

A comprehensive review of lithium salts and beyond for rechargeable batteries: Progress and perspectives

A. Mauger, C.M. Julien, A Paollela, M. Armand, K. Zaghib

▶ **To cite this version:**

A. Mauger, C.M. Julien, A Paollela, M. Armand, K. Zaghib. A comprehensive review of lithium salts and beyond for rechargeable batteries: Progress and perspectives. Materials Science and Engineering: R: Reports, 2018, 134, pp.1-21. 10.1016/j.mser.2018.07.001 . hal-02337513

HAL Id: hal-02337513

https://hal.sorbonne-universite.fr/hal-02337513

Submitted on 29 Oct 2019

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

A comprehensive review of lithium salts and beyond for rechargeable batteries: progress and perspectives

A. Mauger[a], C.M. Julien[a], A. Paollela[c], M. Armand[b], K. Zaghib[c,*]

[a]Sorbonne Université, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie (IMPMC), UMR 7590, 4 place Jussieu, 75005 Paris , France.

[b]CIC Energigune, Parque Tecnologico de Alava, Albert Einstein 48, Ed. CIC, 01510, Miñano, Spain.

[c]Center of Excellence in Transportation Electrification and Energy Storage (CETEES) Hydro-Québec, 1806 Bd Lionel-Boulet, Varennes, Québec, J3X 1S1, Canada.

* Corresponding author: zaghib.karim@ireq.ca

Abstract

The increasing need for energy storage has been the motivation for intensive research in batteries with different chemistries in the recent past. Among the elements of the batteries, the salts and their solvent play an important role. In particular, the cathodic stability at low potential depends importantly on the choice of the cation, while the stability at high potentials is mainly due to oxidation of anions and the ion mobility and dissociation depend primarily on the delocalization of the anion, so that many attempts are made to find the optimum choice of both the cations and anions of the salts, and their solvents. Although lithium-based batteries are almost exclusively used today, efforts are currently made to explore batteries based on sodium, aluminum, magnesium, calcium, potassium. The purpose of the present work is to review the salts and solvents that have been proposed in these different batteries and discuss their properties and their ability to be used in the near future and in the next generation of batteries.

Keywords: Ionic salts; Electrolytes; Ionic liquids; Aprotic solvents; Rechargeable batteries

Contents

1. Introduction
2. Lithium salts
    2.1. Salts in Li-ion batteries
    2.2. Ionic liquids
    2.3. Salts for Li-metal batteries
3. Sodium salts
    3.1. Salts for sodium-ion batteries
    3.2. Sodium salt with non-aqueous solvents
    3.3. Ionic liquids in SiBs
    3.4. Salts in all-solid-state sodium metal batteries
    3.5. Salts in gel-polymer electrolytes
    3.6. General trends
4. Magnesium salts
    4.1. THF-free liquid electrolytes
    4.2. Electroactive cations
    4.3. Ionic liquids
    4.4. Solid-state electrolytes
5. Aluminum salts
    5.1. Al batteries
    5.2. Al-based dual batteries
6. Calcium salts
7. Potassium salts
8. Prospective
    8.1. Environmental issues
    8.2. Cost issues
9. Conclusions
References

1. Introduction

The rapid conversion from fossil to green energy was endorsed at the political level by the Paris agreement to address climate change [1]. The increased average economic growth rate is concomitant with an increase in electricity consumption per capita. In addition, the population on earth is increasing very rapidly. When applied to the present situation, we know that with chain reactions that lead to a first-order transitions, this means a shortage of electricity and forces a drastic change in lifestyle. The challenge for scientists and technologists is to propose solutions to avoid this first-order transition. The solution will not be unique, but requires a variety of energy sources (geothermal, biomass, hydroelectricity, etc.), and energy storage will play an increasing role. Different kinds of energy storage systems are used at different levels to manage the electricity supply from the GWh scale down to kWh used by consumers. A review paper [2] provides a comparison in performance between various energy storage modes, including a discussion on their relative efficiency and cost. Attention is also focused on rechargeable batteries, which constitute a market in exponential growth that has major demand for portable use, electric cars, and large-scale energy storage to solve the problems with intermittence electricity production by windmills and solar plants. Today, the lithium batteries are almost exclusively used for this type of energy storage, while flow batteries are being tested. Na/S and Na/$NiCl_2$ batteries operating at > 300°C are developing slowly after a major incident. In parallel with the research on these batteries to improve their performance and safety, new efforts are under way to identify alternatives to lithium. In particular, recent progress on more abundant sodium, magnesium, aluminum and potassium batteries, as well as lithium-sulfur chemistry, are receiving significant attention. Review papers are available on these advanced batteries. However, these reviews are usually focused on one particular battery system, which is justified by the huge amount of publications. For example, in 2016, 900 research papers were published on Li-S batteries only.

There are numerous reviews on the different components utilized as electrode materials in advanced batteries, with a lesser number on separators. Only a few reviews are devoted to the electrolyte. All the aspects of the electrolyte have been reviewed in 2014 by Xu [3], but usually the reviews focus on the additives chosen to improve the safety or control the solid-electrolyte interface (SEI). In addition, the salts used in the electrolyte are very important as they insure the ionic conductivity and the stability window, but this has not been a major topic of many reviews so far.

These considerations guided us to the present work, which focuses on the electrolyte salts used in

the different battery chemistries mentioned here. Every battery chemistry has its advantages and disadvantage due to the different elements that are used. The salts are effective depending on their concentration and type of solvent in the electrolyte because the electrolyte interacts with the electrodes via SEI formation and the insertion or de-insertion of anions or cation in the electrodes. In addition, the separator plays a role in battery safety, and may also be functionalized to prevent the internal shuttle in Li-S batteries, for example. Therefore, battery performance depends on the compatibility between all the components. Nevertheless, a review that focuses on the salts (in relation to the solvents) is timely, and a discussion of their application in various advanced batteries is useful. One reason is that the performance of a battery is due to the ions in the electrolyte, and the behavior of anions in different batteries are often the same, for example: (1) ion mobility and dissociation depend primarily on the delocalization of the anion; (2) carbon is commonly used as the active electrode component, so the interaction and insertion properties of this anion towards carbon is similar in many batteries; (3) electrolyte conductivity also depends on salt concentration, which usually shows a maximum at 1 molar salt, a compromise between viscosity and concentration of the charge carriers and is optimized to achieve the best conductivity and/or electrochemical properties.

In this work, we review the salts and their solvent employed as electrolytes in non-aqueous batteries. Section II is devoted to salts used in rechargeable lithium batteries. In sections III-VII, we report on the salts-solvents used in sodium, magnesium, calcium, aluminum batteries, which are currently under investigation to prepare the next generation of high density/high power batteries. Section VIII is devoted to a discussion on the different chemistries, their impact on the environment and cost issues that will guide the future research and development of electrochemical energy storage.

2. Lithium salts

2.1. Salts in Li-ion batteries

The salt used in commercial Li-ion batteries is almost exclusively lithium hexafluorophosphate ($LiPF_6$) [4], because its solutions in dipolar aprotic organic solvents, either cyclic carbonates (e.g. ethylene carbonate) or linear carbonates (e.g. dimethyl-, diethyl-, and ethyl-methylcarbonate) show high ionic conductivities, good electrochemical stability and protects the Al current collector against corrosion. There are, however, several drawbacks. First, its thermal stability above 55 °C is poor: at

high temperature it decomposes through the reaction: $LiPF_6 \Rightarrow LiF$ (s) + PF_5 (g) [5-7]. Then, pentafluorophosphorane (PF_5) reacts with the solvents to generate highly toxic chemicals [8], and also initiates polymerization of solvents [9-11]. $LiPF_6$ is also extremely moisture sensitive [10-14], and readily hydrolyzes to form HF and PF_3O by trace amounts of water (or alcohols) [10-14]. As a rule, in carbonate-based dipolar aprotic solvents, the poorly solvated PF_6^- anion is highly reactive even towards weak nucleophiles.

These limitations of $LiPF_6$ have motivated extensive research on other salts. Some properties of usual Li-salts investigated in the 1980s are reported in Table 1, which was reproduced from [15]. Some of the salts are not practical for different reasons; $LiAsF_6$ and $LiClO_4$ are poisonous and explosive, respectively. The anion (BF_4) in $LiBF_4$ is not very conductive and creates problems on the surface of Li [16-18]. However, when the anode is graphite, $LiBF_4$ was claimed to be the only salt that permits full charge-discharge cycles in γ-butyrolactone (GBL)-ethylene carbonate (EC) mixtures [19]. Acceptable electrochemical properties of C-$LiFePO_4$//C-$Li_4Ti_5O_{12}$ cells were obtained with 1.5 mol L^{-1} $LiBF_4$ in GBL-EC (1:1) electrolyte at a temperature of 60 °C when $LiPF_6$ must be avoided because of its poor thermal stability [20] (see Fig. 1). Therefore, $LiBF_4$ is superior to $LiPF_6$, in EC:GBL electrolytes in Li-ion batteries that are used or stored at high temperatures, whether the cathode is $LiFePO_4$ [21] or $LiCoO_2$ [22]. Other anions containing phosphorous were considered [23-27], including $LiPF_3(CF_2CF_3)_3$ (LiFAP) [25-26] or lithium tris[1,2-benzenediolato(2)-O,O] phosphate [28]. However, the former salt is too expensive and produces a large amount of HF in a battery fire, while the latter salt is too resistive because its ion-dissociation is limited and the size of the anion with its rigid phenyl rings increases markedly the local viscosity for practical applications in Li batteries. Many other anions in Li salts were considered: those containing nitrogen [29-31], carbon [32], or boron [33-43] as the central atom, large cluster-based anions [44], and aromatic heterocyclics [45-46]. They include lithium bis(trifluoromethanesulfonyl)imide $Li[N(SO_2CF_3)_2]$ (LiTFSI) [29,47] lithium bis(fluorosulfonyl)imide, $Li[N(SO_2F)_2]$ (LiFSI), lithium bis(oxalato)borate, $Li[B(C_2O_4)_2]$ (LiBOB) [36-39]. Benzimidazole and imidazole lithium salts for battery electrolytes are illustrated in Fig. 2 reproduced from Ref. [46].

