

Fluorine-Free Electrolytes for Lithium and Sodium Batteries

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Fluorinated components in the form of salts, solvents and/or additives are a staple of electrolytes for high-performance Li- and Na-ion batteries, but this comes at a cost. Issues like potential toxicity, corrosivity and environmental concerns have sparked interest in fluorine-free alternatives. Of course, these electrolytes should be able to deliver performance that is on par with the electrolytes being in use today in commercial batteries. This begs the question: Are we there yet? This review outlines why fluorine is regarded as an essential component in

battery electrolytes, along with the numerous problems it causes and possible strategies to eliminate it from Li- and Na-ion battery electrolytes. The examples provided demonstrate the possibilities of creating fully fluorine-free electrolytes with similar performance as their fluorinated counterparts, but also that there is still a lot of room for improvement, not least in terms of optimizing the fluorine-free systems independently of their fluorinated predecessors.

1. Introduction

Since its inception in the 1970s and commercialization in the 1990s, the Li-ion battery has quickly become the *de facto* standard technology for portable electronics and electromobility, where high gravimetric and volumetric energy density is essential. A timely acknowledgement in the form of the 2019 Nobel Prize for chemistry appears to have ushered in the age of the Li-ion battery as the demand for energy storage is surging due to the rapid electrification of the transportation sector. With the currently parallel development of closely related battery chemistries beyond the Li-ion concept, such as Na-ion batteries, this type of batteries is likely to fulfil a significant part of our energy storage needs for a large part of the foreseeable future.^[1,2]

In Li-ion batteries, Li^+ cations are exchanged through an electrolyte between the electrodes to charge compensate the redox reactions taking place within the anode and cathode. By replacing the Li^+ with other cations, such as Na^+ , this technology may also be extended beyond Li for additional sustainability and cost benefits, at the expense of energy density.^[3] Although not directly involved in the charge-storing redox reactions, and not directly influencing either the voltage or capacity of a battery, electrolytes are nonetheless key components with a huge influence over battery performance. The very concept of electrochemical reactions – the separation of oxidation and reduction – is inherently dependent on charge compensation via ionic currents. Since ion transport is typically much slower than electron transport, the power output is directly related to the ion transport capability of the electrolyte. The electrolyte also has a non-negligible mass, volume and cost, leading the electrolyte to not only affect the performance of the battery, but also the volumetric and gravimetric energy densities and the overall cost of energy storage.^[4]

Perhaps even more importantly, although the electrolyte is not involved in the charge-storing redox reactions, it does unfortunately take part in redox reactions elsewhere, and the harsh electrochemical environment of high-energy-density Li- and Na-ion batteries inevitably leads to electrolyte (side) reactions. This gives additional roles to the electrolyte that need to be played to perfection. While there are many different “flavors” of Li-ion battery chemistries in terms of electrode active materials, the electrolyte tends to have the same basic composition of a solution of LiPF_6 in a mixture of organic carbonate solvents. Such solutions are, however, unstable at the low potential of most anode materials such as graphite which makes it necessary for the electrolyte to be able to create a passivating solid electrolyte interphase (SEI) layer; this has largely been accomplished by the inclusion of ethylene carbonate (EC) in the solvent mixture.^[5,6] The situation is similar for Na-ion batteries as well, and the standard electrolyte consists of a mixture of organic carbonate solvents containing NaPF_6 or other sodium salts with heavily fluorinated anions.^[7,8]

The presence of fluorine seems inevitable in high-performance electrolyte systems not only as part of fluorinated anions, but also in co-solvents and electrolyte additives for improved functionality,^[9,10] and in the binder as polyvinylidene difluoride (PVdF) has been the most common binder used to prepare electrodes.^[11] With such a high amount of fluorine used in batteries follows a range of issues not least related to environmental and occupational safety of the battery cells, from their production to their end-of-life. This has naturally spurred research into fluorine-free batteries from a safety and environmental protection perspective. But is this heavy dependence on fluorine really all that necessary to attain high performance in Li-ion and Na-ion battery systems, or can a move towards fluorine-free batteries also be motivated by performance or functionality gains?

In this review, we will present the current status of fluorine-free electrolyte development, with the ambition to provide a balanced perspective on the prospective of utilizing fluorine-free electrolytes in commercially relevant lithium and sodium batteries. The focus will be on the applications perspective and electrolyte systems that have been validated in prototype Li-ion and Na-ion battery cells. Of course, to attain fully fluorine-free systems, the binder also needs to be addressed. There have indeed been promising efforts to develop fluorine-free binders, but that is outside of the scope of this review.

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2. The Case for Fluorine

Alkali metals and fluorine may be extreme opposites in the periodic table, but have a deep symbiotic relationship when it comes to battery functionality.^[9] In both Li- and Na-ion batteries, electrolyte salts with heavily fluorinated counterions are typically used,^[6,8,12] with the archetypal LiPF₆ being a prime example, consisting of a little more than $\frac{3}{4}$ of fluorine by weight. Here, the electron-withdrawing effect of fluorine helps to distribute the negative charges, thereby lowering the lattice energy of the salt, improving ion dissociation and facilitating dissolution of the salt in organic solvents.^[9] In aqueous electrolytes, in contrast, the greater solvation power of water makes such effects less important and the need for fluorine diminishes, enabling simpler salts, such as LiOH and LiNO₃, to be used instead.^[13] However, for non-aqueous systems, LiPF₆ has a particular set of attributes that constitutes a suitable compromise between important electrolyte properties, leading to the almost exclusive reliance on this salt in electrolytes for commercial Li-ion batteries.^[9,14] Of particular importance is the role of the hexafluorophosphate anion in passivation – both the formation of the SEI and its ability to passivate aluminum, preventing corrosion of the cathode current collector at high potentials.^[15]

Within the SEI layer, the presence of fluorinated species has been hailed as essential for its function to passivate the anode surface.^[16,17] Species such as LiF/NaF, fluorophosphates and fluorinated organics have been identified as SEI components, originating from fluorinated anions as well as from fluorinated solvents and electrolyte additives as these take part in and influence the electrolyte degradation reactions and SEI formation.^[18–21] Consequently, improvements in battery performance can be attained by replacing conventional non-fluorinated alkyl carbonate and ether electrolyte solvents with

fluorinated counterparts. As an added bonus, the use of highly fluorinated solvents may also render the electrolyte non-flammable.^[22] This increase in performance is perhaps most notable for Li metal cells, where the fluorinated solvents are beneficial for formation of a highly fluorinated, LiF-rich SEI.^[19] High-rate stripping/plating can be done with higher stability and more longevity when 1-fluoroethylene carbonate (FEC) replaces EC as a co-solvent with dimethyl carbonate (DMC) in the electrolyte.^[10] The effects of this can be clearly seen in the cycling performance shown in Figure 1. This effect also extends to anode-free Li metal battery configurations, where longer capacity retention is seen in highly fluorinated mixtures containing FEC and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether.^[23,24]

Fluorinated solvents can also be equally beneficial on the cathode side. Examples include a combination of 2-(2,2,2-trifluoroethoxy)-1,3,2-dioxaphospholane 2-oxide (TFEP), 2,2,2-trifluoroethyl methyl carbonate (FEMC) and 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether (HFE) that was found to drastically improve the coulombic efficiency and capacity retention during long-term cycling of SiO₂||NMC622 cells through the formation of an elastic and robust SEI layer, but also a highly functional CEI layer (Figure 2).^[25] Another example is the inclusion of 1-fluoroethylene carbonate (FEC), 1,2-difluoroethylene carbonate and 1,1,2,2-tetrafluoroethyl-2,2,3,3-tetrafluoropropyl ether in organic carbonate solvent mixtures, leading to longer cycle life of graphite||Li_{1.2}Mn_{0.56}Co_{0.08}Ni_{0.16}O₂ cells owing to the formation of a stable and protective CEI layer.^[26]

Fluorinated solvents may give similar performance enhancements in sodium systems as well. An electrolyte consisting of 1 M NaClO₄ in FEC was found to be more resistant towards oxidation and induce a robust fluorinated CEI on Na_{2/3}Ni_{1/3}Mn_{2/3}O₂ cathodes, resulting in enhanced cyclability in



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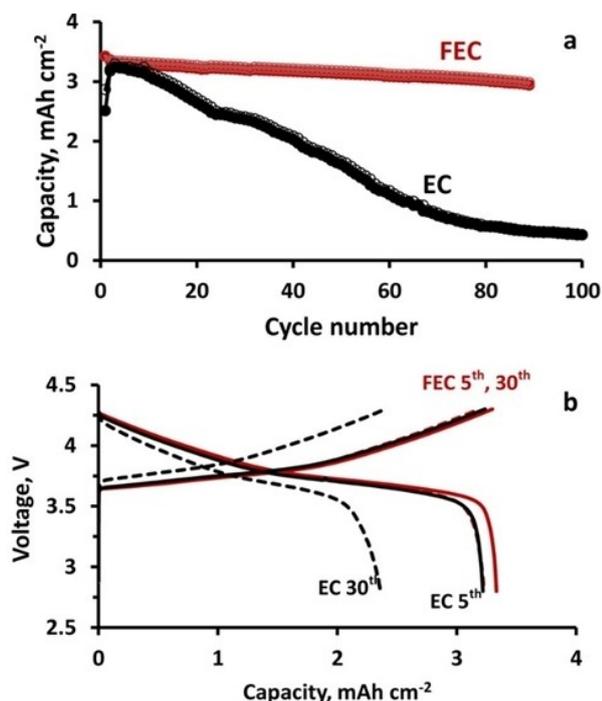


Figure 1. Performance of Li | NMC622 cells containing 1 M LiPF₆ in either FEC/DMC or EC/DMC as electrolyte. Reprinted with permission from Ref. [10]. Copyright (2017) American Chemical Society.

full cells with hard carbon anodes.^[27] For Li–O₂ batteries, the increased solubility of molecular oxygen is another benefit of highly fluorinated solvents,^[28] whereas for Li-S batteries, the low solubility of lithium polysulfides is highly attractive.^[29]

