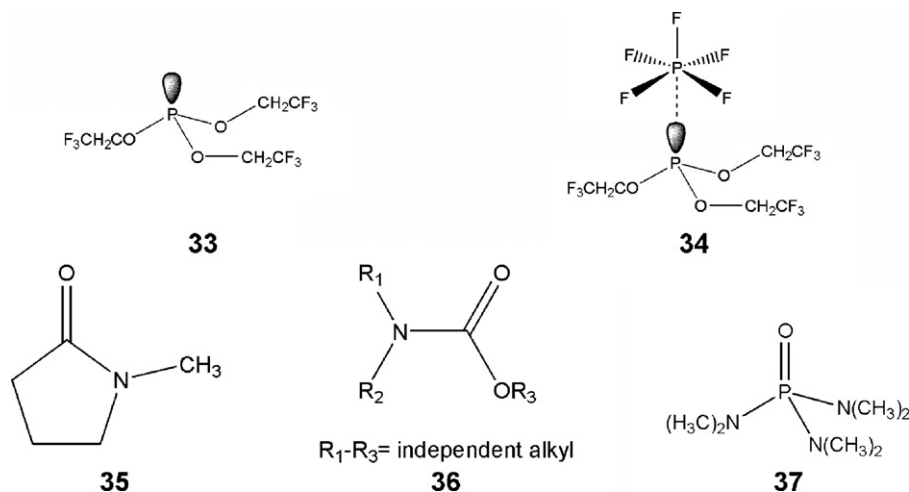
Based on the descriptions above, the functions of the cathode protection agents can be divided into two categories: (1) to scavenge water and acidic impurities, and (2) to combine the dissolved metal ions into a protective surface layer. Since water is inevitably generated by the oxidation of solvents during charging and occasionally overcharging [94], the combination of these two approaches seems the best way to protect the cathode from performance deterioration.

#### 4. LiPF<sub>6</sub> salt stabilizer

Thermal instability of LiPF<sub>6</sub>-based electrolytes is attributed to two factors of: (1) high equilibrium constant of the decomposition “LiPF<sub>6</sub> ⇌ PF<sub>5</sub> + LiF” and (2) high reactivity of the resulting PF<sub>5</sub> with the organic solvents. Beside this, the resulting PF<sub>5</sub> can deteriorate the stability of the SEI on the graphite surface via a series of reactions with most of the SEI components, such as Li<sub>2</sub>CO<sub>3</sub>, RCO<sub>2</sub>Li, and ROCO<sub>2</sub>Li, even in the absence of H<sub>2</sub>O and other acidic impurities, for example:



As a result of these reactions, the content of LiF in the SEI is increased and the pressure inside the battery is build-up by the generated gaseous products. Therefore, the efforts to stabilize the electrolytes have been focused on solving the above two problems. For the first issue, Hiroi et al. disclosed [100] that



Scheme 4. Schematic structure of LiPF<sub>6</sub> thermal stabilizer.



dissolution of as low as 0.05 wt.% LiF into the LiPF<sub>6</sub>-based electrolyte can significantly reduce gas generation. This improvement is attributed to the suppression of decomposition reaction by the excess LiF in a chemical equilibrium principle. Solutions to the second problem have been focused on weakening the reactivity and acidity of PF<sub>5</sub> by adding small amount of Lewis basic additive. Based on the electron-deficient property of PF<sub>5</sub>, electron-rich compounds should be effective for this purpose. Ideally, these compounds should be a weak or mild Lewis base so that their presence does not promote the equilibrium moving forward decomposition. As an example, tris(2,2,2-trifluoroethyl) phosphite (TTFP, **33**, Scheme 4) is capable of stabilizing LiPF<sub>6</sub>-based electrolytes [86,101], which is attributed to the formation of a 1:1 weak complex (**34**) between TTFP and PF<sub>5</sub>. In the similar principle, many amide-based compounds have been reported as the LiPF<sub>6</sub> stabilizer. These compounds include 1-methyl-2-pyrrolidinone (**35**) [102,103], fluorinated carbamate (**36**) [104], and hexamethyl-phosphoramidate (**37**) [105], in which the nitrogen core with its lone-pair electrons being well delocalized by the electron-withdrawing >C=O or >P=O groups acts as the weak base site to deactivate the reactivity of PF<sub>5</sub>.