From Table 1, LiTFSI is the best candidate for a Li salt in lithium batteries and LiTFSI is highly soluble in the usual solvents (see also [48]). Unfortunately, LiTFSI allows severe aluminum corrosion near 3.6 V due to the solubility of $Al(TFSI)_3$ in alkyl carbonates [30]. The only case where this corrosion problem is not significant is in C-$LiFePO_4$//C-$Li_4Ti_5O_{12}$ cells, because the upper operating voltage is less than 3.6 V and the titanium spinel does not build a thick SEI at its operating voltage of

1.5 V vs. Li^+/Li. These cells containing 1 mol L^{-1} LiTFSI in GBL-propylene carbonate (PC) gave remarkable results even at 80 °C [20]. In this case, PC was used instead of DEC, DMC, because of its lower vapor pressure. In other Li-ion batteries using higher potential (layered oxides) active cathode elements, aluminum corrosion prevents the use of LiTFSI alone. To overcome this problem, LiTFSI was mixed with another salt. These salt blends were investigated to combine the advantage of the different components [49-52]. In particular, corrosion of Al foil in the LiTFSI-based electrolytes can be suppressed successfully by the addition of LiBOB as a co-salt [53], which also provides the benefit of higher thermal stability and better tolerance to water of LiTFSI compared to $LiPF_6$ [54]. The LiTFSI-LiBOB mixed salts are much more thermally stable than $LiPF_6$ [53]. The corrosion of aluminum can also be mitigated, at least partly, by mixing LiTFSI with $LiPF_6$ so that the latter still produces the AlF_3 protecting film on the Al current collector [55]. This $LiPF_6$-LiTFSI blend was tested on two of the most important material couples: $LiFePO_4$ vs. graphite (LFP/G) and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ vs. graphite (NMC/G) in EC/DMC (1/1) electrolyte [56]. These tests showed that the LiTFSI additive improved the lifetime, significantly increased residual capacity at end of life even with as little as 5% LiTFSI + 95% $LiPF_6$, and improved capacity after 6 months storage at room temperature and 55 °C. The C-$LiFePO_4$//C-$Li_4Ti_5O_{12}$ cell with a salt blend of 0.5 mol L^{-1} LiTFSI + 1 mol L^{-1} $LiBF_4$ in GBL+EC gave better results than the cell containing 1.5 $LiBF_4$ in GBL+EC at 60 °C [20], which illustrates the superiority of blends to optimize performances by taking advantage of the different salts synergies. Another example is provided with electrolytes comprising a mixture of $LiPF_6$ and $LiPF_3(CF_2CF_3)_3$ (LiFAP) in alkyl carbonates, which were superior to the single salt LiFAP or $LiPF_6$ alone as electrolyte with lithium–graphite anodes at elevated temperatures [57,58]. ARC measurements showed that LiFAP solutions have a higher onset for thermal reactions (>200 °C) but a much larger self-heating rate than $LiPF_6$ [59].

The LiBOB salt forms a thick SEI dominated by semi-carbonates that effectively protects the cathode against corrosion by other components of the electrolyte [60-65]. The SEI is robust enough to suppress the thermal reactivity of lithiated graphite towards the non-aqueous electrolytes [49-50], but the thick SEI is responsible for increased cell impedance when the active element of the cathode is a metal oxide. There is, however an exception: LiBOB is useful with $LiFePO_4$ [51]. In this particular case, LiBOB has other interesting properties – similar to $LiPF_6$, it protects the aluminum current collector, and is more stable than $LiPF_6$ above 55 °C. Even in $LiFePO_4$-based lithium batteries, however, LiBOB has not replaced $LiPF_6$ because it is not soluble enough in carbonate solvents [4,39],

so that it is only used in a salt blend or ether-containing solvents limited to 4 V. The $LiPF_6$/LiBOB blend combines the advantage of good conductivity, owing to $LiPF_6$, while LiBOB improves thermal stability [49-51]. This blend was recognized as a potential candidate for high-power lithium-ion batteries, especially for transportation applications [66]. Due to the unique case of $LiFePO_4$ and LiBOB, however, the salt blends containing LiBOB were mainly tested with $LiFePO_4$ cathodes. Zhang et al. [53] showed that both $LiBF_4$-LiBOB and LiTFSI-LiBOB mixed salts are much more thermally stable than $LiPF_6$ and LiTFSI-LiBOB mixed salt produced the best result as a promising electrolyte candidate for Li-ion batteries in wide-temperature applications.

The LiFSI-LiBOB mixed salt exhibited very good electrochemical results in a cell with a $LiFePO_4$ cathode and graphite anode in 1.0 mol L^{-1} $LiPF_6$/EC/EMC electrolyte containing 0.2 mol L^{-1} LiFSI and 0.2 mol L^{-1} LiBOB salt, proving that LiBOB passivates Al and suppresses corrosion attributed to FSI anions in similarity to LiTFSI [67] (see Fig. 3).

Li@borate salts with orthoborate chelate-type anions were introduced by Barthel et al., e.g. lithium bis[1,2-benzenediolato(2-)$^{-}$O,O'] borate (LBBB) [68-70]. However, similar to LiBOB, LBBB forms a poorly conducting solid electrolyte interface, and exhibits poor solubility/dissociation in commercial-type solvents that produces electrolytes with low conductivity. The lithium tetrakis(perhaloacyloxy)borate exemplified by $[Li(CF_3CO_2)_4B]$ (LiTFAB) [40] and lithium bis(fluoromalonato)borate salts [71] also suffer from low conductivity. Meanwhile, lithium difluoro(oxalato)borate $Li[F_2BC_2O_4]$ (LiDFOB) exhibits higher ionic conductivity, high Li transference number, high thermal stability and good SEI formation ability [43,72-76]. These properties helped LiDFOB achieve comparable performance to that of a mixture of LiBOB and $LiBF_4$.

A new type of imidazole-based salt was proposed [77], 2-trifluoromethyl-4,5-dicyano-imidazole (TDI) based on the principle of negative charge stabilization in conjugated 5-membered rings (Hückel rule), which has the properties needed for application in lithium-ion batteries: high stability, +4.6 V vs. Li against aluminum collectors, +4.0 V vs. Li anode in PEO (limitation by the polymer), and thermal stability at over 200 °C. Its only drawback is a conductivity 65% of that of $LiPF_6$ in the same solvents.

First-principle calculations showed that Li@carborane ($LiCB_{11}H_{12}$) is a superhalogen that can be used as a building block for halogen-free electrolytes in lithium-ion batteries [78]. However, the synthesis of this derivative is tedious. $Mg(CB_{11}H_{12})_2$ was synthesized, and experiments showed that it is a promising electrolyte for Mg batteries with a smooth plating/stripping of Mg [79]. First-principle calculations also suggest that $B_{12}(CN)_{12}$ clusters have potential applications for halogen-free

electrolytes in both Li and Mg batteries [80].

2.2. Ionic liquids

The ionic liquids (Ils) or molten salt liquids contain only ionic species and are a field in their own. By definition, these salts are liquid below 100 °C, but in the context of batteries, this term is used for salts that are already liquid at room temperature. These ionic liquids are composed of a "onium" unsymmetrical cation and a delocalized anion, largely TFSI and FSI. In turn, these molten salts can dissolve a lithium salt (LiTFSI or LiFSI) resulting in a transport of this metal cation representing @ 20-30% of the total conductivity. To these true ILs, we regroup here the solvates formed by LiTFSI or LiFSI with some glymes (G*n*: ($CH_3O(CH_2CH_2O)_nCH_3$)) [81-84]. They have some advantages over organic molecules as electrolyte solvents; they are less flammable and practically non-volatile. The very low charge to radius ratio of both the anion and the cation explains their very small lattice energy and low melting point. However, they also have disadvantages - high cost, low conductivity at low temperature, high viscosity and poor wetting characteristics with some electrodes due to high contact angle [85].

The main problem with ILs is the cathodic stability at low potential, which is attributed mainly to the cations. ILs containing nitrogen in a heterocyclic structure (imidazolium family) cannot be used with carbon anodes because the imidazolium cations are reduced or decomposed at the carbon electrode when the potential is polarized down to 0.7 V vs Li^+/Li. The electrochemical stability of ILs is improved in the negative voltage region with the addition of lithium salts [43-45] forming a SEI. In the case of Li-metal, the SEI is formed from ionic species that prevent further the electrochemical reduction of cationic species.

The stability at high potentials is relatively good and is due to oxidation of anions [86]. The 1-ethyl-3-methylimidazolium (EMI)-based ionic liquid has stimulated interest because of its low viscosity, high conductivity, and its oxidative potential is almost 5.0 V, but with the reducive potential at + 1 V vs. Li^+/Li, in practice the electrochemical window is 4 V. Anions with higher oxidation resistance are highly fluorinated ions such as tetra-fluoroborates [87], hexafluorophosphates but result in highly viscous liquids [88].

In most cases, the hydrophobicity of ILs is improved by the use of highly fluorinated anions ($[(R_FSO_2)_2N^-]$) with R_F = CF_3, C_2F_5, C_4F_9, although cation-containing perfluorinated alkyl chains have

also been beneficial [89,90].