From these examples a pattern emerges: In the context of fluorinated electrolytes, FEC fills a niche of its own and is ubiquitous throughout the literature both as an electrolyte solvent and as an additive. The effects of this fluorinated substitute for EC are particularly beneficial for use with the anode materials silicon and Li metal, where the large volume changes and, in the latter case, a particularly harsh and chemically reactive environment, has rendered FEC an indispensable electrolyte component.^[16] With the formation of an SEI consisting of LiF, Li₂O and fluorinated organics by the

defluorination and rapid interfacial reduction of FEC, as well as etching of the surface of the silicon particles, the lithiation kinetics and the coulombic efficiency are improved.^[30,31] Compared to the functionally similar additive vinylene carbonate (VC), the SEI layer formed by FEC on Li metal anodes contains structured LiF nanocrystals that improve Li⁺ conductivity and render the system suitable for high-power applications.^[32,33]

The positive effects of FEC also extend to sodium systems,^[34] with protective powers towards both the anode- and the cathode-side of sodium cells.^[18] In combination with NaPF₆ as the electrolyte salt in organic carbonate electrolytes, 0.5% FEC helps to create a thin but efficient fluorinated passivation layer on hard carbon anodes that enables excellent long-term capacity retention.^[35] The same protective effect of FEC is also seen in non-flammable electrolytes based on organic phosphates.^[36]

In addition to FEC, there are several other fluorinated electrolyte additives with positive effects on battery cycling. Lithium difluoro(oxalato)borate (LiDFOB) works as a salt-type additive to improve the cycling stability of batteries with Li-rich cathodes and graphite anodes, contributing to forming an LiF-rich SEI on the anode, at the same time as it decreases the formation of LiF on the cathode surface.^[37] When used in higher concentrations,^[38] and in combination with FEC,^[39] a stabilizing effect is seen for anode-free Li metal batteries through the formation of nanostructured LiF in the SEI.^[38] In the same battery cell configurations, difluoro- and trifluoroacetic anhydride additives have also shown to give improved reversibility of lithium plating.^[40] Fluorophosphates have also been identified as effective additives at low concentrations for both Li- and Na-ion batteries.^[41,42] LiPO₂F₂ not only contributes to the interfacial reactions that form the SEI, but also suppresses transesterification reactions in the bulk electrolyte.^[43]

3. The Case against Fluorine

There is undoubtedly a strong case for fluorinated compounds in batteries, but at the same time, when scratching the surface, the use of fluorinated species comes with its own set of

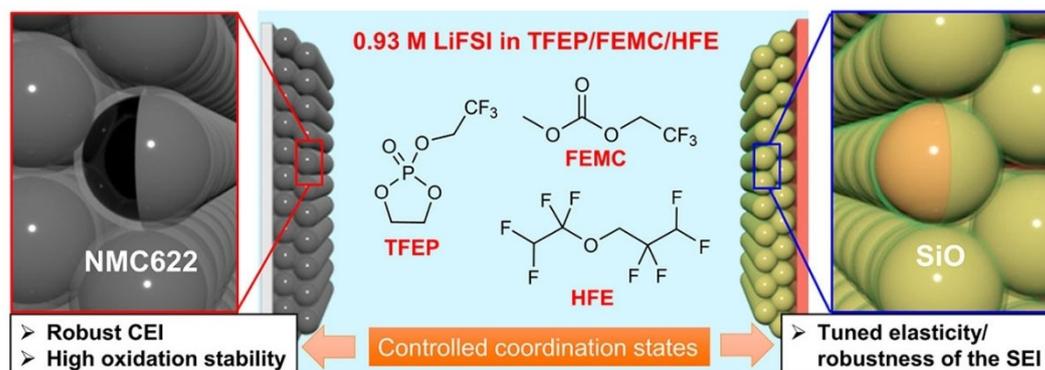


Figure 2. Schematic illustration of the effects of an electrolyte based on LiFSI in a mixture of fluorinated solvents on cycling of SiO | NMC622 cells. Reprinted (adapted) with permission from Ref. [25]. Copyright (2021) American Chemical Society.

problems. This is partly related to the very function of the fluorinated species themselves, which is not always as intended. This is probably best illustrated by FEC. While effective in providing a protective SEI on silicon and Li metal, it is incapable of doing the same on graphite anodes when replacing EC as an electrolyte solvent.^[44] The benefit of using FEC as an additive is also limited with certain cathodes, such as the high-voltage material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), with high concentrations resulting in poor cycling performance and low concentrations behaving similarly to cells without the additive.^[45] The effect of FEC is also questionable in sodium systems, where certain hard carbon anodes form a better and more conductive SEI in additive-free non-fluorinated organic carbonate electrolytes.^[46]

Even when properly functioning in a protective role, the protective function of FEC is connected to its continuous consumption on Si/graphite electrodes. Thus, while FEC is able to efficiently protect the other electrolyte components from reduction, it does so while being degraded itself, such that the lifetime of the electrodes is determined not by the concentration, but the total available amount of FEC in the electrolyte.^[47] Add to this the inherent instability of FEC that

causes it to gradually decompose when combined with LiPF_6 in the electrolyte even in the absence of electrochemical cycling, leading to a cascade of potentially detrimental reactions (Figure 3).^[48–50] This is particularly detrimental at elevated temperatures; e.g., the protective effect in Li metal cells at room temperature becomes almost completely lost at 55°C (Figure 4). Considering this, it becomes evident that FEC is perhaps not such an omnipotent electrolyte component after all.

The temperature-accelerated degradation of FEC is closely associated with the well-known temperature instability of LiPF_6 that makes it decompose to LiF and PF_5 . The highly reactive PF_5 then goes on to wreak further havoc in the electrolyte by reacting with and decomposing the organic carbonate solvents.^[51] These reactions are further exacerbated by trace amounts of protic impurities, such as water, that are near-impossible to fully remove, leading to the formation of, among a large range of anion- and solvent-derived reaction products, also highly toxic and corrosive HF .^[52–54] The HF may further contribute to transition metal dissolution from cathode materials such as $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$.^[55–57]

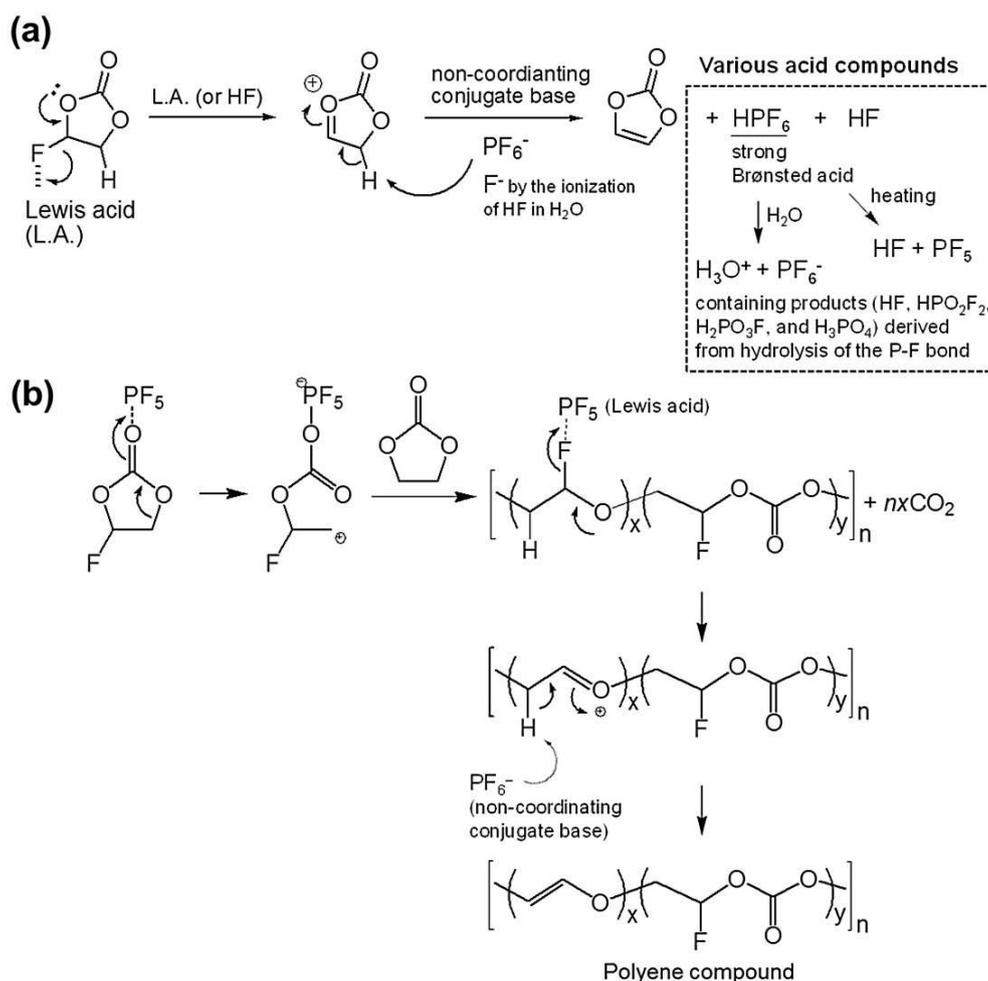


Figure 3. Illustration of the cascade of reactions resulting from the degradation of FEC in combination with LiPF_6 as suggested by Kim et al. Reprinted with permission from Ref. [49]. Copyright (2016) Elsevier.

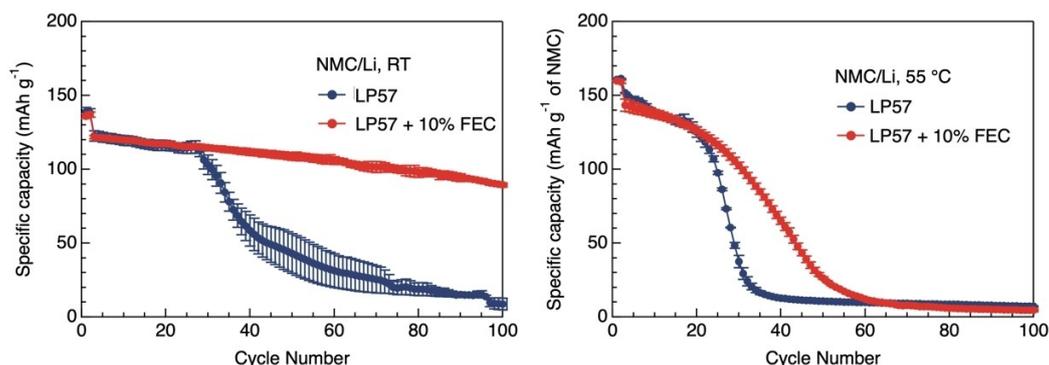


Figure 4. Cycling of Li | NMC111 cells with LP57 electrolyte with and without 10% FEC at room temperature (left) and 55 °C (right). Reprinted (adapted) with permission from Ref. [50]. Copyright (2019) American Chemical Society.