## 5. Safety protection agent

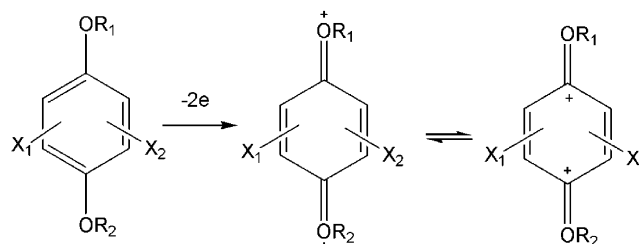
### 5.1. Overcharge protector

According to the function, the overcharge protection additives can be classified as redox shuttle additive and shutdown additive. The former protects the cell from overcharge reversibly, while the latter terminates cell operation permanently. Idea of the redox shuttle is not new, its initial study started with I<sub>2</sub>/I<sub>3</sub><sup>-</sup> redox couple to protect 3 V lithium batteries [106,107]. Basically, the shuttle molecules are required to be oxidized reversibly at slightly higher potentials than the normal end-of-charge potential of the positive electrode. When overcharging, the shuttle molecules are oxidized at the positive electrode and the oxidized shuttle species diffuse to the negative electrode and are reduced back to the neutral molecule. In this way, the shuttle molecules act as an internal discharger and the potential of the positive electrode is indefinitely locked at the oxidizing potential of the shuttle molecules while the current supplied in the overcharge is converted to heat. The maximum current that the shuttle additive can carry depends on several factors, including the concentration of the shuttle molecules in the electrolyte, the diffusion constant of the shuttle molecules, and the number of charges carried by the shuttle molecules [108,109]. Ideally, the shuttle additive should meet these requirements of: (1) the shuttle reaction must be highly reversible, (2) its oxidation potential must be slightly higher than the normal end-of-charge potential of the positive electrode but lower than the decomposing potential of electrolytic solvents, (3) it must be electrochemically stable within the cell operating potentials, and (4) its oxidized and reduced forms must be highly soluble and mobile (high diffusion) in the electrolyte. There are thousands of organic molecules showing reversible redox in the time scales of cyclic voltammetry [110], however, only few fairly have been found to meet the requirements above [111]. The search for the potential candi-

date for the redox shuttle additive in the past decade has been carried out mainly on a trial-and-error basis until recently a quantum chemical calculation software (Gaussian ver. 03<sup>TM</sup> 20) was developed to accelerate the screening process [112].

Early-investigated shuttle additives include metallocenes [108,113–117], tetracyanoethylene, tetramethylphenylenediamine [118], dihydrophenazine derivatives bearing either 2-hydroxypropyl or ethyl substituents on both N atoms [119], and a series of substituted aromatic or heterocyclic compounds and their alkali metal salts [109]. Since all these compounds have a redox potential ranging between 2.8 and 3.5 V, they are only suitable for low voltage lithium batteries. Meanwhile, these compounds show some adverse impacts on the cell performance. For example, metallocenes are strongly adsorptive to the surface of cathode materials, which blocks ionic conduction path and results in the loss of both rate and power capability [115]. Aromatic and heterocyclic compounds have low solubility and slow mobility in the electrolyte, which limits their shuttle effectiveness (current) [119]. Some metal complexes of Fe, Ru, Ir, or Ce with phenanthroline or bipyridine have around 4 V versus Li<sup>+</sup>/Li of reversible redox potentials, however, they did not work well due to their low solubility and mobility [120].