The interest in ILs for Li-ion batteries was first investigated with ILs based on perfluoroanions that were already studied as counter-anions for lithium salts, in particular BF_4^- and $TFSI^-$ [91]. In practice, however, ILs based on $TFSI^-$ were preferred because they are immiscible in water so that the residual products such as alkali metal salts can be removed by washing in water. This is not possible with borate-based ILs, which are miscible with water [92]. In addition, the viscosity of the borate-based ILs (over 300 mPa s) [93] at room temperature is greater than that of the corresponding $TFSI^-$-based ILs (69 mPa s) [94]. In particular, $TFSI^-$ and further FSI forms low viscosity ILs even with aliphatic quaternary ammonium cations (AQA) mainly pyrrolidinium or piperidinium [95], which have wider electrochemical window [96] and are compatible with Li-metal [97-99] so they can be used at > 4 V. The AQA was used successfully in a cell with a lithium metal anode and $LiCoO_2$ cathode without any additive [100]. The onium cations, such as AQA and imidazolium-based C_{nmim+}, do not participate in the electrochemical process in lithium batteries, and their unique role is to maintain the IL in the liquid state.

With carbon anodes, ILs alone do not work due to the co-intercalation of the cationic species [46]. Although the addition of lithium salt is beneficial to solve the problem, the viscosity increases by adding LiTFSI salt is a drawback. The FSI anion ILs are as said above, less viscous, and even with concentrated LiFSI addition (50 mol.%) show very promising Li/LFP electrodes behavior. Another solution is to add carbonates [101,102], but the increased volatility and flammability become problematic. More recently, however, promising results were obtained [102] (see Fig. 4).

Li[FTFSI], where $FTFSI^-$ represents the (fluorosulfonyl)-(trifluoromethylsulfonyl)amide anion $[(FSO_2)(CF_3SO_2)N]^-$, was tested as a model of a pure lithium ionic liquid without any solvent molecules and also without a long alkyl and/or alkoxy moiety in the anionic species [103]. This salt melts at 100 °C and was tested at 110 °C in cells with lithium anode and either $LiFePO_4$ or $LiCoO_2$ cathodes. The electrochemical properties were encouraging, but the tests only lasted two cycles, so the aging and cycling life are unknown. These results showed that Li[FTFSI] is a unique lithium single ionic liquid that is promising in batteries used above 100 °C with an electrolytic window exceeding 4 V. Other electrolytes that satisfy these criteria are alkali molten salts at eutectic point: Li[TFSI]−K[TFSI] and Li[TFSI]−Cs[TFSI], Li[FTFSI]−Cs[FTFSI] and their mixtures [104]. However, Li-ion batteries are useful near room temperature, while the operating temperature for lithium metal-polymer batteries is typically 70 °C because the conductivity of the polymer at room temperature is too

small and this is considered as a handicap.

The introduction of siloxyl groups improves hydrophobicity [105,106], and this property was used to synthesize a new family of ILs composed of tetraalkylammonium cations with increased hydrophobicity; one alkyl chain is the (trialkyl-siloxy)ethyl group and anions of bis(perfluorosulfonyl)amide (TFSI, FSI, and FTFSI) [107]. All of them are liquid at room temperature except N-(2-Trimethylsiloxyethyl)-N-methylpyrrolidinium TFSI. The cathodic stability is improved owing to the silylation of the OH group rendering the electrolyte stable to 0 V vs. Li^+/Li. The electrochemical window may exceed 5 V, depending on the anion that is used. Various ILs were tested with different anions, but in practice the best choice is the $TFSI^-$ anion because of its superior stability due to the fact that it contains no hydrolysis-sensitive fluorine atoms as FSI^- does. A family of molten salts that is based on the *N*-alkyl, *N*-alkyl pyrrolidinium cation and the $TFSI^-$ anion was proposed [95, 108]. Some of these molten salts are highly conductive, or form highly conductive plastic crystals upon doping with LiTFSI [109].

The disadvantage of TFSI-based ILs is the lower conductivity with LiTFSI in the electrolyte compared with FSI-based ones [110]. Another problem that limited the use of ILs in Li-ion batteries is their decomposition on graphite anodes. This problem was resolved by using an ILs-based electrolyte containing TFSI anions and an additive of vinylene carbonate (VC) that suppresses ILs reduction and stabilizes the SEI [111-114]. This finding was extended to the use of ILs blended with organic electrolytes (EC-DEC) to take advantage of the low vapor pressure and high non-flammability of ILs to improve safety, and inherit the high conductivity of organic electrolyte, even though adding carbonates [101] is effective in increasing the conductivity and the fluidity. A thorough study of the IL, with TFSI anions combined with EMI cations, which was selected because of its relatively high conductivity and low viscosity was reported [115]. The conductivity and viscosity of the EMI-TFSI ionic liquid/EC-DEC mixtures at different concentrations of EMI-TFSI are reported in Fig. 5. When the IL concentration in the mixture increases from 0 to 60%, the conductivity rises as the "salt" (IL) is added to the solvent EC-DEC. However, the conductivity reaches a maximum and decreases at higher concentrations to return to the lower conductivity of the pure IL. The viscosity increases with the IL concentration up to 60%, so there is an optimum concentration of IL around 60% in the mixed electrolyte where the viscosity is still low (16-17 Pa s), and the conductivity is still acceptable (greater than 10 mS cm^{-1}). Moreover, the electrolyte was not flammable at this composition, and the evaporation temperature increased by 252% with respect to the organic electrolyte. Therefore, this new

electrolyte is an improvement, with the three properties needed for an electrolyte: high conductivity, low viscosity and non-flammability. The tests on a $LiFePO_4$ half-cell showed that the addition of 60% EMI-LiTFSI Il in the organic electrolyte did not affect cell performance at 2C rate.

2.3. Salts for Li metal batteries

The only industrial systems that use Li are the "Bluesolution" batteries, in a car pay-and ride scheme in several cities, the largest fleet deployment being in Paris. The electrolyte is a solid polyether, mainly PEO, and the salt LiTFSI. The temperature of operation of the batteries is on average 70 °C. Effectively, the development of lithium metal/polymer batteries has been impeded by the difficulty in finding solid electrolytes with good ionic conductivity and mechanical properties that minimizes dendrite formation at the lithium surface. The difficulty arises from the fact that these properties are antinomic. The best conductivity in PEO electrolytes is obtained with LiFSI. Other hosts polymers with remarkable conductivities are polyesters, like random copolymers of trimethylene carbonate and co-ε-caprolactone [116] or poly(ethylene carbonate) [117]. Solid-state batteries with these polymers and TFSI were able to operate at RT, albeit at low current densities. A distinct advantage of the polyesters is a higher transference number ($t_+ > 0.4$) as compared with PEO ($t_+ \approx 0.2$) especially at high salt concentrations, reducing the establishment of a salt gradient. A recent review [118] on electrolytes and the fabrication of lithium films describes encouraging progress on the development of all-solid lithium batteries. Mendemark et al. have reviewed the "Beyond PEO Electrolytes" [119]. There is also considerable activity worldwide for Li metal-based batteries using a liquid electrolyte to meet the conductivity requirement and the choice of the solvent is sovereign since it contains most of the organic components that forms the SEI, which in turn determine the morphology of the lithium deposit and the electrochemical properties [120]. The most popular solvent in such batteries is 1,3-dioxolane (DOL), first proposed by Aurbach and co-workers [121]. The salts in the electrolyte are also important to stabilize the SEI and prevent dendrite. The salts used with Li-metal are limited but include $LiPF_6$, LiTFSI, LiFSI, TDI [118]. An interesting salt is $LiNO_3$, which participates, mainly as additive, in the formation of a stable passivation film on the lithium surface [122,123]. It thus protects against the attack of polysulfides in Li-S batteries [124] and potentially suppresses gas generation [125] (see Fig. 6). However, from other sources, above 40 °C, $LiNO_3$ itself produces gas and causes swelling [126], so cells containing this salt cannot pass Test 2 of UN38.3 Transport of Dangerous Goods Certification

[127] and cannot be used in mass-produced commercial batteries. In batteries with lithium anodes, including Li-S batteries (see [128] for a review), ionic liquids containing $TFSI^-$ anions are often used because they improved Li metal cycling efficiency, but only at low C-rates. The reason is that the larger number of F atoms in TFSI form a LiF passivation layer at the lithium surface. The rate capability remains a problem because LiF forms an insulating layer. The first salt blends tested in Li-metal batteries were not successful because of low conductivity [129]. However, more recent salt blends were much more successful. In particular, the mixture LiTFSI/LiFSI with DOL solvent mitigated dendrite formation at the lithium surface, even at current densities as high as 10 mA cm^{-2} [130]. The success of this salt combination was due to the synergetic effect of LiFSI that provides high conductivity and improves the interfacial behavior, while LiTFSI acts as stabilizer. A catalytic action tertiary amine base is admixed with the LiFSI in order to prevent polymerization of DOL. Adding dimethoxymethane (DME) as co-solvent improves further the solubility of LiFSI. The LiFSI-LiTFSI/DOL-DME solution was tested in Li//Li symmetric cells and in cells with Li anode and $LiFePO_4$ or sulfur composite (38.7% S). In all these cases, high cycle efficiency of ca. 99% and dendrite-free Li deposit were achieved. The excellent cycling performance and favorable lithium morphology were obtained, even at a high current density of 10 mA cm^{-2}. The combination of LiTFSI and LiBOB in a carbonate solvent mixture also formed an effective SEI at the lithium surface in Li-metal batteries because of the highly conductive sulfur-rich components found in the SEI film [131].