In addition to causing unwanted reactions in the battery during normal operation, accidental release of electrolyte components is cause for concern. The most well-known cause for concern is undoubtedly HF, both when released as a degradation product from battery operation and when formed from hydrolysis of the hexafluorophosphate anion when exposed to the humidity of the ambient atmosphere.^[58] Toxic and corrosive compounds, such as HF and PO₃F₂, are also formed on combustion of the electrolyte in case of a battery fire, where the release of the toxic fluoride gases constitutes a serious risk if, e.g., an electric vehicle catches fire, particularly in confined spaces.^[59]

Fluorinated electrolyte components are also a cause a concern during recycling of used batteries, as they may cause significant safety and environmental hazards during handling and processing, including the liberation of toxic HF and PF₅.^[60,61] Treating the waste streams to recover fluorine is therefore important both to avoid the release of these species to the environment and due to their value.^[62] Designing electrolytes that are devoid of fluorinated components would thus be an important step towards creating more recycling-friendly batteries.^[62]

4. Alternatives to Fluorine

Following the aforementioned issue with the presence of fluorine in battery electrolytes, developing non-fluorinated anions to replace PF₆⁻ therefore becomes an important exercise. Such fluorine-free anions need to fulfill a variety of demands, but the most important property is perhaps the ionic conductivity provided by the fluorine-free salts in battery electrolytes. The dissolution of electrolyte salts in non-aqueous solvents (or water as well, for that matter) involves the two steps of i) dissociation of the cation (Li⁺ or Na⁺) from the anion, and ii) the formation of a coordination structure between the cation and the solvent molecules.^[63] The properties of the anion have a major influence on the first step. This is why simple salts like LiF with high lattice energy cannot be used as electrolyte salts because the dissociation of the cation and the anion requires more energy than what can be compensated for by

the formation of the coordination structure. The focus has therefore been on designing salts with weakly coordinating anions^[64] where the charge is delocalized over the anion and thus the dissociation energy becomes lower. In terms of ionic conductivity, many of these non-fluorinated salts have shown to be competitive with the “standard” battery electrolytes based on LiPF₆/NaPF₆ and carbonate solvents. This means that ionic conductivities in a wide range of 1–20 mS cm⁻¹ have been demonstrated for fluorine-free electrolytes both for Li- and Na-ion batteries, which indicates that there does not seem to be a definitive competitive edge of fluorine-containing anions in this regard.

Several different anions based on N, S, B, C, O, P and Cl have been developed and investigated in research studies, but in most cases these anions also contain fluorine. There exist, however, a few fluorine-free anions such as perchlorate (ClO₄⁻), bis(oxalato)borate (known as BOB), tris(oxalato)phosphate, tetracyanoborate and dicyanotriazolate,^[65–69] which are described in more detail in the following sections. The main challenge with these fluorine-free salts is their relatively poor performance in passivating the aluminum cathode current collector at high potentials. Indeed, one reason why LiPF₆ has traditionally been used in Li-ion batteries is its ability to passivate aluminum, mainly thanks to its fluorine atoms, although other fluorine-based salts, such as LiTFSI and LiFSI are unable to provide the same passivation. In this regard, corrosion studies with LiBOB-based electrolytes show that the BOB anion is able to passivate aluminum similar to BF₄⁻ or PF₆⁻ and it has been suggested to be thanks to the borate-containing species formed on aluminum,^[65] especially AlBO₃ as determined by EQCM.^[70] These results indicate that fluorinated electrolytes are not necessarily required for passivation of aluminum and there are other alternatives that can also fulfill that role. There are, however, also other issues often cited with regards to fluorine-free anions, such as the safety concerns with perchlorate (ClO₄⁻) and the formation of an efficient SEI or too resistive SEI on the anode material.^[71]

Another source of fluorine in battery electrolytes is the additives such as FEC. Fluorine in such additives serves more or less the same aforementioned purposes to passivate Al and to improve the SEI. So, to remove fluorine, one could similarly try

to use additives based on elements such as B, P, C, N, etc. A few commonly used fluorine-free additives are vinylene carbonate (VC), tris(trimethylsilyl)phosphite (TMSP), and also fluorine-free salts which, when used in low concentrations, could be considered additives, e.g., LiBOB and LiNO_3 . If one simply discards the idea that an efficient and robust SEI needs to contain LiF or other fluorinated species, there is in fact a wide variety of non-fluorinated additives that can potentially fulfil the same role using other chemical routes.^[72]

5. Progress towards Fluorine-Free Systems: Lithium

Since the major source of fluorine in commercial Li-ion battery electrolytes is the LiPF_6 salt, the route towards creating a fluorine-free system involves finding competitive fluorine-free anions to replace PF_6^- . With the initial quest for alternative anions to be used in batteries, Johansson developed computational approaches to correlate the anion's structure with its oxidation stability leading to a wide range of possibilities for new lithium salts.^[73] Other authors have also joined the search, also providing experimental details and their application in Li-ion batteries. The most common examples of anions that have been investigated are perchlorate, phosphates, and heterocyclic and boron-based anions.

5.1. Lithium perchlorate (LiClO_4)

The reported advantages of LiClO_4 and the reasons why it used to be a popular lithium salt are its low cost, high solubility and high ionic conductivity in carbonate-based solvents (9 mS cm^{-1} in EC/DMC at 20°C) as well as acceptable anodic stability (4.5 V vs. Li^+/Li).^[74] However, the main disadvantage that has prevented its use in Li-ion batteries is safety concerns. Perchlorates are strong oxidants due to the high oxidation state of chlorine (VII), and they are prone to react violently with organic species.^[75,76] In 2010, Marom et al. reconsidered the use of LiClO_4 as an electrolyte salt; however, the results showed poorer electrochemical performance compared to LiPF_6 and its thermal reactions are more exothermic.^[77] Therefore, this salt is not considered for commercial Li-ion batteries, although it is sometimes used on a laboratory scale.^[78]

5.2. Phosphates

Similar to the traditionally used LiPF_6 salt, other phosphate anions have also been considered for Li-ion batteries, some of them being fluorine-free. *Ab initio* as well as experimental studies have suggested lithium tris(oxalato) phosphate (LiTOP; 1, Figure 5) as an analogue of LiPF_6 and LiBOB to be used in Li-ion batteries.^[67,79] This salt can be readily dissociated due to the delocalizing effect of the six carbonyl functionalities of the oxalate ligands making it highly soluble in carbonate-based solvents and with high ionic conductivity. It is thermally stable until $150\text{--}190^\circ\text{C}$, between its analogues LiPF_6 and LiBOB.^[67] The electrochemical performance of this salt has been investigated

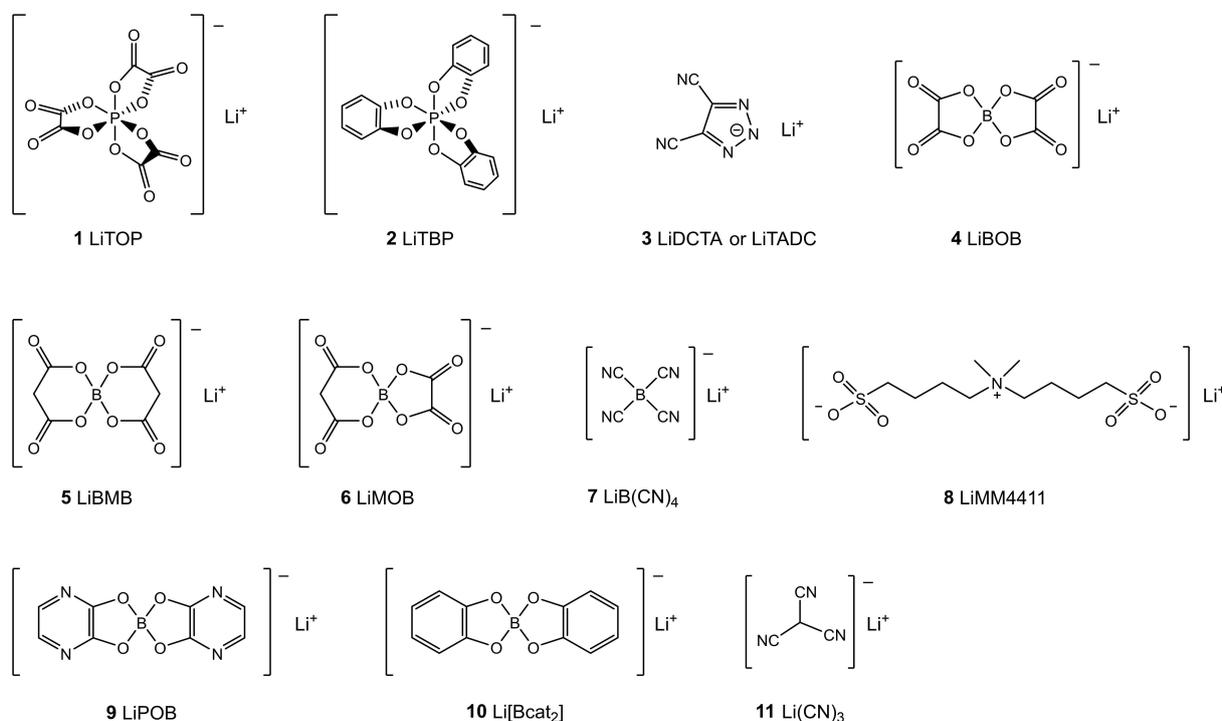


Figure 5. Chemical structures of fluorine-free lithium salts.

in graphite half-cells demonstrating its ability to reversibly (de)intercalate lithium ions into graphitic materials. In the first cycle, a reductive peak appeared at 2.15 V vs. Li^+/Li suggesting the formation of an SEI layer by the TOP anion. Coulombic efficiency and capacity retention remained close to 100% for the reported 9 cycles.^[67] Furthermore, this salt has shown to have a remarkably high stability against anodic decomposition (~ 5 V vs. Li^+/Li); however, it has not yet been tested with cathode materials or in full-cell Li-ion batteries. Therefore, despite the promising preliminary results, its viability to be used as a salt in Li-ion batteries has not been demonstrated due to the lack of experiments to demonstrate long-term cycling and stability towards relevant cathode materials.