Extensive investigations have been focused on anisole-family compounds [111,120–123] because of their relatively high redox potential and high solubility in the lithium battery electrolytes. The shuttle mechanism of these compounds can be generally described as below:



where R<sub>1</sub> and R<sub>2</sub> are independent alkyl groups, and X<sub>1</sub> and X<sub>2</sub> are H, halogen, or independent alkyl groups. The potentials of these redox shuttle molecules are affected by the type and position of the substituents linking to the aromatic ring, and in most cases are ranged in 3.8–4.0 V versus Li<sup>+</sup>/Li with a reversible electrochemical window up to 4.2 V [120,122]. Meanwhile, the position of alkoxy groups and substituents and the type of the substituents affect the reversibility and shuttle efficiency of these compounds. For example, Adachi et al. [120] investigated a series of anisole compounds and found that only those having two methoxy groups at 1,2- (ortho-) and 1,4- (para-) positions showed reversible redox at the 4.0 V region, while the 1,3- (meta-) counterpart was oxidized irreversibly. This is due to that the 1,2- and 1,4-positions are more favorable for the delocalization of radical cation (RC, the oxidized product), which is responsible for the high reversibility of redox shuttle. The effect of delocalization was furthermore confirmed by substituting hydrogen at the 4-position for a bromine, which significantly increased the shuttle efficiency [120]. This is because the p-orbit and its two lone-pair electrons in the bromine core participate into the conjugated structure, which in turn stabilizes the RC.

In the similar principle, 2,5-ditertbutyl-1,4-dimethoxybenzene shows excellent redox shuttle behavior at 3.85–3.92 V versus  $\text{Li}^+/\text{Li}$  because the presence of two ditertbutyl groups at the 1- and 4-positions stabilizes the RC [121–123]. According to their redox potentials and electrochemical stability, the anisole-family compounds are most suitable for  $\text{LiFePO}_4$ -based Li-ion batteries. Other aromatic compounds that have been reported to have the similar functionalities are monomethoxy benzene class compound [124], hexaethyl benzene [125], bipyridyl or biphenyl carbonates [126], difluoroanisoles [126], and some S- or N-containing heterocyclic aromatic compounds such as thianthrene and 2,7-diacetyl thianthrene [127], as well as phenothiazine-based compounds [128].

Recently, Dantsin et al. [129] introduced a new approach toward the development of the redox shuttle additive. They reported that the weakly coordinated perfluoroborane cluster salts, i.e., lithium fluorododecaborates ( $\text{Li}_2\text{B}_{12}\text{F}_x\text{H}_{12-x}$ ), not only function as the electrolyte salt but also serve as a redox shuttle. The doubly charged anion,  $(\text{B}_{12}\text{F}_x\text{H}_{12-x})^{2-}$ , can be oxidized reversibly to the singly charged anion at about 4.5 V, which is the highest potential that the redox shuttle molecules have been known to reach without structural deterioration. Therefore, this unique oxidation chemistry provides inherent protection against the overcharge and may be well suited to the high voltage cathode materials such as  $\text{LiCoO}_2$  and  $\text{LiMn}_2\text{O}_4$ . Equal interest is in the redox potential that can be changed by controlling the degree of fluorination in the fluorododecaborate anion. It has been demonstrated [129] that the small graphite/ $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cell incorporating this salt exhibited 1C-overcharge protection for almost 100 h without visible discharge capacity loss.

The “shutdown additive” is based on the idea that at high potentials, the additive molecules polymerize to release gas, which in turn activates the current interrupting device (CID), while the resulting polymer is covered onto the surface of cathode to isolate the cathode from further overcharge. Without few exception [29], majority of such additives belong to the aromatic compounds, such as xylene [130], cyclohexylbenzene [29,131], biphenyl [29,131–140], 2,2-diphenylpropane [139], phenyl-*tert*-butyl carbonate [141], phenyl-R-phenyl compounds (R = aliphatic hydrocarbon, fluorine substituted) [139], and 3-thiopheneacetonitrile [139]. Lee et al. described that mixing cyclohexyl benzene (CHB) and biphenyl gave much more effective protection than CHB alone and the mixture expanded the safety region up to 12 V/2 A for a 0.76 Ah graphite/ $\text{LiCoO}_2$  Li-ion battery, which the CHB alone can never reach [131]. This result suggests a new approach toward the more efficient shutdown protection against the overcharge. More recently, Abe et al. [136] described that some benzene derivatives (biphenyl and *o*-terphenyl) and heterocyclic compounds (furan, thiophene, *N*-methylpyrrole, and 3,4-ethylenedioxythiophene) could be electrochemically oxidized to form a very thin film on the cathode surface during the battery cycling, and that the resulting film is electrically conductive (therefore they called it as “electroconducting membrane (ECM)”). In the case of slight amount of addition, therefore, the ECM film could improve the cycleability of the cathode. In addition, most of these shutdown additives described above could serve as a wetting agent to increase the

wettability of liquid electrolyte to the non-polar polyolefine separator because of their non-polar property. The negative impact of these compounds is on the long-term operation and storage performance of the Li-ion batteries due to the slow and irreversible oxidation of these compounds.