Utilization of graphite as both the anode and cathode is possible and constitutes an example of dual-ion battery. $LiPF_6$ salt was chosen, because both Li^+ and PF_6^- ions can be inserted in graphite. Li^+ intercalates into the negative electrode, and PF_6^- intercalates into the positive electrode when the cells are charged, depleting the electrolyte of salt. The ions return to the electrolyte during discharge. The cell potential during anion intercalation rises to over 5 V, so the solvent chosen for such a battery is ethyl methyl sulfone (EMS), which oxidizes only above 5.5 V. A capacity of 100 mAh g^{-1} was obtained with a $LiPF_6$/EMS electrolyte [132]. Comparable capacities with very good cycle life were obtained with for dual-graphite cells using ionic liquid-based electrolytes, where the anion was $TFSI^-$ [133,134]. Since the chemical compatibility of LiTFSI with graphite is rather poor, dual-batteries with LiTFSI salt utilized Li anodes instead of graphite [135-137], in combination with graphite cathodes. The electrolyte was a mixture of LiTFSI and *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide ($Pyr_{14}TFSI$), in which only LiTFSI is active, while $Pyr_{14}TFSI$ increases the ionic conductivity and stays a liquid. Another electrolyte was proposed by Meister at al. [138] fluorosulfonyl-

(trifluoromethanesulfonyl)imide ($FTFSI^-$) in Pyr14FTFSI, that takes advantage of the smaller size of the $FTFSI^-$ ion compared to the $TFSI^-$ ion. However, the results were not much different, with capacities in the range 43-50 mAh g^{-1} and a cut-off voltage of 4.8 V. When the cut-off voltage is raised to 5.2 V, the capacity increases to 99 mAh g^{-1}, but the capacity fade is much more important (see Fig. 7) and the coulombic efficiency decreased. Another anion insertion battery with Al-metal anodes will be discussed later in the section on Al-based batteries.

This use of $Pyr_{14}TFSI$ illustrates the interest in pyrrolidinium-based electrolytes. Not only Pyr_{14}^+, but also N-propyl-N-methyl-pyrrolidinium Pyr_{13}^+ cations are used in lithium batteries. The Pyr_{13}^+ cation is slightly smaller than the Pyr_{14}^+ cation, so we can expect better ionic conductivity at low temperature. The $Pyr_{13}TFSI$-$Pyr_{13}FSI$ blends have ionic conductivities greater than 10^{-4} S cm^{-1} at -20°C, and an optimized TFSI:FSI mole ratio of 2:3 [139]. The $TFSI^-$ anions increase the stability towards oxidation, and the FSI^- anions increase the ionic conductivity. The fact that the blend is a liquid with high ionic conductivity even at -20°C was attributed to the combination of the two ionic liquids, which hinders crystallization of the resulting mixture. An electrolyte with LiTFSI salt in this ionic liquid mixture was tested with the optimized concentration of 0.1LiTFSI-0.3$Pyr_{13}TFSI$-0.6$Pyr_{13}FSI$, and good compatibility was observed with a high-voltage cathode (NMC) and graphite anode [140]. The next section discusses the important role of pyrrolidinium-based ionic liquids in sodium-ion batteries.

2.4 Salts for use in organic battery

The discussion focused on results obtained with Li salts added to electrolytes so far. However, a carbonyl-based Li salt of tetrahydroxybenzoquinone ($Li_4C_6O_6$) can be both reduced to $Li_2C_6O_6$ and oxidized to $Li_6C_6O_6$ [141]. Lithiated oxocarbon salt ($Li_{2+x}C_6O_6$) has a very large theoretical capacity of 580 mAh g^{-1}, from x=0 to x=4. In this compound, each Li is coordinated to four oxygen ions of two or four neighboring C_6O_6 units. The main stabilizing force comes from the formation of extra aromatic systems after electron injection. The $Li_4C_6O_6$ compound shows good electrochemical performance vs. Li with a sustained reversibility of ~200 mAh g^{-1} at an average potential of 1.8 V. This battery chemistry displays a more stable cycle compared to inorganic electrode materials, but the operating voltage is too low. Since then, a novel quinone-based oligomeric lithium salt of poly(2,5-dihydroxy-p-benzoquinonyl sulfide) with average polymerization degree of 7 was used as a cathode in a lithium-metal battery. High reversible capacity (268 mAh g^{-1}), high cycling stability (1500 cycles, 90%) and high rate capability (5000 mA g^{-1}, 83%) were obtained. The high capacity compensates for the low

potential (the main charge/discharge process was in the range 1.8-2.3 V) [142].

To achieve the sustainability required for next generation energy storage systems, the development of rechargeable batteries with a low CO_2 footprint is desirable. This is the motivation for extended research to replace the inorganic electrodes by organic electrodes. The dual-battery with graphite anode and cathode mentioned in the previous section is an example. The use of the salts mentioned in the present section also belongs to this approach. A huge amount of work devoted to organic-based lithium and sodium batteries justifies a separate review that we are presently writing, which should be published by next year. Therefore, the oxocarbon salt we have mentioned should be considered only as an example in this context. The reason of this choice is that, except 5,7,12,14-pentacenetetrone, $Li_2C_6O_6$ is the only example of four-Li uptake, due to the fact that $C_6O_6^{4-}$, when reduced, forms an additional aromatic system (benzene in this case) to help stabilization [143Y. Liang, P. Zhang, J. Chen. Function-oriented design of conjugated carbonyl compound electrodes for high energy lithium batteries. Chem. Sci., 2013, 4, 1330-1337]. Replacing Li by Na, we obtain the $Na_2C_6O_6$ sodium rhodizonate dibasic (SR) sodium salt that has tested as a cathode for sodium-ion batteries [144]. Structured in nanorods with uniform diameters of ca. 200 nm, SR delivered 190 mA h g^{-1} at current density of 0.1C and retained 90% of its second cycle capacity after 100 cycles.

3. Sodium salts

3.1. Salts for sodium-ion batteries

The studies of Na-ion batteries (SiBs) are taking place in parallel with the studies of Li-ion batteries. The Li-ion battery dominates the market today because of its high rate capability and energy density. Sodium is abundant and a low-cost element for energy storage devices but has a propensity for dendrite formation [145]. Some reviews on Na batteries have addressed the electrolytes, for example, non-aqueous electrolytes [146], while other reviews discussed aqueous liquid electrolytes and solid electrolytes [147]. Reviews of anodes and cathode materials for Na-based batteries are available [148-151], which suggest that there is significant interest in SiBs. A review on SiBs including electrolyte salts, solvents, additives and binders can be found in Ref. [152]. The use of aqueous solvents will not be addressed here for several reasons:

(1) electrochemical window possible for aqueous SiBs is only 1.23 V;

(2) energy density is low (below 80 mAh g^{-1} in practice for the electrodes);

(3) cycle life is low, partly due to corrosion of the current collectors.

3.2. Sodium salt with non-aqueous solvents

The usual non-aqueous solvents in LiBs are also used in SiBs: binary or ternary systems of cyclic (PC, EC) and linear (EMC, DEC, DMC) carbonate esters. One key difference between the component in LIBs and SiBs is the choice of negative electrode. Graphitized carbon is the most popular anode material in LiBs, while for SiBs, hard carbons (HCs) are used, presumably because the Na-C system lacks suitable binary intercalation compounds. This issue was circumvented by co-intercalation that occurs in diglyme-based electrolytes, in which a SiBs with graphite anodes is able to deliver a capacity close to 100 mAh g^{-1} for 1000 cycles [153]. However, graphite cannot be used in SIBs with carbonate ester-based electrolytes, a major difference with LIBs, and the reason for the choice of hard carbon in SiBs. Hard carbons do not co-intercalate solvent molecules, which is responsible for exfoliation of graphite. Consequently, PC that is prohibited in LiBs is now a potential solvent in electrolytes with hard carbon in SIBs [154], especially when sodium polyacrylate is used as a binder with hard carbon, because this binder covers the surface of hard carbon and the passivation is highly improved in comparison to poly(vinylidene fluoride) (PVdF) binder [155].

The salts that are used with carbonate ester solvents in SiBs are almost exclusively either $NaClO_4$ or $NaPF_6$. Similar to $LiPF_6$, $NaPF_6$ is sensitive to moisture, while $NaClO_4$ has safety problems that will forbid a commercial use. In addition, the oxidative stability of ClO_4^- anions is less than that of PF_6^- in EC:DEC solvents [156]. Despite its combination of very electronegative element, ClO_4^-, electrolyte decomposition occurs at >4.5 V vs. Na^+/Na, which limits the cut-off voltage to 4.5 V when $NaClO_4$ is used [157,158]. Therefore, $NaPF_6$ is preferred, especially in dual-ion cells with graphite cathode and Na-metal counter-electrode in 0.5 mol L^{-1} $NaPF_6$/EC:EMC electrolyte that delivered 86.2 mAh g^{-1} discharge capacity at the 120th cycle at C/4 rate, and with coulombic efficiency of nearly 97% [156]. However, this performance is still not as good as that achieved with the lithium-based counterpart (Li-metal anode, graphite cathode, $LiPF_6$/EC:EMC electrolyte). A tin-graphite dual-ion battery with 1 mol L^{-1} $NaPF_6$ in EC:DMC:EMC (1:1:1 v/v/v) delivered 74 mAh g^{-1} at 2C (1C corresponding to 100 mA g^{-1}), 94% capacity retention after 400 cycles and high coulombic efficiency of 95% in a voltage window of 2.0–4.8 V [159] (Fig. 8).