Another example of chelated phosphates is lithium tris[1,2-benzenediolato(2-)-O,O']phosphate (LiTBP; **2**, Figure 5). The highest solubility and conductivity of this salt was found with a binary mixture of EC and THF, 0.5 M and 3.89 mS cm^{-1} , respectively. These values are lower than the conventional LiPF_6 due to the high viscosity of the solutions with LiTBP.^[80] The oxidative stability was reported to be 3.7 V vs. Li^+/Li , limiting its performance to rather low-voltage cathodes.^[80,81] The electrochemical performance of this salt was tested in $\text{Li} \parallel \text{V}_2\text{O}_5$ cells with an output voltage of 3 V vs. Li^+/Li .^[80] Further developments of this salt were done introducing fluorine atoms and not towards other phosphate-based fluorine-free anions.^[81] The initial discharge capacity and capacity retention was lower for the fluorine-free LiTBP than the fluorinated analogue (3-FLTBP) and both lower than LiPF_6 (Figure 6). The poorer performance compared to LiPF_6 suggests that these phosphate salts are not suitable candidates to fully replace LiPF_6 . However, the addition of a small amount of the fluorinated analogue 3-FLTBP did improve the cycling efficiency and morphology of passivating films.^[81]

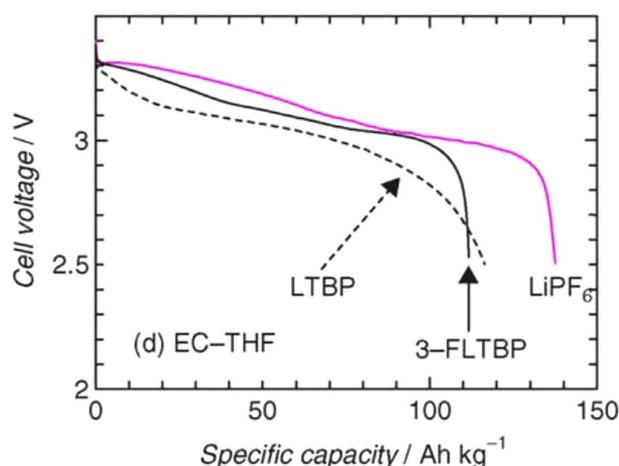


Figure 6. Discharge profiles of 0.5 M LTBP, 3-FLTBP (lithium tris[3-fluoro-1,2-benzenediolato(2-)-O,O']phosphate) and LiPF_6 in EC-THF (mole ratio 1 : 1) in $\text{Li} \parallel \text{V}_2\text{O}_5$ cells at 25°C and 1 mA cm^{-2} . Adapted with permission from Ref. [81], Copyright (2004) Elsevier.

5.3. Heterocyclic anions and cyano-based anions

Another category of lithium salts is that based on heterocyclic anions. They were proposed due to their extensive charge delocalization which allows dissociation of the salt in the typical solvents used in Li-ion batteries and therefore providing high solubility and ionic conductivity. The most well-known example is lithium 4,5-dicyano-1,2,3-triazolate (LiDCTA, also known as LiTADC; **3**, Figure 5). The coordination of lithium takes place through the nitrogen atoms in the planar five-membered ring, as revealed by *ab initio* and experimental studies.^[82] In addition, this salt has high thermal stability up to 300°C .^[83] With regards to its electrochemical properties, a lower anodic stability has been reported for this salt in PC compared to other fluorinated salts such as LiPF_6 or LiTFSI. This also explains the poorer electrochemical performance of LiDCTA in PC in $\text{LiFePO}_4 \parallel \text{Li}$ cells. Nevertheless, the choice of solvents plays an important role. For example, replacing PC with poly(ethylene glycol) dimethyl ether (PEGDME) leads to improved cell performance,^[84] and even better when using a mixture of adiponitrile and sulfolane with or without EC (Figure 7).^[85] In addition, this salt has also been investigated in solid polymer electrolytes with poly(ethylene oxide) showing good solubility and a conductivity of $10^{-4} \text{ S cm}^{-1}$ at 55°C , although this system has not yet been tested in battery devices.^[66]

Through *ab initio* studies, it has been reported that by increasing the $-\text{CC}\equiv\text{N}$ substitution in the anion, the Li-ion affinity decreases, and thus the dissociation ability increases. Furthermore, the oxidative stability also increases, making them better candidates for their application in Li-ion batteries. Although this has been proven with fluorinated anions,^[86] similar behavior could be expected for fluorine-free analogues which could be another family of anions to investigate, especially for high-voltage cathode materials that require high anodic stability of the electrolyte.

5.4. Boron-based anions

Despite all the aforementioned candidates for fluorine-free salts, the most studied and promising is lithium bis(oxalato)borate (LiBOB, **4**, Figure 5), which is synthesized by mixing lithium tetramethanolborate and di(trimethylsilyl) oxalate.^[87,88] The electron-withdrawing carbonyl groups of the anion help delocalizing the charge and facilitates dissociation of the salt. Hence, high solubility and ionic conductivity can be obtained in organic solvents. For example, 1 M LiBOB in 1,2-dimethoxyethane (DME) has a conductivity of 14.9 mS cm^{-1} at 25°C , although introducing EC to the solvent mixture decreases the solubility and conductivity. On the contrary, cyclic esters such as gamma-butyrolactone (γ -BL) increase the solubility up to 2.3 mol kg^{-1} LiBOB.^[89]

Other advantages of LiBOB compared to LiPF_6 are its higher thermal stability up to 302°C and more benign decomposition products, such as LiBO_2 and LiOCCOOH , compared to the toxic POF_3 and HF from LiPF_6 .^[87] Regarding the purity of this salt, the main contaminant found is lithium oxalate which

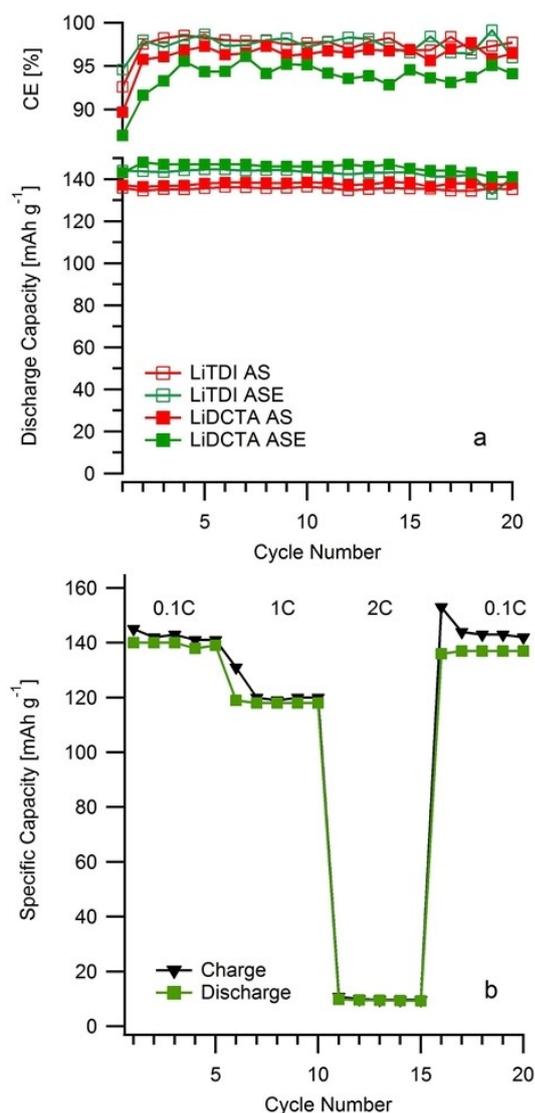


Figure 7. a) Coulombic efficiencies (CE) and discharge capacities for Li || LFP cells with LiDCTA with AS (adiponitrile:sulfolane) and ASE (adiponitrile:sulfolane:EC) electrolytes and b) specific capacity at different C-rates for Li || LFP cells with LiDCTA with ASE electrolytes. Reprinted with permission from Ref. [85], Copyright (2016) Elsevier.

hinders the solubility of LiBOB in carbonate solvents and increases the cell impedance.^[90] Therefore, the purity of the salt is an important aspect to consider and check prior to its use in electrochemical cells.^[71,90–92] Another source of impurities is water, as it can lead to salt decomposition resulting in lower solubility and high-resistance byproducts.^[90] Nevertheless, it still has more tolerance towards water than LiPF₆-based electrolytes, which is another advantage of LiBOB over the state-of-the-art salt.^[91]

The electrochemical performance of LiBOB-based electrolytes has been assessed mostly vs. graphite anodes but new studies with silicon-based anodes are also emerging. The main advantage of this salt compared to LiPF₆ is its ability to form an SEI on graphite. This layer prevents the exfoliation of graphite when PC is used as solvent leading to better cell performance

compared to LiPF₆.^[93] The formation of the SEI layer has been associated with the irreversible plateau commonly observed at 1.6 V vs. Li⁺/Li. However, a stable SEI layer is fully formed with reduction products of the BOB anion only when the voltage is decreased to 0.5 V vs. Li⁺/Li.^[94] Thus, the former plateau can instead be assigned to oxalate ester impurities from the synthesis reaction of LiBOB.^[71] Furthermore, the extent of this plateau differs with the choice of solvents, being larger for cyclic esters, which could be due to the higher solubility of such impurities in these solvents.^[89]