On the other hand, it has been reported [142] that LiBOB can act as a shutdown additive to provide excellent overcharge tolerance. In a 1C-overcharge test on 8 Ah cylindrical Li-ion batteries, the LiBOB battery only experienced mild vent with the maximum temperature not exceeding 100 °C and it did not catch any fires and sparks, while the  $\text{LiPF}_6$  counterpart battery not only caught fire but also resulted in a violent explosion with the maximum temperature reaching 400 °C. The excellent overcharge tolerance of LiBOB battery is attributed to the fact that the oxalate molecular moieties of LiBOB are preferably oxidized to produce  $\text{CO}_2$  by the oxygen released from the cathode [75]. This process generates much less heat than the oxidization of solvents as occurred in the  $\text{LiPF}_6$  battery. As a result of the mild oxidization of LiBOB, the internal pressure is rapidly built up by the released  $\text{CO}_2$ , which consequently opens safety vent before thermal runaway occurs. The similar result also was presented by Amine et al. [143], who described that the graphite/LiBOB/spinel Li-ion cells exhibited excellent abuse tolerance.

## 5.2. Fire-retardant additive

Safety concern has been a main obstacle for the application of Li-ion batteries in hybrid electric vehicles and electric vehicles, which is greatly related to the high flammability of the liquid electrolytes. Therefore, many researches have been focused on the development of fire-retardant (FR) additive to lower the flammability of the liquid electrolytes. The concept of the FR additives has been long known and studied for the protection of the solid polymers and woods [144,145]. There are two mechanisms proposed to explain the flame retardation: (1) physical char-forming process, which build-up an isolating layer between the condensed and gas phases to stop combustion process [146,147], and (2) chemical radical-scavenging process, which terminates radical chain reactions responsible for the combustion reaction in the gas phase [147,148]. Although these two processes are coexistent in most cases, the former is more applicable to the condensed phase while the latter to the vapor phase. So far most of FR additives used in the liquid electrolytes are based on organic phosphorus compounds [148–155] and their halogenated derivatives [156–160], and the radical-scavenging mechanism seems to be more acceptable [147,148,161]. Among various testing methods, differential scanning calorimetry (DSC), accelerating rate calorimeter (ARC), and self-extinguishing time (SET) have been most extensively adopted for the evaluation of the FR effectiveness. Generally, the presence of FR reduces the self-heating rate and delays the temperature at which the propagating self-heating initiates.

Trimethyl phosphate and triethylphosphate are among the earliest investigated FRs [148–151,154,155]. Unfortunately, both of them are unstable against the low reductive potentials on the

graphite anode surface [149,151]. Due to the high content of phosphorus, trimethyl phosphate has better FR effectiveness but shows inferior reductive stability on the graphite anode surface [149,151]. This fact indicates a trade-off relationship between the FR effectiveness and reductive stability. The reduction in flammability with the addition of these FRs has to be realized at an expense of the other performances such as ionic conductivity of the electrolyte and reversibility of the cell. Therefore, Xu et al. [151] concluded that it is impractical to use alkyl phosphates as the FR in Li-ion batteries. In their continued efforts, Xu and co-workers [156–160] synthesized a series of partially fluorinated alkyl phosphates and found that the presence of fluoride not only improved reductive stability but also increased FR effectiveness. When 20 wt.% of tris(2,2,2-trifluoroethyl) phosphate was added, for example, the electrolyte became non-flammable while having no any adverse impacts on both graphite anode and cathode of the Li-ion batteries [156,158]. Other successful examples to improve the reductive stability of phosphates are: (1) to increase the number of carbons in the alkyl groups [152], (2) to partially replace alkyl groups with the aryl (phenyl) group [152,153], and (3) to form cyclic structural phosphate [154]. On the other hand, cyclophosphazene family compounds seem to be a very promising FR [101,162,163]. The advantages of these compounds include: (1) the increased FR effectiveness due to the high content of phosphorus related to their ring structure, and (2) the excellent stability at low potentials with respect to the graphite anode. It was evaluated [151,162,163] that hexamethoxycyclotriphosphazene had no any negative effects on the graphite anode, while provided highly effective FR and remained stable up to 5.0 V against the anodic potentials.