The reason why graphite is viable for Na-ion storage in cells with ether-based electrolytes is due to co-intercalation of solvent molecules and Na^+-ions to form ternary graphite intercalation compounds (t-GICs) [160,161]. Different results were obtained in cells with Na-metal counter-electrodes [162-164]. The remarkable cycle life is strong evidence that graphite in ether-based electrolytes is compatible with sodium metal. Cui et al. suggested that when the salt is $NaPF_6$, in ether solvents (except triglyme) forms a uniform and thin SEI layer mainly composed of Na_2O and NaF to protect the surface of sodium [164], which suppresses dendritic growth and promotes high coulombic efficiency and high cycle life.

Crystalline polymeric Schiff bases are able to electrochemically store more than one Na atom per azomethine group at potentials between 0 to 1.5 V vs. Na^+/Na. These Schiff-base anodes provided reversible capacities of up to 350 mA h g^{-1} in SiBs with an electrolyte consisting of NaFSI in methyltetrahydrofuran (Me-THF) [165].

Organic electrolytes have the advantage of good conductivity, but their flammability can result in safety hazards. The safety hazard was overcome with an electrolyte composed of 0.8 mol L^{-1} $NaPF_6$ in trimethyl phosphate (TMP) plus 10 vol.% fluoroethylene carbonate (FEC) as a SEI-forming additive. TMP is a liquid organic phosphate that is nonflammable and a very appropriate choice for safe electrolytes in SiBs [166] (see Fig. 9). Note the TMP decomposes electrochemically on carbonaceous anode, which is the reason why it cannot be used in lithium-ion batteries, and it prohibits the use of hard carbon as an anode in SiBs. The SiB using this electrolyte with Sb-based anode and $NaNi_{0.35}Mn_{0.35}Fe_{0.3}O_2$ cathode delivered a capacity of 300 mAh g^{-1} at current density of 50 mA g^{-1}. This performance is attributed to the stable SEI film formed by FEC decomposition on the anode and cathode.

3.3. Ionic liquids in SiBs

Perfluoroanions, which were evaluated as counter-anions (e.g. BF_4^- and $TFSI^-$) for lithium salts were also used in SiBs with EMI cations because of its relatively high conductivity and low viscosity [167-169]. However, the electrochemical window of EMI-based ionic liquids is limited to 4 V. EMI-TFSI oxidative potential is almost 5.0 V, but the reducive potential is + 1 V vs. Li^+/Li. In practice its use as electrolyte is limited, in the absence of a SEI builder, to anode materials like $Li_4Ti_5O_{12;}$ this material intercalates lithium, but the result is a two-phase mixture. The potential window for

electrolytes in SiBs was increased by adding $NaBF_4$ to $EMIBF_4$ but was detrimental to the ionic conductivity [169].

For these reasons, attention was focused on pyrrolidinium-based ionic liquids (Pyr_{14}^+ and Pyr_{13}^+ cations) for SiBs, similar to those in lithium batteries. NaFSI in $Pyr_{13}FSI$ was considered as electrolyte for Na/$NaCrO_2$ SiBs [170,171] and Na/HC half-cells [172]. These cells, however, have good electrochemical properties only at high temperature (90°C), and the performance depends significantly on the salt concentration. For Na/$NaCrO_2$ cells at 90 °C, the optimum concentration is 40 mol.% NaFSI, while the best composition for Na/HC at 90 °C is 10 mol.% NaFSI. The capacity of the HC reached 260 mAh g^{-1} at 50 mA g^{-1}, and 211 mAh g^{-1} at 1000 mA g^{-1} [173]. A high salt concentration (1 mol L^{-1} NaFSI) gives poor results with Na metal, but better results than conventional organic electrolytes in full cells (HC anode, $Na_{0.44}MnO_2$ cathode), where the cathode capacity was 117 mAh g^{-1} at 0.1C rate, with 3% decay after 100 cycles [174].

Pyr_{14}^+-based electrolytes were explored in parallel with Pyr_{13}^+. The analog to Pyr_{14}^+ cations in electrolytes is NaFSI in $Pyr_{14}FSI$ ionic liquid [174]. The interface between this electrolyte and Au(111) was investigated as a function of salt concentration [175], and confirmed the general trend already observed in lithium batteries that the decomposition potential of the cation shifts to more negative potentials when metal salts are added to ILs [176]. In most cases, however, the Pyr_{14}^+ cations are associated to the $TFSI^-$ anions rather than FSI^-. A study of $Pyr_{14}TFSI$-NaTFSI was conducted [177,178], and this electrolyte was tested with different salt concentrations in a $NaFePO_4$/Na cell [179]. An optimum capacity of 125 mAh g^{-1} was observed in 0.5 mol L^{-1} NaTFSI in $Pyr_{14}TFSI$ at 50 °C, and 65% capacity was retained at 1C. However, the capacity decreased by a factor 2 at room temperature, which confirms that ionic liquids are preferred to organic electrolytes only at higher temperatures. Different salts ($NaClO_4$, $NaBF_4$, NaTFSI, $NaPF_6$) were tested in $Na_{0.44}MnO_2$/Na cells in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (BMP -TFSI) [87]. The best performance was obtained with $NaClO_4$, with a capacity of 115 mAh g^{-1} at 0.05C and 75 °C, and 85% of the capacity was retained at 1C, owing to the lower SEI resistance of the cathode and anode. Meanwhile, a capacity of 120 mAh g^{-1} was obtained at room temperature in a full cell $Na_{0.66}Ni_{0.22}Fe_{0.11}Mn_{0.66}O_2$/Sb-C with NaTFSI in $Pyr_{14}TFSI$ [180] at an average working potential of 2.7 V.

NaFSI combined with other ionic liquids were tested as electrolytes in full SiBs at high temperature [181-183]. For instance, a [NaFSI]-[C_3C_1pyrr][FSI] (C3C1pyrr: N-methyl-N-propylpyrrolidinium) electrolyte in Na//$NaCrO_2$ cells at 80 °C delivered a capacity of 106 mAh (g-

$NaCrO_2)^{-1}$ that was stable over 100 cycles [170]. This electrolyte has good conductivity and high stability up to 5 V, and thus is a potential electrolyte for SiBs [184], but has not been tested.

3.4. Salts in all-solid-state sodium metal batteries

So far, solid polymer electrolytes with sodium have not been successfully deployed, as is the case with lithium batteries with its only exception, which is attributed to several reasons. The solid polymer must be used at higher temperatures, typically >60 °C, because of its low conductivity, but since the melting point of sodium is 98 °C, the practical temperature range to use Na anodes with polymer electrolytes is very limited. In practice, the temperature in solid sodium metal-polymer batteries must be reduced to 60 °C, where the conductivity of the polymers is usually low. The main efforts to overcome this problem is to reduce the activation energy for the ionic conductivity of the polymers. PEO-based electrolytes were investigated many years ago with different salts: $NaClO_4$ [185], $NaPF_6$ [186], $NaClO_3$ [187], and $NaLaF_4$ [188] (a crystalline solid electrolyte with fluorite structure). However, the ionic conductivity of these salts in PEO-based electrolytes is only about 10^{-6} S cm^{-1} at RT. Recently, NaTFSI and NaFSI were tested with PEO [189]. A higher conductivity was obtained with NaTFSI because of the stronger interaction between FSI^- with Na^+ compared to $TFSI^-$. The ionic conductivity of NaTFSI-$(PEO)_9$ is 4.5×10^{-5} S cm^{-1} at 20 °C. A conductivity of 2×10^{-5} S cm^{-1} was obtained with PEO-PEGDME blend host polymer with SiO_2 particles that were functionalized by grafting with sodium 2-[(trifluoro-methane-sulfonylimido)-N-4-sulfonylphenyl]ethyl salt [190]. The grafting on the polymer immobilized the F-bearing anions, which increases the transference number of the sodium ions to close to unity, and the conductivity increased to close to 1.3×10^{-4} S cm^{-1} at 60 °C. An even better conductivity was measured at the same temperature with $NaClO_4$ in the ceramic-polymer electrolyte, TiO_2:PEO, at an optimum composition 5 wt.% TiO_2, EO/Na=20 [191]. However, the electrochemical properties were disappointing, so compatibility with sodium metal is questionable.

Other polymer-salt combinations were also considered: poly(vinyl alcohol) with NaBr salt [192], poly(vinyl pyrrolidinone) with $NaClO_3$ [193] and $NaClO_4$ [194], NaF [195]. However, the only combination that produced electrolytes with an appreciable conductivity (7.1×10^{-4} S cm^{-1}) that is greater than that of ceramic-polymer blends is polyacrylonitrile (PAN) with 24 wt.% $NaCF_3SO_3$ (sodium triflate, also denoted NaTf) [196].

Sodium triflate $NaCF_3SO_3$ (NaTf) was also evaluated in a hybrid solid electrolyte that is based on a poly(vinylidene fluoride-co-hexafluoropropylene) (PVdF-HFP) matrix with a NASICON ceramic

powder $Na_3Zr_2Si_2PO_{12}$, PVdF–HFP binder, and 1 mol L^{-1} NaTf/TEGDME liquid electrolyte in a 70:15:15 weight percentage. The conductivity of this electrolyte is 1.2×10^{-4} S cm^{-1} at 0 °C. Studies of the electrolyte in a half cell with a $NaFePO_4$ cathode yielded a capacity of 131 mAh g^{-1} at 0.2C, and 330 mAh g^{-1} relative to the negative for the full cell, $NaFePO_4$//hard carbon, with good rate capability and cyclability [197]. These results are much better than the performance obtained with inorganic ceramic electrolytes, which have better bulk ionic conductivity. Note, however, that owing to the presence of TEGDME plasticizer, this electrolyte already belongs to the family of gel-polymer electrolytes.