The chemical composition of the SEI formed with LiBOB-based electrolytes has been mainly studied with XPS and FTIR. Sample preparation for *ex situ* experiments involving LiPF₆ has been done by cleaning the surface of the electrode with DMC to remove residual salt and solvents. However, the low solubility of LiBOB in DMC results in salt precipitation upon cleaning. Therefore, a mixture of γ -BL with DMC has been proposed for LiBOB-based cells, although there is a risk of dissolving SEI species with the strong solvation power of γ -BL.^[95] The main difference in the composition of the SEI between LiBOB- and LiPF₆-based electrolytes is the oxygen-rich layer formed with the former and a fluorine-rich formed with the latter.^[96] The oxygen species found with LiBOB electrolytes have been assigned to semicarbonates-like compounds originating from the reduction of LiBOB; the mechanism is shown in Figure 8.^[95] These compounds on the SEI protect graphite against solvent cointercalation as well as chemical erosion at elevated temperatures.^[95,97] Additional compounds found on the SEI with LiBOB are orthoborates also formed from the decomposition of the anion (Figure 8). Despite the ability of LiBOB to form a stable SEI layer on graphite, it has also been reported that the presence of EC is still required as it forms an initial compact and highly insulating layer on graphite due to its high reduction potential, followed by the reduction of the BOB anion. In the absence of EC, only reduction products of the BOB anion are observed throughout the SEI layer.^[98]

Overall, LiBOB-based electrolytes have shown promising electrochemical performance with graphite anodes similar to the state-of-the-art LiPF₆.^[65,89,94,95,98] However, the main limitation comes from the higher cell resistance observed for this fluorine-free electrolyte.^[96,99] On the other hand, the main advantage of LiBOB is seen at elevated temperatures, where LiBOB-based electrolytes clearly outperform conventional LiPF₆-based electrolytes thanks to the higher thermal stability of the LiBOB salt, allowing longer cycle life at 60 °C.^[65,92,96,100]

Most efforts towards the development of LiBOB-based electrolytes have focused on its interaction with graphite anodes. However, Xu has also shown the importance of the choice of cathode material and surfaces for fluorine-free electrolytes based on LiBOB.^[89] Capacity retention in half-cells at 60 °C between 2.5 and 4.1 V vs. Li⁺/Li is lower for LCO and NMC, followed by spinel LMO and the best-performing LFP and NCA (Figure 9).^[71,89] Similar trends have also been reported for large-format Li-ion cells at 60 °C even outperforming commercial cells with LiPF₆-based electrolytes.^[92] This confirms the improved thermal stability of cells containing LiBOB-based electrolytes. The poorer performance with Co-rich cathode

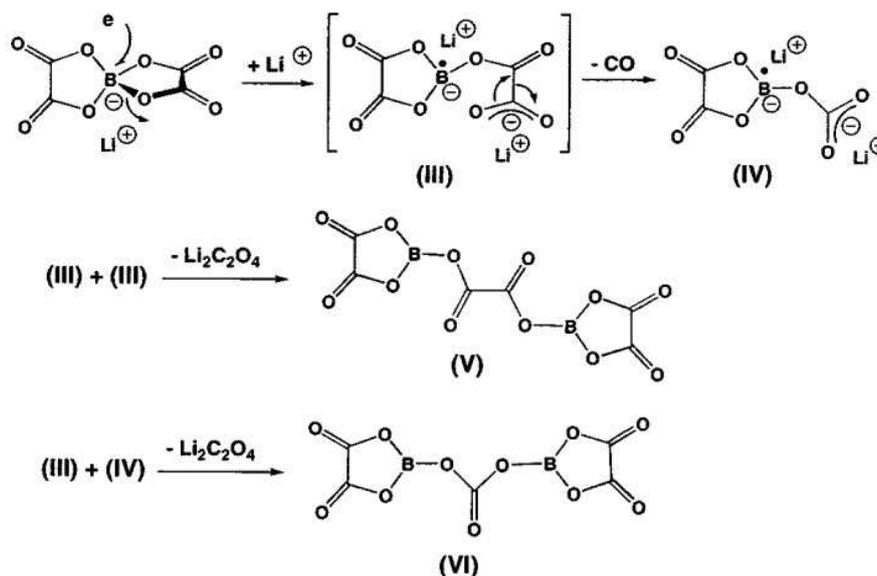


Figure 8. Proposed decomposition mechanism for BOB anion. Reprinted with permission from Ref. [95]. Copyright (2003) The Electrochemical Society.

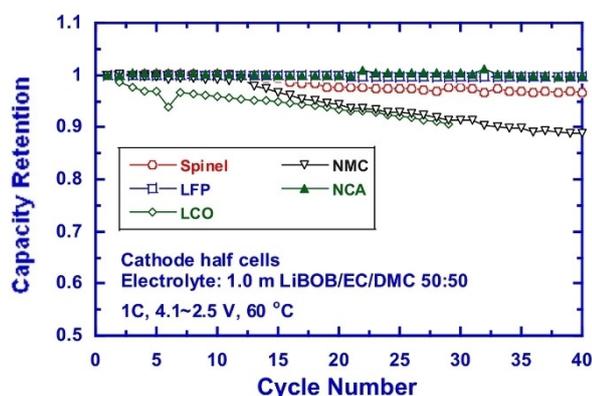


Figure 9. Stability of LiBOB-based electrolytes at 60 °C in half cells with different cathode materials: spinel $\text{Li}_x\text{Mn}_2\text{O}_4$, LiFePO_4 , LiCoO_2 , $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$, and $\text{LiNi}_{0.85}\text{Co}_{0.10}\text{Al}_{0.05}\text{O}_2$. Reprinted with permission from Ref. [89]. Copyright (2008) The Electrochemical Society.

surfaces has been ascribed to an anodic decomposition of the BOB anion catalyzed by Co sites on the cathode.^[71,89] However, further studies are needed to confirm this hypothesis.

Besides the typical electrode materials, other iron-based materials have been used with electrolytes containing LiBOB and fluorine-free binders in order to build safer and more sustainable batteries. Cells consisting of nanostructured iron oxide in a deeply lithiated $\text{Fe}/\text{Li}_2\text{O}$ state as anode and LiFePO_4 as cathode have shown to exhibit higher capacity retention (91.2% after 100 cycles) than with the conventional LiPF_6 -based electrolyte (89.2% after 100 cycles).^[101] Towards higher-energy-density materials, silicon is widely used with graphite to boost the capacity of the latter but also as the solely active material of the anode. Some studies have investigated the effect of LiBOB-based electrolytes with silicon and silicon/graphite composites. Thin-film silicon electrodes have shown improved capacity retention with LiBOB salt over LiPF_6 (83.5% and 50.8%

respectively after 100 cycles). This has been ascribed to the ability of LiBOB to form a stable SEI layer on the silicon electrode.^[102] Furthermore, composite electrodes with graphite and silicon have shown lower specific capacity but improved capacity retention with LiBOB compared to LiPF_6 .^[99] When additives are included in the electrolyte formulation, full cells containing silicon/graphite and NMC111 featured improved discharge capacity and capacity retention at low current densities with the fluorine-free electrolyte compared to a highly fluorinated electrolyte (Figure 10). However, such improvement was not maintained at higher rates due to the higher cell resistance with the LiBOB-based electrolyte.^[96] Further investigation of additives to match the performance of LiPF_6 -based electrolytes also at higher cycling rates clearly has the potential to render LiBOB-based electrolytes competitive with state-of-the-art electrolytes also when paired with high-energy-density active materials.

LiBOB-based electrolytes have also been tested in Li-metal batteries with LiFePO_4 cathodes. A thin lithium foil (30 μm) was used and protected with a controlled exposure to pure O_2 gas. Compared to LiPF_6 , a fluorine-free electrolyte containing LiBOB showed improved performance with extended cycle life at various current densities without failure or signs of dendrites (Figure 11).^[103] The main advantage of LiBOB was reported to be its ability to form a stable passivating layer on lithium^[65] while LiPF_6 requires SEI-forming additives such as FEC.^[50]

From studies with accelerated rate calorimetry (ARC), a higher onset of self-heating reactions was observed for lithiated mesocarbon microbeads with LiBOB (170 °C) compared to LiPF_6 (80 °C), as well as lower self-heating rate for the non-fluorinated electrolyte. The reason for the lower thermal stability of lithiated graphite with LiPF_6 is a substantial amount of deintercalated carbon with LiPF_6 , while it remains lithiated with LiBOB, as shown by XRD after heating to 170 °C.^[104] While cells containing LiBOB have shown slower reactivity of the negative

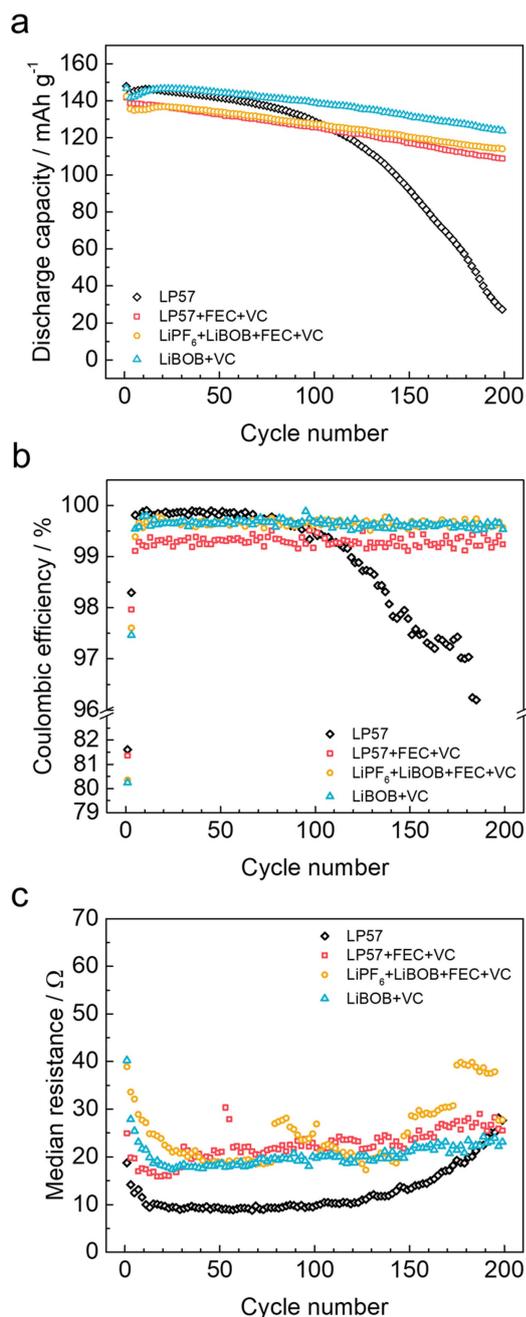


Figure 10. Electrochemical performance of NMC111 || Si/graphite cells cycled at C/10 at room temperature with electrolytes LP57 (1 M LiPF₆ in EC:EMC) (black), LP57 + 10% FEC + 2% VC (red), 0.38 M LiPF₆ and 0.5 M LiBOB in EC:EMC + 10% FEC + 2% VC (yellow), and 0.7 M LiBOB in EC:EMC + 2% VC (blue). a) Discharge capacity, b) Coulombic efficiency, and c) median resistance during discharge. Reprinted from Ref. [96]. Copyright (2020) The Authors.