In addition to P(V) phosphate and phosphazene, the phosphites with P(III) also have been reported as the very effective FR [86,101,155,164]. The advantages of P(III) phosphate over the P(V) phosphate are that: (1) it is superior in facilitating SEI formation [155] and (2) it is capable of deactivating PF<sub>5</sub> [86]. Among these compounds, tris(2,2,2-trifluoroethyl) phosphite was found to be very promising, which not only reduced the flammability of the liquid electrolyte, but also improved the cycleability of the Li-ion cells [101,164]. For example, adding 5 wt.% TTFP as the additive into a 1.0 M LiPF<sub>6</sub> 1:1:3 PC–EC–EMC electrolyte significantly improved the cycleability of Li-ion cells although this amount was not sufficient to retard flaming. When the content of TTFP was increased to 20 wt.% as the co-solvent, the electrolyte became non-flammable and the Li-ion cells using it could be cycled at 60 °C for 200 cycles without visible capacity loss.

On the other hand, fluorinated propylene carbonates [165] and methyl nonafluorobutyl ether (MFE) [166–168] have been studied as the non-phosphorus FR. The “no flash point” electrolytes by the addition of these solvents were obtained only when they became the major solvent (>70% by volume). This is because they themselves are neither radical-scavenging nor char-forming. Their function of making electrolyte non-flammable is only to dilute the other highly volatile and flammable co-solvent. As an example, DSC results showed that they were able to delay the exothermal peak temperature of the mixture of the fully charged LiCoO<sub>2</sub> powder and solvent up to 40 °C, depend-

ing on the number of fluoride substituents [165]. Fluorinated propylene carbonates were superior to MFE in both FR and cell performance. For MFE, Arai evaluated MFE electrolyte using Li/graphite and Li/LiCoO<sub>2</sub> half-cells by comparing it with the counterpart LiPF<sub>6</sub> EC–EMC. Results showed that the MFE electrolyte provided nearly same performance for Li/LiCoO<sub>2</sub> cell, however, it resulted in very high polarization for Li/graphite cell [168]. Therefore, further work should be carried out for the MFE-based electrolytes.

## 6. Li deposition improver

Additives to improve the cycling efficiency of metallic Li have been long investigated for use in rechargeable Li batteries. These additives are of special importance to develop high power Li-ion batteries. In fact, power loss of the Li-ion batteries is in a great degree related to Li plating on the graphite anode, which promotes undesirable growth of the SEI since Li plating often occurs in the late period of charging Li-ion battery at constant current, especially at high rate or low temperatures [53]. The poor cycleability of metallic Li is mainly attributed to two factors: (1) high reactivity of Li with the electrolyte solvents, and (2) poor morphology of the plated Li such as the formation of needle-like dendrite and very porous sponge-like Li. The reactivity of metal Li is affected not only by the inherently chemical property but also by the surface specific area. Therefore, most of previous efforts were focused on the second problem to improve the morphology of Li deposition. The idea was based on the formation of an ion-conducting surface layer or a Li–metal alloy to facilitate a uniform deposition of Li.

In early efforts, it was found that low concentration (ppm level) inorganic compounds such as SO<sub>2</sub> [169], polysulfide [40,41], CO<sub>2</sub> [170,171], and even water [169] were effective to improve the cycling efficiency of Li on an inert metal substrate in LiClO<sub>4</sub>–PC solution. This improvement was attributed to the fact that these compounds incorporated to the formation of a Li<sup>+</sup>-conductive film, which resulted in smoother surface morphology. In the similar manners, the increased coulombic efficiencies of Li cycling in LiClO<sub>4</sub>/PC or PC–DME solution were obtained by the addition of some organic compounds such as 2-methyltetrahydrofuran [172–174], 2-methylthiophene [173], and nitromethane [169]. This is because these compounds are preferably reduced before Li plating, and the resulting products build-up to form a SEI, which subsequently suppresses the formation of Li dendrites. More interestingly, their presence favors decreasing electric resistance at the electrode–electrolyte interface [173].