3.5. Salts in gel-polymer electrolytes

Gel-polymer electrolytes are distinguished from polymer-salt electrolytes by the use of a solvent or plasticizer to improve the ionic conductivity. For example, a solution of NaTf in EMI triflate (EMITf) ionic liquid immobilized in PVdF-HFP increased the conductivity to 5.74×10^{-3} S cm^{-1} at room temperature for a gel polymer electrolyte EMITf:PVdF-HFP (4:1 w/w) + 0.5 mol L^{-1} NaTf [198].

The most common salt in gel-polymer electrolytes is $NaClO_4$, which is found in poly(methyl methacrylate (PMMA) with SiO_2 nanoparticles and 1 mol L^{-1} $NaClO_4$/EC-PC [199], cross-linked PMMA and 1 mol L^{-1} $NaClO_4$/PC-FEC [198], PVdF-HFP with 1 mol L^{-1} $NaClO_4$/EC-DC-DEC [200], PVDF-HFP plus glass-fiber paper and polydopamine (PDA) coating with 1 mol L^{-1} $NaClO_4$/PC [201]. The gel polymer electrolyte with a conductivity of 5.4×10^{-3} S cm^{-1} produced the best results [202]; an initial capacity of 120 mAh g^{-1} that decreased to @100 mAh g^{-1} after 100 cycles was obtained in a cell with $Na_2MnFe(CN)_6$ cathode and Na metal anode.

3.6. General trends

The ionic conductivity of the electrolyte in SiBs receives the most attention. The conductivity depends on all of the components in the electrolyte. The salt plays a major role, for example, the conductivities of PC-based electrolytes (1 mol L^{-1} salt) with $NaPF_6$, $NaClO_4$ and NaTFSI, are 8, 6.5 and 6.2 ($\times10^{-3}$ S cm^{-1}) at room temperature, respectively [157,158]. However, when the salt is added to ionic liquids, promising conductivities are also observed. For instance, the conductivities of ionic liquid $Py_{1,4}$-TFSI with $NaBF_4$, $NaClO_4$, NaTFSI and $NaPF_6$ are 1.9, 1.0, 0.5 and 0.4 ($\times10^{-3}$ S cm^{-1}) [87]. The

lowest conductivity was obtained with $NaPF_6$ in the IL electrolyte, while in the PC-based electrolyte, it yielded the highest conductivity. This illustrates the synergy between the salt and other components of the electrolyte, particular the solvent, in determining the ionic conductivity. For instance, monoclinic $Na_2Fe_2(CN)_6.2H_2O$//graphite cell with 1 mol L^{-1} $NaBF_4$/tetraglyme electrolyte showed excellent capacity retention at 35 mAh g^{-1} (anode + cathode) over 3000 cycles at C/4 rate and 2.3 V average operating potential [203], which is a much better performance than in case carbonate-based electrolytes are used either with $NaPF_6$ or $NaClO_4$.

The electrochemical stability shows a general trend. With a carbon gas diffusion layer as the electrode, the electrochemical stability of the $NaPF_6$-based electrolyte is 5.0 V, much higher than that of $NaClO_4$ [50]. This is consistent with the trend $PF_6^- > ClO_4^- > CF_3SO_3^-$ observed in lithium batteries [186]. The salt plays a crucial role in electrolyte stability, as illustrated with electrolytes containing difluoro(oxalato)borate salt that are stable up to 5.5 V in PC, EC/DEC or EC/DMC, while none of these electrolytes are stable to such high potential when the salt is $NaClO_4$.

4. Magnesium salts

Magnesium batteries are very attractive despite the lower theoretical capacity of Mg, 2061 mAh cm^{-3} than that of lithium (3862 mAh cm^{-3}). Magnesium has several advantages over lithium:

- Mg is abundant and much cheaper than Li,
- Mg is not prone to dendrite formation [204],
- Mg is more stable than lithium in air.

The major problem with Mg remains the lack of a suitable solvent-electrolyte combination [205] because the SEI formed at the Mg surface in common electrolytes blocks ion transport [206,207]. In addition, the electrolyte must be stable at the Mg redox potential (-2.37 V vs. NHE, compared to that of Li, -3 V), and the cathode active element that may operate at + 1 V vs. NHE. In addition, Mg is reactive to many polar solvents and anions [208,209], so that in practice the choice of electrolyte has been limited to inert ethereal solvents [210-213]. The first results on rechargeable Mg-batteries were obtained with an electrolyte obtained by electrolysis of Grignard, organo-borate and amino-magnesium reagents, with ethereal solvents such as tetrahydrofuran (THF) [206]. Different solutions were proposed in the 1990s, but they did not solve the poor cycle life and rate capability. There are several reviews on Mg-batteries that were published a few years ago [214,215]. The major challenge is to identify suitable salts and non-polar solvents for the electrolyte that have an acceptable potential stability window.

Aurbach et al. [212] reported a major breakthrough with an electrolyte that has improved oxidative stability, which was obtained by a Grignard reagent combined with Al-based Lewis acid including an alkyl group. This finding initiated further research on other organohalo-aluminate electrolytes by the same group [211, 216,217] and others [218], which further improved the performance by developing an electrolyte with oxidative stability up to 3.2 V vs. Mg and higher current densities [218]. The oxidative stability was raised to 3.5 V and 3.7 V by using phenylmagnesium chloride with a boron-based Lewis acid in tetrahydrofuran, such as tris(pentafluorophenyl)borane [205], or tri(3,5-dimethylphenyl)borane [212]. The fluorinated alkoxyaluminate magnesium electrolytes [219], and fluoroalkoxyborate electrolytes [220] also have oxidative stability > 3.5 V vs. Mg, which is typical for electrolytes with aluminum trichloride as the Lewis acid. The fluorinatedaryl magnesium reagents or fluorinated organo aluminates can react explosively. It is highly recommended to replace the fluorinated aluminates by borates because the latter are not explosive [205].

The electrolytes containing organometallic reagents are unstable to air and water, and until recently, it was assumed that inorganic electrolytes did not work in Mg batteries. However, Doe et al. [216] made a breakthrough by synthesizing $Mg_mAl_nCl_{[2m+(3n)]}$ salts by acid–base reaction of $MgCl_2$ and the Lewis acidic compound $AlCl_3$ and demonstrating upwards of 99% coulombic efficiency with anodic stability of 3.1 V [221]. Further studies were pursued on this new family of magnesium-aluminum chloride-complex (MACC) electrolyte that avoided the onerous conditioning process [222]. As-prepared MACC is inactive for Mg deposition, and therefore conditioning the electrolyte is required to enhance Mg electrodeposition [223,224]. The onerous conditioning process was successfully overcome by using a higher Mg/Al ratio in the synthesis procedure [225]; however, there are some drawbacks. The presence of free chloride ions in the salts/complexes results in corrosion of non-noble metals, which prevents the use of Al or stainless steel current collectors [205,212,226,227]. Tutusaus et al. [79] applied an ion-exchange pathway to synthesize an active, non-corrosive electrolyte ($Mg(CB_{11}H_{12})_2$/tetraglyme (MCC/G4) and MCC/triglyme) with high oxidative (3.8 V vs. Mg) stability. Another strategy to improve the stability in air and moisture is to enhance the stability of the modified Grignard reagents by replacing phenoxides [212,228] with alkoxides [229]. The non-Grignard magnesium halide salts [230,231] show very good electrochemical properties and better stability towards air, compared to those of Grignard reagents, because THF is the solvent. However, THF is not desirable because of its high volatility and its tendency to form peroxides, so recent efforts were focused on electrolytes that are THF-free and chloride-free.

4.1. THF-free liquid electrolytes

Boron hydride $Li(BH_4)$ is of interest for lithium batteries because of its high ionic conductivity and relatively strong reducing power of BH_4^-anions, which led to the proposal to investigate magnesium borohydride $Mg(BH_4)_2$ for Mg batteries [232]. $Li(BH_4)$ has many applications, and one example is for hydrogen storage, which was the subject of a recent review on its synthesis and structure [233]. As expected, this salt facilitates Mg deposition and stripping when a standard Chevrel phase cathode is chosen [232]. By mixing the two borohydride salts, $LiBH_4$-$Mg(BH_4)_2$, in dimethoxyethane (DME, monoglyme) solvent, Mohtadi et al. produced a cell with Coulombic efficiency of 94%, and a peak stripping current density of 25 mA cm^{-2} that was achieved due to the higher conductivity when $LiBH_4$ is added. A Mg-battery with an electrolyte containing 0.5 mol L^{-1} $Mg(BH_4)_2$/1.5 mol L^{-1} $LiBH_4$ in tetraglyme and TiO_2 cathode retained a capacity of 140 mAh g^{-1} over 80 cycles. A coulombic efficiency close to 100% was reported with the electrolyte 0.1 mol L^{-1} $Mg(BH_4)_2$/1.5 mol L^{-1} $LiBH_4$ in DGM solution with $LiBH_4$ [234]. DGM is a diglyme (a tridentate ligand) with boiling and flashpoint temperatures of 162 and 57 °C, respectively, which produces a much safer Mg battery than one using THF. To understand the remarkable improvement linked to the addition of $LiBH_4$, Chang et al. investigated the electrodeposition of Mg on the anode in this electrolyte and attributed the effect to the co-intercalation of Li and Mg ions [235]. These results suggest that $MgBH_4^+$ is the electroactive species in magnesium borohydride electrolytes. The anodic-stability potential on stainless steel in 0.5 mol L^{-1} $Mg(BH_4)_2$/1.5 mol L^{-1} $LiBH_4$/tetraglyme solution was 2.4 V vs. Mg. 100% Mg deposition/dissolution efficiency was obtained, with high cycling reversibility [236] (see Fig. 10). Such a high coulombic efficiency was also achieved with another THF-free electrolyte, namely 0.35 mol L^{-1} $(HMDS)_2Mg–2AlCl_3$ in diglyme, where HMDS is bis(hexamethyldisilazide anion) [205]. The salt blend $(HMDS)_2Mg$ with $MgCl_2$ instead of $AlCl_3$ has the advantage of a simpler synthesis [237]. This result also illustrates that the solubility of non-Grignard magnesium halide salts, which is low when they are used individually in ethereal solution, is greatly enhanced by adding a second salt [238,239]. In the same way, ternary electrolytes consisting of non-Grignard magnesium chloride, $Mg(TFSI)_2$), and triglyme were proposed, and tests showed seemingly good electrochemical properties at 100 °C [240].