electrode, they have also shown increased reactivity of the positive electrode below 200 °C, particularly with cells containing LiCoO₂.^[105] Nevertheless, it has also been shown that half-cells with LiNiO₂ are stable with electrolytes containing LiBOB while cells with LiCoO₂ are not.^[71] Therefore, further studies regarding the thermal stability of LiBOB in full cells as well as the effect of the cathode active material, especially when containing cobalt, are required to fully understand this different

behavior. Safety studies during overcharging of Li-ion cells have also shown improved results with LiBOB-based electrolytes compared to LiPF₆.^[92] The reason behind this is the oxidation of the BOB anion on the cathode side releasing CO₂ that triggers the safety vent and prevents thermal runaway. In addition, the generated CO₂ can also assist in suppressing flames as well as cooling down the reactive sites on the cathode.^[92,106] Nevertheless, there is also a trade-off as gassing in Li-ion cells can lead to swelling and poor electrochemical performance.^[71]

Overall advantages of LiBOB are the higher thermal stability, higher safety and environmental friendliness at the expense of slightly higher resistances and lower rate capability. Nevertheless, these shortcomings can likely be improved with a better design and optimization of the solvents and additives for this particular salt.

A derivative of LiBOB comprising a 6-membered ring with a -CH₂- group between the two carbonyls, lithium bis(malonato)borate (LiBMB; 5, Figure 5) has also been studied. The ion coordination properties of this salt have been investigated with *ab initio* methods showing a stronger coordination of Li⁺ by the BMB anion than by the similar BOB anion.^[79] This is in agreement with experimental results that show limited solubility of this salt in PC (0.08 M). The only conductivity experiments reported are with DMSO as solvent where 0.5 M concentrations are feasible, but the values are lower than for LiBOB and fluorinated salts although the conductivity becomes increasingly competitive as the temperature increases.^[87]

To continue the efforts of developing new orthoborate anions, lithium (malonatooxalato) borate (LiMOB; 6, Figure 5) was introduced and its properties investigated with *ab initio* methods. This salt has stronger coordination to Li due to the partial loss of conjugation when introducing a CH₂ group in the molecule.^[79] From these results poor solubility and conductivity would be expected for this salt although it has not been confirmed experimentally.

Another type of borate salt is lithium tetracyanoborate (LiB(CN)₄; 7, Figure 5). The boron atom is here stabilized by four electron-withdrawing nitrile groups. Computational studies predict valuable properties for this salt to be used in battery applications, due to a good oxidative stability and weak coordination to lithium ions.^[68] LiB(CN)₄ has been experimentally investigated with ionic liquids but the solubility is low due to the strong ion-ion interactions in

larger aggregates. On the other hand, the solubility is improved with strong Li⁺-coordinating oligomers such as poly(ethylene glycol) dimethyl ether (PEGDME). This electrolyte was tested in Li || LiFePO₄ cells with good stability up to 4 V vs. Li⁺/Li and 99% capacity retention after 22 cycles.^[107] It has also been explored in glyme-based gel polymer electrolytes, but the results are poorer than with state-of-the-art LiPF₆-based electrolytes with instability issues above 4 V vs. Li⁺/Li and poor coulombic efficiency.^[84]

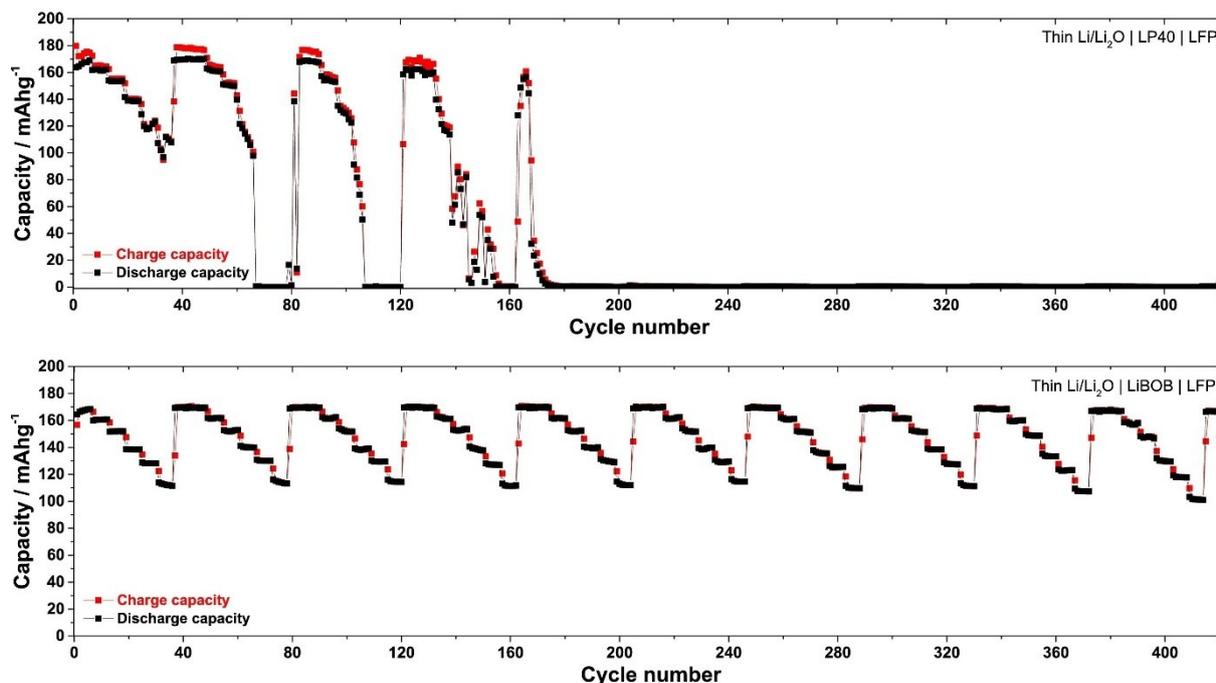


Figure 11. Long-term capacity retention at various C-rates (ranging from 0.2 C to 6 C) for protected Li || LiFePO₄ cells with LP40 (top) and LiBOB-based (bottom) electrolytes. Adapted with the authors' permission from.^[103]

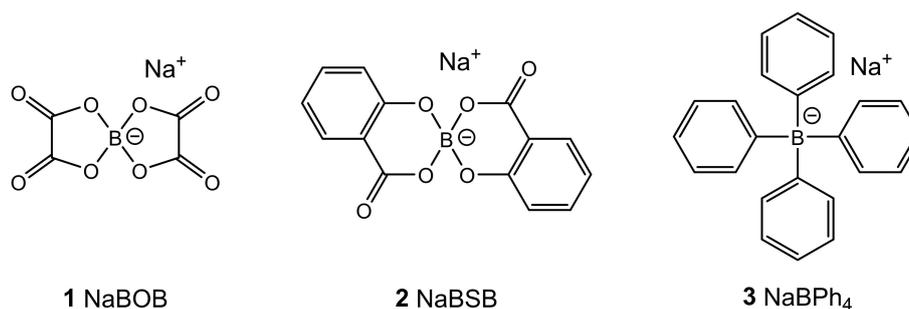


Figure 12. Cyclic voltammetry of NaBOB in NMP, TMP, and 50/50 mixtures of both solvents showing a) reduction and b) oxidation on carbon-coated aluminum. c) Long-term cycling performance of TEP:NaBOB electrolyte in Prussian white/hard carbon full cells and associated voltage profiles. Adapted from Refs. [114,115]. Copyright (2021) The Authors.

5.5. Other salts

Besides the aforementioned lithium salts which have been explored in Li-ion batteries to some extent, there are other alternative salts that have been proposed but not yet tested in battery devices. One example is 4,4'-(dimethylammonio)bis(butane-1-sulfonate) (LiMM4411; **8**, Figure 5). It is a pseudo-delocalized anion as the charge is not completely localized to a unique region nor delocalized as for other weakly coordinating anions. However, due to the strong interaction of the two SO₃⁻ groups in the anion to Li⁺, this salt is only soluble in protic solvents such as water. The ionic conductivity of this Li-based aqueous electrolyte is 30 mS cm⁻¹ and the electrochemical stability window is 2 V, higher than the thermodynamic stability of water but still very much limited by water decomposition.^[108] Other reported examples are the synthesis and crystal structure of borate anions, such as bis(2,3-oxy-pyrazine)borate (LiPOB; **9**,

Figure 5)^[109] anion and bis[1,2-benzenediolato(2-)-O,O']borate (Li[Bcat₂]; **10**, Figure 5).^[110] However, there is no information about their solubility, conductivity or other relevant properties for Li-ion batteries.