Based on the principle of the surface layer to promote smooth and uniform deposition of Li, both ionic and non-ionic surfactants were proposed to improve Li cycling efficiency. It is assumed that the surfactant molecule can be physically absorbed on the surface of Li, and the adsorption depends on the local morphology of the Li surface. Physically, the dendrite sites are preferably absorbed due to their much higher specific surface area, and in this way the growth of dendrites is suppressed. The surfactants that have been studied and found to be effective include tetraalkylammonium chlorides with a long alkyl chain

[175], cetyltrimethylammonium chlorides [175], lithium and tetraethylammonium salts of perfluorooctanesulfonate [176], perfluoropolyethers [177]. Based on the SEM observation, Ribes et al. [176] concluded that the presence of surfactants favored the deposition of less porous Li due to an enhanced and more uniform nucleation, and the improvement was attributed to the morphological properties of the Li surface. On the other hand, it was reported [178] that the addition of the other surfactant-like compounds such as nitrile sucrose and nitrile cellulose could significantly reduce the interface resistance between Li and electrolyte.

Another approach is based on the formation of Li–metal alloy, which has been verified to be very effective in increasing the cycling efficiency of Li. So far only two salts,  $\text{AlI}_3$  and  $\text{SnI}_2$ , have been studied by Ishikawa et al. [174,179,180], who concluded that the formation of Li–metal alloy layer could limit the growth of Li dendrites or brittle Li, and stabilize the interfacial resistance of Li. For example, addition of hundreds of ppm  $\text{AlI}_3$  into a 1.0 M  $\text{LiN}(\text{C}_2\text{F}_5\text{SO}_2)_2$  PC–DMC electrolyte could increase the cycling efficiency of Li by 5–10% [180]. More interestingly, the increased efficiency was retained even if the Li was transferred to the blank electrolyte without  $\text{AlI}_3$  after the first deposition of Li. They thought that the residual Al was permanently remained in a form of Li–Al alloy on the surface of Li, which provided durable Li interface with better Li cycleability.

Beside the approaches above, acidic HF was proposed to improve the morphology of Li deposition [181–183]. The idea of this method is based on the fact that the uneven current distribution caused by non-uniform SEI layer on Li surface is the main reason for the deposition of dendrite Li [179,184–186], and all the components to build SEI on the Li surface are strong alkali [187]. Acidic HF can react with the alkali SEI components, such as lithium akalycarbonate, lithium alkyoxide, and  $\text{Li}_2\text{CO}_3$ , to form more even and LiF-rich SEI. Results showed that the presence of  $5 \times 10^{-3}$  to  $20 \times 10^{-3}$  M HF in the electrolyte could very effectively suppress the growth of Li dendrite [181,182], which was attributed to the formation of a LiF-rich SEI. Probably in the same mechanism, Mogi et al. [43] described that the addition of 5 wt.% fluoroethylene carbonate into 1 M  $\text{LiClO}_4$  PC electrolyte significantly improved the cycling efficiency of Li. An in situ observation using atomic force microscope (AFM) indicated that the surface of Li was covered with a uniform and closely packed layer of particle-like deposit of about 100–150 nm diameter, and the film had lower resistance compared with that formed in the additive-free solution. As described in Section 2.2, there is a chemical equilibrium of “ $\text{FEC} \rightleftharpoons \text{VC} + \text{HF}$ ”. Thus, the FEC may slowly release HF that in turn severs as the additive for Li deposition. Due to the above merits, FEC seems to be a very promising additive for the efficient deposition of Li.

The opposite results about the impact of VC on the Li deposition have been reported by different authors [43,188]. Mogi et al. [43] observed that the surface of the Li deposited from a 5 wt.% VC-containing electrolyte contained more solids and had higher resistance, while Ota et al. [188] found that the addition of 2 wt.% VC increased the cycling efficiency of Li and the deposited Li had lower surface resistance. This difference could be associated with the concentration of VC contained the solutions, and it clearly indicates the importance of the selection for an appropriate concentration of the electrolyte additives.