4.2. Electroactive cations

The electroactive species in halide-based electrolytes is $MgCl^+$ or $Mg_2Cl_3^+$ [241-248]. The organohalo-aluminate electrolytes obtained by reaction between a Grignard reagent and $AlCl_3$ [241], was a subject of a review publication [249]. The $Mg_2Cl_3^+$ ion is one of the active species in HMDS-based electrolytes [213] that has attracted significant interest because of its oxidative stability (3.3 V) and applications in haloaluminate-based electrolytes [218] and carboranyl-MgCl electrolytes [250].

The promising performance of a Mg/TiS_2 cell with $MgCl^+$ electroactive ions in a standard electrolyte, $[Mg_2Cl_3]^+[AlPh_2Cl_2]^-$ + THF and $Py14^+Cl^-$], was reported [251]. The TiS_2 cathode was expanded by intercalation of $Py14^+$ [1-butyl-1-methylpyrrolidinium] ions during full discharge. A reversible intercalation of 1 and 1.7 magnesium monochloride cations per titanium at 25 and 60 °C, respectively, was observed, corresponding to 400 mAh g^{-1} capacity based on the mass of TiS_2; the capacity at 240 mA g^{-1} was 150 mAh g^{-1} and remained above 100 mAh g^{-1} after 500 cycles. Similar tests with a THF-free electrolyte have not been performed, consequently the possibility of eliminating THF from commercial cells remains unanswered.

4.3. Ionic liquids

The high volatility of alkyl carbonates or of THF and monoglyme that leads to safety hazard is an issue in both Li-ion batteries and Mg batteries. Therefore, the same remedy was investigated for both types of batteries, namely the use of ionic liquids as an alternative to volatile solvents. Magnesium triflate in an imidazolium-based ionic liquid was proposed for Mg batteries [252], but it was not compatible with Mg electrodes (unstable SEI problems) [253]. However, phenyl magnesium bromide [254] and alkylmagnesium bromide [255] are viable options in ionic liquid solvents containing the salts of N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium $DEME^+$ cation like DEMETFSI dissolving LiFSI and $Mg(TFSI)_2$ [256]. This finding motivated studies on DEME-based ionic liquids as a solvent and an electrolyte consisting of Grignard reagent (ethylmagnesiumbromide in THF) and $[DEME]^+[TFSI]^-$ ionic liquid was evaluated [255], but effective plating/stripping of Mg was obtained only if THF is added as co-solvent. Stripping peaks for magnesium were observed in solutions of phenylmagnesium chloride in BMP -TFSI, but only at 150 °C [254]. $MgCl_2$ reacts with $AlCl_3$ in ionic liquids to produce an electrolyte that co-deposits Al and Mg [256-258], like the $MgCl_2/AlCl_3$ (MACC) electrolyte in the initial cycles [259]. Watkins et al. reported that the chelating ILs with a polyether chain from the organic pyrolidinium cation from the IL forms a complex with the magnesium ion in the ionic salt [260]. The presence of a polyether chain in the IL improves electrochemical performance

[261-269].

$Mg(TFSI)_2$ salt was also used [270], which is compatible with Mg, and it showed good cyclability even at 1C rate in a liquid electrolyte of $Mg(TFSI)_2$ dissolved in glyme/diglyme [271]. Furthermore, this liquid electrolyte was compatible with aluminum, stainless steel and copper electrodes. The large polarization of the Mg plating/stripping process was eliminated by adding triphenolate-borohydride anions, $[B(OPh)_3H]^-$ as $Mg[B(OPh)_3H]_2$ to $Mg(TFSI)_2$ in glyme containing a small amount of $MgCl_2$ [272]. The addition of $MgCl_2$ improves the electrochemical performance, but its amount must be small, because it renders the electrolyte more corrosive [238, 273,274]. Higher oxidative stability is obtained by switching from $Al(Cl)_3$ to aluminum triphenoxide $C_{18}H_{15}AlO_3$ [219].

4.4. Solid-state electrolytes

Ionic liquids were not successfully employed yet in Li-batteries, consequently, alternatives such as solid or gel-electrolytes are being pursued. In the case of Li-batteries, some success was achieved, and Mg should be more promising, because it is not prone to dendrite formation. The conductivity of magnesium ions in solid-state electrolytes is very low so the temperature must be raised to 500 °C to be useful [261-262]. An exception, however, is borohydride-based solid electrolytes, if BH_4^- is partly substituted with $Mg(BH_4)(NH_2)$ salt to enlarge the anion cage to enable migration of Mg ions [263,264]. The addition of $Mg(BH_4)(NH_2)$ salt, which promotes good ionic conductivity at 150 °C, also leads to improved cycle life in Mg batteries at this temperature [265]. Recently, a high magnesium conductivity was claimed in a magnesium scandium selenide spinel but only by NMR. Should these results be confirmed, the scarcity of both Sc and Se leaves these materials as a curiosity, as the philosophy behind Mg batteries is widespread availability [275].

The 150 °C of $Mg(BH_4)(NH_2)$ are still too high, especially considering that solid-state lithium batteries are operational at 70 °C. Therefore, efforts are focused on identifying polymers and salts that are compatible, and that have good cycle life. The same classic polymer electrolytes used in Li batteries, namely PVDF plus poly(ethylene oxide) (PEO) are also of interest for Mg batteries [266]. So far, the best electrochemical performance in Mg batteries was observed with gels consisting of tetraglyme, PVdF and $Mg(AlCl_2EtBu)_2$ that is stable to oxidation up to 2.2 V vs. Mg^{2+}/Mg and forms an organo-haloaluminate electrolyte with Grignard reagents (THF, DME, TEGDME) as solvents. Other gel-electrolytes were tried, but they used Mg salts such as $Mg(ClO_4)_2$ that are not compatible with Mg

metal [266-269]. The abovementioned studies suggest that liquid electrolytes are promising for commercial magnesium cell, in particular with TiS_2 cathodes also described elsewhere [251].

5. Aluminum salts

5.1. Aluminum batteries

Research on rechargeable Al-ion batteries has been underway for about 30 years. These batteries are attractive because of their potentially high energy density due to the redox reaction Al^{3+} <=> Al^0 involving three electrons. In addition, aluminum is abundant and very low-cost. However, Al-ion batteries have encountered technical problems such as poor cycle life and significant capacity fade. The high corrosion and hydrogen evolution prohibits the use of aqueous electrolytes with Al has stimulated the investigation of IL- based electrolytes [274-277].

Promising results were obtained recently with $AlCl_3$ dissolved in an Al-conducting ionic liquid, 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) [278,279]. A cell containing this electrolyte with a V_2O_5 cathode and Al anode delivered an initial discharge capacity of 305 mAh g^{-1} that decreased to 273 mAh g^{-1} after 20 cycles. Lin et al. used the same kind of electrolyte with a graphitic cathode [280], but the voltage is decreased to 2 V, and the specific capacity was reduced to 70 mAh g^{-1}. However, the high conductivity of the graphitic carbon yielded remarkable rate capability, and the cycle life was outstanding with an optimal ratio of $AlCl_3$/[EMIm]Cl of 1.3-1.5. Also, the coulombic efficiency was 98%, and the cell showed charging times of 1 minute with a current density of 4 A g^{-1}, retaining the initial capacity over 7500 cycles, but the areal capacity was very small. These results clearly demonstrate that Al-ion batteries with high power density and very long cycle life are feasible, and that the diffusion of intercalated $AlCl_4^-$/$Al_2Cl_7^-$ ions in graphite is very fast. Jiao et al. developed an Al-ion battery with a higher voltage plateau [281] in which the expensive ionic liquid was replaced by a much cheaper molten salt electrolyte prepared by melting a mixture of $AlCl_3$ and NaCl (molar ratio of ~1:63), close to the eutectic temperature of 108 °C. The ionic conductivity increased, but the drawback is that the battery works at 120 °C close to the melting point of the salt mixture. At this temperature, the battery with Al//graphite electrodes delivered a discharge capacity of 190 mA h g^{-1} at a current density of 100 mA g^{-1} and showed excellent cyclic performance, even at an extremely high current density of 4000 mA g^{-1}, a capacity of 60 mA h g^{-1} was observed after 5000 cycles and 43 mAh g^{-1} capacity after

9000 cycles, with a coulombic efficiency constantly higher than 99% [282]. This performance was attributed to the unique dynamic equilibrium between Al^{3+}, $AlCl_4^-$ and $Al_2Cl_7^-$ in $NaAlCl_4$ melts. The power density of the battery was calculated to be equivalent to ~3000 W kg^{-1} and an energy density of 50 Wh kg^{-1}. In addition, the battery is projected to be low cost, so it shows good prospects for commercialization for some applications, even though the energy density is about three times less than that of Li-ion batteries.