Furthermore, new fluorine-free salts have been developed and used with solid polymer electrolytes. One example is lithium tricyanomethanide (LiTCM; **11**, Figure 5), which has been mixed with poly(ethylene oxide) and compared to LiTFSI. The ionic conductivity is slightly lower for LiTCM, especially below the melting point of the polymer host, and the anodic stability is also lower at a reported 4 V vs. Li⁺/Li. The latter value is surprising as the cyano groups are expected to increase the anodic stability of the salt.^[86] Despite these initially poor properties, they have shown clear improvements in lithium-sulfur solid-state cells, thanks to a robust and highly ionically conductive passivation layer.^[111]

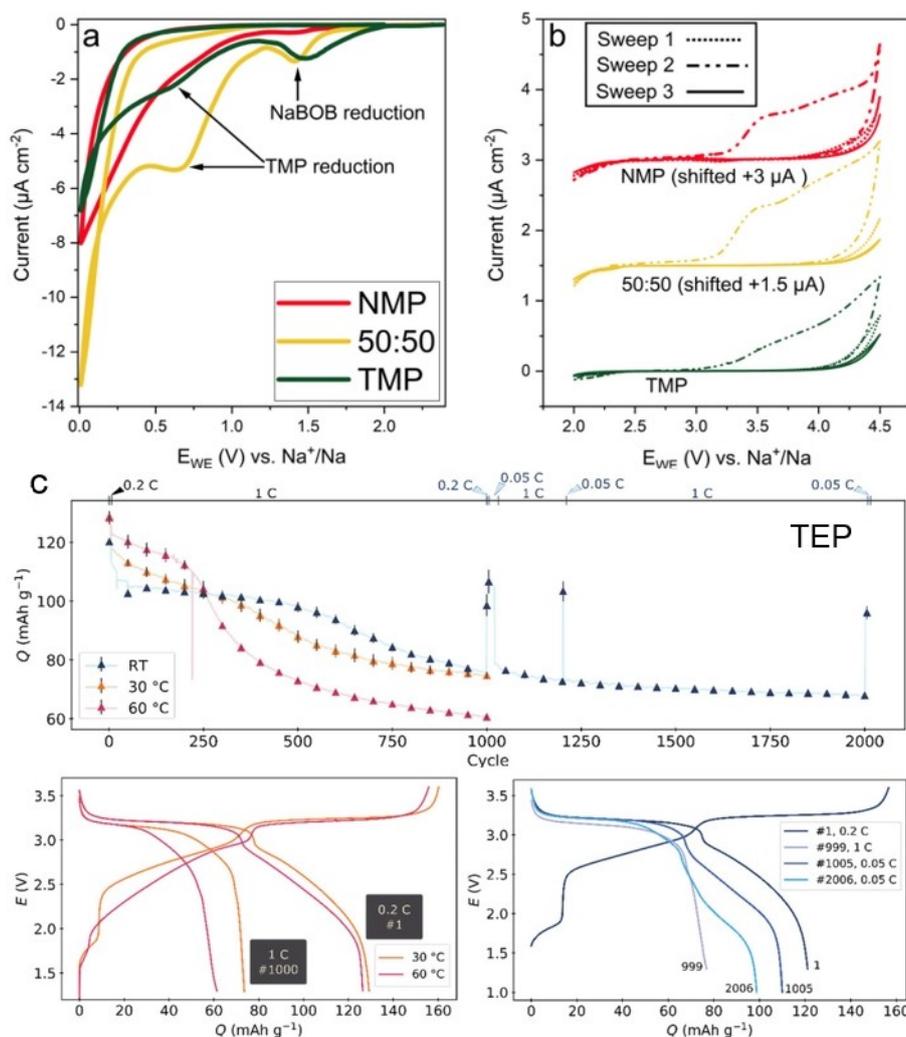


Figure 13. Structures of bis(oxalato)borate (NaBOB), sodium bis(salicylato)borate (NaBSB) and sodium tetraphenylborate (NaBPh₄) salts.

6. Progress towards Fluorine-Free Systems: Sodium

Sodium-ion batteries have much the same reasons for avoiding fluorinated salts as Li-ion batteries with the major difference that Na-ion batteries are even more cost-sensitive with regards to all components due to the envisioned large-scale use of said chemistry. While there are many fluorine-free sodium salts that have been used for non-aqueous electrochemistry such as NaI, NaSCN and NaNO₃, it is impossible to speak about Na-ion batteries without starting with sodium perchlorate (NaClO₄). Sodium perchlorate was considered the standard salt in Na-ion batteries for a long time until the hexafluorophosphate anion became dominating. Perchlorate seems like a perfect match for a Na-ion battery, being relatively cheap, made from abundant elements, and displaying excellent solubility in many solvents. The voltage stability of sodium perchlorate is slightly worse than NaPF₆ for both oxidation and reduction according to some sources^[112] while others say that the performance is comparable.^[113] As mentioned earlier, the strongly oxidative nature of perchlorates presents a major hurdle for commercial-

ization of NaClO₄; this salt does, however, show that fluorine-free salts are able to provide more than acceptable performance at a reasonable cost. Despite the arguments about commercial feasibility, sodium perchlorate is actively researched to this day for both aqueous^[116] and non-aqueous systems and remains one of the most popular salts in Na-ion battery research. Perchlorates will, however, not be discussed further in this review since they do not really provide any novelty, and the focus will instead be on newer salts.

6.1. Boron-based anions

Boron-based salts have been widely used in Na-ion batteries and by far the most common is NaBF₄ that often is seen as a cheaper but inferior alternative to NaPF₆ due to the lower solubility. Several fluorine-free borate anions have seen use in batteries and some show quite promising performance. These candidates include salts such as sodium bis(oxalato)borate (NaBOB), sodium bis(salicylato)borate (NaBSB)^[117] and sodium tetraphenylborate (NaBPh₄)^[118] (Figure 12). Furthermore, several

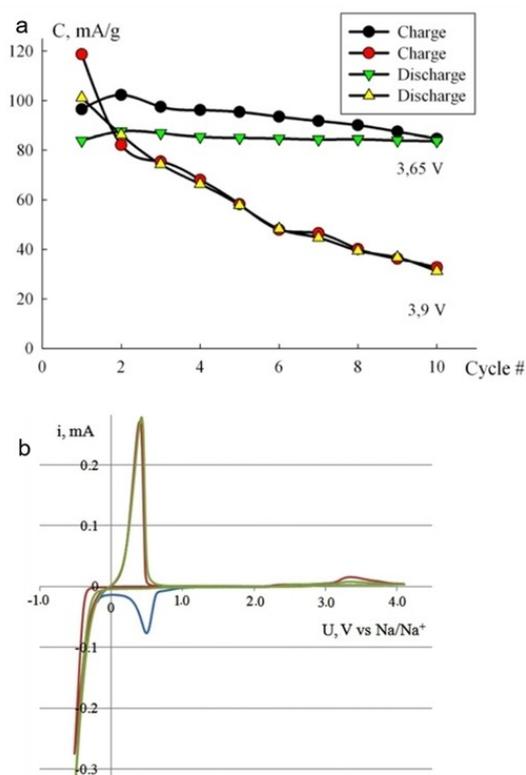


Figure 14. a) Cycling performance of $\text{Na}_{0.95}\text{Cr}_{0.95}\text{Ti}_{0.05}\text{O}_2$ cathode vs. Na metal using an electrolyte consisting of 0.25 mol kg^{-1} NaBSB in GBL. b) Cyclic voltammogram of the electrolyte performed at 10 mV s^{-1} showing cycles 1, 2, and 5. Adapted with permission from Ref. [117]. Copyright (2018) Elsevier.

promising BOB derivatives have been synthesized^[119] although low conductivities are reported in carbonate solvents. Many of the BOB derivatives remain untested in combination with common solvents, and should be tested with the solvents that has proven successful for the most investigated candidate, NaBOB.

NaBOB was first synthesized by Whittingham et al.^[120] and the physical properties of the NaBOB salt include good thermal stability ($> 300^\circ\text{C}$) and stability in ambient conditions although NaBOB will hydrolyze if dissolved in water. When it comes to electrochemical properties, NaBOB shares many of the good properties of LiBOB, although the solubility of NaBOB is extremely low in most common solvents.^[121,122] A shared trait for the two mentioned salts is that they decompose at quite high potentials to form a passivation layer. This can be both good and bad since this leads to rather robust SEI formation with good passivation but also a rather high impedance, as this is quite similar to LiBOB it is likely that the decomposition of NaBOB follows closely what has been described earlier for LiBOB (Figure 8). Another aspect of the NaBOB salt is that it appears to passivate the aluminum cathode current collector, and this too probably occurs in a similar reaction to LiBOB,^[70] although this mechanism has yet to be investigated. In terms of practical application of NaBOB, it is currently restricted to use with amides such as *N*-Methyl-2-pyrrolidone (NMP)^[114] and alkyl phosphates such as trimethyl phosphate (TMP)^[69] and

triethyl phosphate (TEP),^[115] as these solvent classes often show much higher solubility of NaBOB than carbonates or ethers. The highest ionic conductivity (8.83 mS cm^{-1}) is attained by NaBOB in the solvent NMP at saturation concentration which corresponds to 0.66 M . The literature on NaBOB in batteries is somewhat limited thus far, especially in terms of how well it can handle higher-voltage chemistries but it has been shown to provide decent initial coulombic efficiency (up to 82%) with hard carbon anodes. In fact, full cells based on hard carbon and Prussian white have retained 57% capacity at 1000 cycles using TMP solvent and 2000 cycles with 80% retention using TEP, although the power fade was quite significant in the latter case.^[69,114,115] Based on cyclic voltammetry performed on carbon-coated aluminum substrates (Figure 13), the voltage stability of NaBOB in TMP and NMP is rather low until passivation has occurred. Reduction occurs as early as $1.5 \text{ V vs. Na}^+/\text{Na}$ while the oxidation occurs at ca. 3 V although in practice the stability will allow cycling of sodium half-cells and cathodes up to $4 \text{ V vs. Na}^+/\text{Na}$ due to both anodic and cathodic passivation.