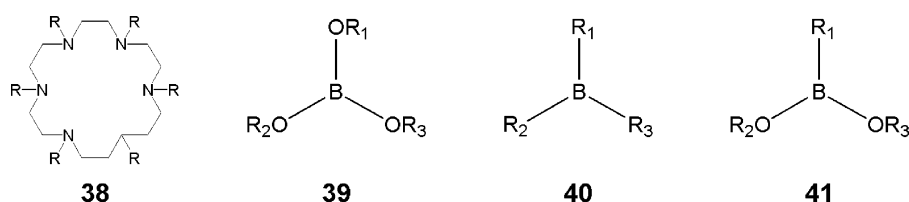
## 7. Other

### 7.1. Ionic salvation enhancer

It has been long known that 12-crown-4 is of excellent selectivity to coordinate  $\text{Li}^+$  ion, and in this way its presence effectively promotes the solubility of Li salts and increases ionic conductivity [189–191]. As a result of the increased geometric size of the solvated  $\text{Li}^+$  ion, the mobility of  $\text{Li}^+$  ion is definitely decreased so that the increased conductivity is mainly contributed by the anion. Furthermore, the strong chelating interaction between crown ligand and  $\text{Li}^+$  ion enhances the activity energy of the desolvation that must take place on the electrolyte–electrode interface before  $\text{Li}^+$  ion intercalates into the electrodes. These disadvantages and high toxicity make it impossible to use crown ether in the Li-ion batteries.

To increase the transference number of  $\text{Li}^+$  ion, Zhang and co-workers [192,193] and Lee et al. [194] independently proposed an “anion-receptor” concept to coordinate selectively anion of the salt. Based on this concept, Zhang and co-workers [192,193] designed a series of borate compounds where the boron core is electron-deficient, while Lee et al. [194,195] synthesized a series of linear and cyclic aza-ether compounds (**38**) where nitrogen is linked by a strong electron-withdrawing substituent to make it electron-deficient. Their results showed that both approaches were successful. In the continued efforts, Lee et al. designed and synthesized numerous boron-based anion-receptors with partially or per-fluorinated substituents. According to the chemical structure, these compounds can be categorized as borate (**39**) [84,85,192,193,196–198], borane (**40**) [80,81,84,85,196,197], and borole (**41**) [199,200], as indicated in Scheme 5.

Results indicated that all these anion receptors (**39–41**) are in different degrees capable of coordinating the anion and increasing the solubility of salts such as LiF, LiCl, and LiBr, and theoretically they can coordinate anion to form a 1:1 complex. Among these boron-based anion-acceptors,



Scheme 5. Schematic structure of the anion receptors.



tris(pentafluorophenyl) borane (TPFPB) has been most extensively studied. In many organic solvents or their mixtures, TPFPB can dissociate up to 1.0 M LiF and the resulting solutions are electrochemically stable [84,85]. For example, with a 1:2 EC–DMC mixture, the resulting electrolyte has an about 5.0 V of electrochemical window on a glass carbon electrode and its cathodic potential is limited by metallic Li plating at 0 V versus Li<sup>+</sup>/Li [198]. Furthermore, the solution was thermally more stable than the counterpart LiPF<sub>6</sub> electrolyte [197,198], and hence it could support Li/LiMn<sub>2</sub>O<sub>4</sub> cell cycling at 55 °C for 50 cycles with only 16% of capacity loss versus 44% in the counterpart LiPF<sub>6</sub> electrolyte [198]. In addition, better electrolyte retention in the separator has been observed as a result of the interaction between TPFPB and DMC [201]. In contrary to the addition of crown ethers, the addition of TPFPB decreases total ionic conductivity and increases the transference number of Li<sup>+</sup> ion [198,201]. There was no further report on the effect of the decreased conductivity on the rate and power performance of the battery. Since TPFPB anion receptor offers a verity of merits, its application in the Li-ion batteries seems very promising if its cost and toxicity can be acceptable in industry standards.