For other salts similar to NaBOB like NaBSB, very little literature exists and the solubility in different solvents is not quite as well investigated. In a paper by Diamant et al.,^[117] the solubility in GBL was shown to exceed 1 mol kg^{-1} , albeit with a low ionic conductivity going from a maximum of 3 mS cm^{-1} at 0.5 mol kg^{-1} to less than 2 mS cm^{-1} at 1 mol kg^{-1} . Cyclic voltammetry shows similarity to NaBOB with the early onset of a reduction peak that could indicate comparable passivation behavior (Figure 14). During galvanostatic cycling of sodium half-cells utilizing a chromium oxide cathode, a significant impact of the higher cut-off voltage was revealed although it is not clear whether this was due to the properties of the electrolyte or the cathode material.^[117]

Sodium tetraphenylborate (NaBPh_4) is a well-known salt that was applied to Na-ion batteries fairly recently by Yamada et al.^[118] NaBPh_4 is an interesting salt since it seems highly resistant to reduction and thus allows impressive plating and stripping performance in sodium half-cells when combined with glymes such as DME (Figure 15). NaBPh_4 is highly soluble in ethers and attains its maximum ionic conductivity of 6 mS cm^{-1} in DME at ca. 0.5 M concentration. Although stable and high-rate half-cell cycling using both hard carbon and $\text{Na}_2\text{V}_3\text{O}_7$ has been demonstrated, it is likely that the low oxidative stability of NaBPh_4 at ca. $3.4 \text{ V vs. Na}^+/\text{Na}$ will be major issue for most Na-ion cathodes.^[123]

6.2. Percyano-substituted anions

Percyano-substituted sodium salts such as NaTIM, NaPCPI and NaTCP (Figure 16) are very promising salts since they are entirely composed of abundant materials and possess many of the requirements that are needed of an electrolyte salt. The literature on these salts is mostly from polymer electrolytes^[124] although some information on common solvents is also available from patents.^[125] Percyano-substituted anions are aromatic (Hückel-type) anions with cyanide substituents. The π -

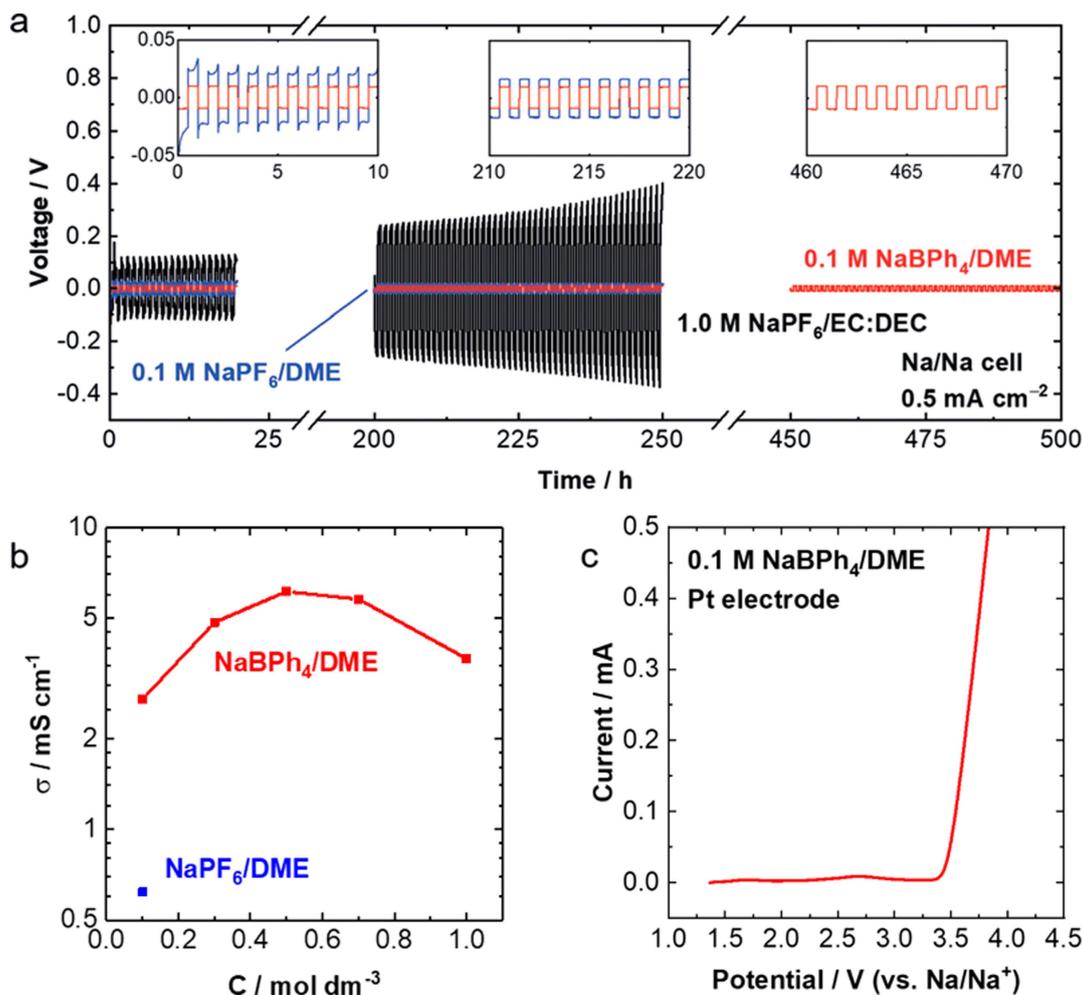


Figure 15. a) Comparison of plating and stripping performance of Na metal on copper for 0.1 M DME NaPF₆, 1 M NaPF₆ in EC:DEC, and 0.1 M NaBPh₄ in DME electrolytes. b) Ionic conductivity and c) oxidation stability for 0.1 M NaBPh₄ in DME. Adapted from Ref. [118]. Copyright (2020) The Author(s).

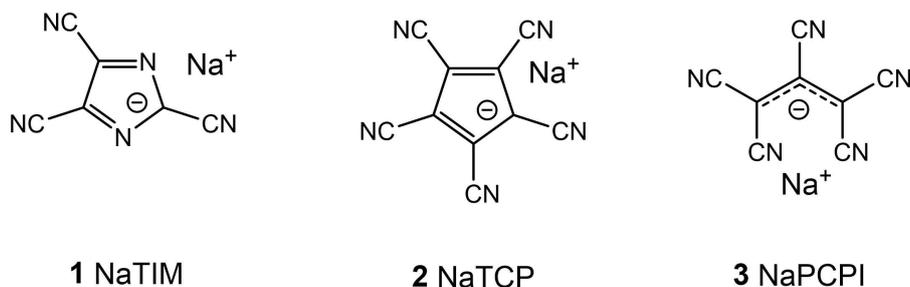


Figure 16. Structures of sodium 2,4,5-tricyanoimidazolate (NaTIM), sodium 2,3,4,5-tetracyanopyriolate (NaTCP), and sodium pentacyanopropenide (NaPCPI) pericyano-substituted salts.

bonds in the aromatic ring allows the negative charge to be delocalized and this results in salts with high solubility. The thermal stability of this class of anions is quite extraordinary with the stability extending to above 500 °C for many salts. When it comes to electrochemical stability not much is known although cyclic voltammograms in the patents indicate very robust oxidation stability (> 4 V vs. Na⁺/Na) in propylene carbonate for NaTCP and NaTIM. What is most impressive for this class of salts is the ionic conductivity that reaches 16.53

and 13.53 mS cm⁻¹ at 0.75 mol kg⁻¹ in EC:DMC for NaTIM and NaTCP respectively, this being a fair bit higher than NaClO₄ at 10.2 mS cm⁻¹ at 1 mol kg⁻¹ in PC.

7. Summary and Outlook

Over the last decades, most of the electrolyte development, understanding and improvement for Li-ion batteries has been

done with fluorinated electrolytes containing LiPF_6 , with a similar situation for Na-ion batteries. To a large extent, this explains why this category of electrolytes is the overall best-performing and still the state-of-the-art electrolytes. In contrast, the research on fluorine-free alternatives is still in its infancy, and when studied, typical solvents and additives that work well for traditional fluorinated electrolytes have largely been used. As we have shown throughout this paper, the choice of additives and solvents needs to be carefully chosen to match the requirements from the salt and therefore more efforts should be placed into developing and designing effective electrolyte formulations specifically for fluorine-free salts. Since the beneficial effects of fluorine are largely related to the formation of SEI and CEI species through “functional degradation” rather than its effect on the innate electrolyte properties, the key to replacing fluorine is to find new, innovative ways to tailor the formation of these passivation layers. Clearly, the SEI formation protocols are not sufficiently developed and what works for electrolytes containing fluorinated species may not necessarily work for fluorine-free systems. The key here is therefore to consider the fluorine-free systems not as direct descendants of the traditional systems, but to develop them in their own right with formulations, additives and cycling protocols specifically for these systems. Still, fluorine-free electrolyte systems have indeed shown promising performance – especially formulations based on the BOB anion. On the other hand, fluorine-free formulations are to a large extent unexplored and not fully optimized, including formulations based on BOB. It appears that fluorine is not strictly necessary to either attain high ionic conductivity or form effective SEI layers and we therefore feel confident to challenge the preconception of fluorinated components being indispensable in high-performance lithium and sodium battery systems.^[9] Still, we would like to reiterate that fluorine-free electrolyte formulations are still in an early stage of development and are not yet quite ready for commercial applications. It thus appears that – at least in the short term – LiPF_6 still reigns supreme. Even when considering fluorinated electrolyte formulations, it may not be necessary to use fully-fluorinated electrolytes. Rather, by tailoring how fluorine is used and distributed in the interphases, it can be better utilized, allowing for a reduction of the total amount necessary.^[16]

The focus of this review has been on the practical implementation of non-fluorinated electrolytes in battery cells. Consequently, there are many salts that have been proposed and even had their properties analyzed but have not made it to a device and so have been left out. Therefore, we urge the community to continue exploring different anions and testing them in relevant devices in order to assess their true potential for use in Li- and Na-ion batteries. This is important because only focusing on the solubility, conductivity or even the electrochemical stability window determined with inert electrodes does not provide a good overview of their application in real devices, as the conditions of such experiments do not necessarily correlate to good electrochemical performance in real cells.^[122,126]

In the end, cheap and environmentally friendly electrolytes are very important not least for Na-ion batteries, that are typically posed as cheaper and more sustainable alternatives to their lithium counterparts, and to this end it is somewhat surprising how little has been done in this field thus far. Many of the results presented here provide a very good starting point for further studies and trials in batteries. It is our hope that the research community will be inspired by the work done so far and further develop salts, that are a better fit for Li- and Na-ion batteries without being unstable, explosive or expensive, and together with new solvent and additive combinations create a new generation of electrolyte formulations with improved functionality in real battery systems. There is indeed great potential for research and innovation within this area!

Acknowledgements

The authors would like to acknowledge ECO²LIB and SIMBA (European Union H2020 research and innovation programme under Grant agreement No 875514 and No 963542, respectively) and STandUP for Energy for financial support.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: electrolytes · fluorine-free · lithium · sodium · batteries · sustainability

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Manuscript received: November 30, 2021
Revised manuscript received: February 18, 2022
Accepted manuscript online: February 28, 2022