### 7.2. Al corrosion inhibitor

Al corrosion in Li-ion electrolytes has been recognized for many years, extensive studies revealed that the corrosion mainly depends on the Li salt, instead of the electrolyte solvents [202–205]. Spectroscopic analyses indicated that molecular moieties of the salt anion were inevitably present on the passivation layer for these Al surfaces without corrosion [204,205]. This fact reveals that the salt anion plays an essential role in promoting passivation of Al surface. Based on this idea, some Li salts that are known to passivate Al very well have been proposed as the corrosion inhibitor to protect Al from corrosion. As an example, Tsujioka et al. [206,207] selected either LiBOB or LiODFB to suppress Al corrosion in the PC–DEC or EC–DMC solution of lithium bis(perfluoroalkyl sulfonyl) imide (Li-imide, having a general formula of LiN(SO<sub>2</sub>C<sub>n</sub>F<sub>2n+1</sub>)<sub>2</sub>, with  $n = 2, 3, \text{ or } 4$ ). Their results showed that when 5 mol.% LiBOB or LiODFB was added to the solution (total salt concentration was 1 M), the Al corrosion could be completely suppressed, as indicated by the zero current flow during a 5.0 V dc-polarization and by the microscope observation showing no any changes of the Al surface before and after polarization test. This protection is due to that one or more of O–B bonds in LiBOB or LiODFB anion break and the resulting new anion constantly combines with Al<sup>3+</sup> to form a very stable passivation layer with network structure [75].

### 7.3. Wetting agent and viscosity diluter

Wetting agent would be used when the electrolyte cannot quickly and sufficiently wet the non-polar polyolefin separator. This case normally occurs when the content of cyclic carbonate or ester, such as PC, EC, and  $\gamma$ -butyrolactone (GBL), in the electrolyte is increased to improve the high temperature performance of the batteries. Ionic and non-ionic surfactants are

among the best candidates for the wetting agents. Cyclic alkyls and aromatic compounds with low molecular weight also can be considered. The minimum criterion for the selection of wetting agents is that their introduction should not bring other negative impacts on the cell performance. As mentioned in Section 5.1, some of shutdown additives for the overcharge protection are of wet-enhancing function. In the other efforts, Wang et al. [103] introduced that the Li/graphite cells with 2–5% cyclohexane added into the electrolyte (1 M LiPF<sub>6</sub> 1:2 EC–DEC) exhibited higher reversible capacity (354 mAh g<sup>-1</sup> versus 347 mAh g<sup>-1</sup>) and coulombic efficiency (91% versus 84%) in the first cycle than those without the addition of cyclohexane. This improvement is probably due to that cyclohexane improved the wettability of the electrolyte to the separator and electrodes, which hence increases the utilization of the electrode materials. In addition, it was reported that the addition of an appropriate amount of trialkyl phosphate [208] or linear esters with high molecular weight [209], such as methyl decanoate, dodecyl acetate, and a series of esters of tertiary carboxylic acids, was very effective to enhance the electrolyte permeation into polyolefin separator.

On the other hand, Zhong and Sacken [210] claimed that the addition of small amount of P<sub>2</sub>O<sub>5</sub> into the electrolyte could effectively reduce the viscosity of LiPF<sub>6</sub>-based electrolytes. Since the issue of viscosity mostly appears at the low temperatures, this approach could be of great interest in the development of the low temperature Li-ion batteries.

## 8. Conclusions

There are numbers of electrolyte additives available for the Li-ion batteries. Each additive exhibits one or more of unique functions to improve the battery performance. However, in many cases use of an additive more or less introduces other negative impacts while improving the targeted performance. For example, appropriate amount of VC is favorable for the SEI formation and Li cycling, however, excess VC results in the cells low cycling efficiency and high self-discharge rate. Among numerous additives, LiBOB seems to be the only one that is multifunctional for the improvement of Li-ion batteries. The functions that have been found from LiBOB include: (1) it cooperates to SEI formation and stabilizes SEI, (2) it reduces dissolution of the cathode materials, (3) it provides excellent overcharge tolerance, and (4) it facilitates Al passivation in the electrolyte solution. In addition, LiODFB is expected to have the similar functions as LiBOB due to their similar structure. Desirable improvement may be achieved by combining several additives together provided that they are not interfered with each other.

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