An Al battery using aluminum as the anode, graphite as the cathode, and a ionic liquid as electrolyte was tested in [283, 284]. The IL was nonflammable 1-ethyl-3-methylimidazolium chloroaluminate (EMIC-$AlCl_3$). A ratio of $AlCl_3$/EMIC = 1.3 by mole was used such that $Al_2Cl_7^-$ was present in the (acidic) electrolyte to facilitate aluminum deposition. This battery exhibited a cathode specific capacity of ~70 mAh g^{-1} with a Coulombic efficiency (CE) of 97–98%, and ultrahigh charge/discharge rate (up to 5,000 mA g^{-1}) for over 7,000 cycles. The same group proposed to replace this electrolyte by a cheap ionic liquid analog electrolyte made from a mixture of $AlCl_3$ and urea in a 1.3:1 molar ratio (urea is 50 times cheaper than EMIC, and eco-friendly) [285]. The aluminum deposition proceeded through two pathways, one involving $Al_2Cl_7^-$ anions and the other involving $[AlCl_2 \cdot (urea)_n]^+$ cations that were detected by FTIR. The cathode capacity was 73 mA g^{-1} at 100 mA g^{-1} (1.4 C) stable over 150-200 cycles. The rate capability was much less than with the EMIC-$AlCl_3$ electrolyte because of the increase of viscosity, but the much reduced cost makes it an attractive option for use on large scales and non-mobile energy storage units.

5.2. Al-based dual batteries

Graphite is the anode material in the commercial Li-ion batteries because Li^+ ions readily intercalate between the graphite layer planes. Therefore, graphite is a useful anode as an Al counter-electrode for dual-ion batteries, provided an electrolyte is available with a salt anion that can also intercalate graphite. The principle processes in dual batteries is as follows: Upon charge, the salt anions intercalate in graphite, while the Li^+ ions in the electrolyte deposit on the aluminum counter-electrode where they form an Li-Al alloy or they enter graphite layers. During discharge, both the salt cations and anions diffuse back into the electrolyte. In an earlier section, the discussion on lithium batteries showed that LiTFSI satisfies this condition, as both Li^+ and $TFSI^-$ intercalate reversibly in graphite. The electrolyte consists of LiTFSI in $Pyr_{14}TFSI$, plus ethylene sulfate (ES). The ES additive forms a

SEI layer at the graphite surface to prevent the intercalation of the large Pyr_{14}^+ ions, which would result in the exfoliation of the graphene layers [286]. A capacity of 96 mAh g^{-1} was achieved. An alternative to LiTFSI is the $LiPF_6$ salt, in which both Li^+ and PF_6^- intercalate reversibly in graphite [287] (this has been discussed in the Li part). The conventional liquid electrolytes in Li-ion batteries use $LiPF_6$ salt in carbonates. However, it cannot be used for dual-batteries because they tightly bind to PF_6^-, thus preventing their intercalation in graphite [288]. On the other hand, a novel aluminum-graphite dual-ion battery (AGDIB), with $LiPF_6$ salt in an ethyl-methyl carbonate (EMC) electrolyte plus 2 wt.% VC additive to form the SEI layer on the aluminum surface delivered a capacity of 100 mAh g^{-1} and capacity retention of 88% after 200 charge–discharge cycles at 2C (1C corresponding to 100 mA g^{-1}). At the pack level, this result would amount to a specific energy density of ~222 Wh kg^{-1} at a power density of 132 W kg^{-1}, and ~150 Wh kg^{-1} at 1200 W kg^{-1}, better than the performance of commercial lithium-ion batteries [289] (Fig. 11). These results are an improvement with respect to a dual-ion battery where the counter electrode to Al-metal was mesocarbon microbeads instead of graphite [290]. The dual-ion battery delivered a capacity of 93 mAh g^{-1} at 2C (1C corresponding to 100 mA g^{-1}) with 89.4% capacity retention after 1000 cycles. The energy density was ~204 Wh kg^{-1} at a high-power density of 3084 W kg^{-1} (15 C, charging/discharging within 4 min), which is twice as large as most commercial lithium-ion batteries. However, the main difficulty with an Al electrode is the volume change during cycling, which limits the cycling life. To accommodate the volume change between Al and Li_9Al_4, a 3D porous Al (pAl) foil coated with a carbon layer (pAl/C) was synthesized for use as the negative electrode and current collector in a dual-ion battery [291]. Used in combination with graphite as the positive electrode, and an electrolyte composed of 4 mol L^{-1} $LiPF_6$ in ethyl methyl carbonate (EMC) plus 5 wt.% VC additive (needed to stabilize the SEI film formation on the Al anode) gave good electrochemical properties, delivering a reversible capacity of 104 mAh g^{-1} at 2C, and 85 mAh g^{-1}at 20C. Most of all, the battery demonstrated excellent long-term cycling performance. After 1000 cycles, the discharge capacity at 2C rate was 93 mAh g^{-1}, which amounts to 89.4% capacity retention with a Coulombic efficiency of 93.1% [291]. This battery reached energy density of 204 Wh kg^{-1} at a high-power density of 3084 W kg^{-1}, which confirms that this chemistry is very promising. Note the electrolyte was the same composition as in Ref. [289], except that the optimum amount of VC additive was raised from 2 to 5 wt.% to adjust for the porosity.

6. Calcium salts

Calcium is almost disqualified as an electrode because of its high reactivity due to its strong reducing power and high solubility in molten salts, but the feasibility of plating/stripping was proven by Ponrouch et al. [292] using the salt mixture $Ca(ClO_4)_2$ and $Ca(BF_4)_2$, in EC:PC solvent in a cell at 100 °C. Therefore, instead of Ca metal alone, secondary batteries were constructed with solid calcium alloy negative electrodes (Ca-Al, Ca-Mg, Ca-Si). Some results were obtained with metal sulfide positive electrodes (FeS, NiS or CoS) in the molten salt electrolyte LiCl-NaCl-$CaCl_2$-$BaCl_2$ [292-294], but they were not competitive with Li-ion batteries, and the project was terminated. The only attractive calcium battery is the calcium-based liquid-metal batteries that have higher cell voltages and lower costs than lithium systems [295]. These batteries are described as Ca in metal A/molten salt electrolyte/Ca in metal B, where A is the negative electrode host metal (Mg, Zn, or Al and B) the positive electrode (Bi, Sb, Sn or Pb). The Bi-Ca positive electrode and the molten salt electrolyte, LiCl-NaCl-$CaCl_2$-$BaCl_2$, used by Argonne National Lab [293-295] was investigated by Kim et al. [296,297] in the temperature range 500-700 °C. Excellent reversibility up to current densities of 200 mA cm^{-2} was observed with high coulombic efficiency >98% at electrode equilibrium potentials between 0.8 and 1.0 V versus Ca. However, problems occur at high C-rates in this molten salt electrolyte, because of the formation of $Ca_{11}B_{10}$ dendrites mixed with the electrolyte, detached from the bulk electrode. The formation of such intermetallics is the big challenge, even if the introduction of barium could be one strategy to minimize the formation of these Ca-Bi intermetallics.

7. Potassium salts

Potassium has recently emerged as a potential vector element for secondary batteries. With a melting point of 63.5 °C the temperature span of a K electrode is reduced. Like calcium, potassium is cheap and abundant, but it is also reactive with the electrolyte components, so a SEI is needed to stabilize the interface [298], and until recently, it was a challenge to obtain good capacity retention with cycling. K^+ intercalates in graphite to KC_8. It is difficult to find a cathode in which K^+ ions can intercalate because the ionic radius of K^+ ions are significantly larger than that of Li^+ ions. The potassium Prussian blue, $K_{0.220}Fe[Fe(CN)_6]_{0.805}\cdot 4.01H_2O$ (KPB), nanoparticles were proposed as a potential cathode material by Zhang et al. [299] who proved that this material delivers a reversible capacity of 73.2 mAh g^{-1}, high discharge voltage 3.1-3.4 V, and 52.4 and 44.7 mAh g^{-1} are retained

over 150 cycles at the rate of 200 and 300 mA g^{-1}, respectively, which amounts to a decay rate of ≈0.09% per cycle [299] in an organic electrolyte. The authors also determined that the redox pair, $[Fe^{II}(CN)_6]^{4-}/[Fe^{III}(CN)_6]^{3-}$, dominates the K^+ ion storage. An increased capacity was obtained by substituting one Fe by Mn because $MnFe(CN)_6$ accepts reversibly almost 2 K^+ ions per formula unit, as both Mn and Fe are active. Both Fe^{3+}/Fe^{2+} and Mn^{3+}/Mn^{2+} redox couples have voltage plateaus at 3.6 V [300] (Fig. 12). The cathode, however, must be in the discharged state $K_xMnFe(CN)_6$ ($x \approx 2$) before use to avoid instabilities associated to the Jahn-Teller Mn^{3+} ions. The capacity of 142 mAh g^{-1} and operating voltage of 3.6 V are promising, when using a saturated $KClO_4$ in PC containing 10 wt.% FEC as electrolyte. However, the cycling life and rate capability still need improvements to be competitive with current Li-ion batteries. Other electrodes have also been proposed [301,302].

These results show that there are electrodes that are able to insert and release K^+ ions with a very good ionic diffusivity. However, the electrolyte above mentioned must be improved, because the low content of K^+ ions in conventional organic liquids limits use at high C-rate. To remedy this problem, some other electrolytes with containing K^+-salts were investigated, taking benefit of the prior works on Li- and Na-batteries. For example, $LiPF_6$ is the preferred salt in lithium-ion batteries, and $NaPF_6$ salt in diglyme is a good electrolyte for sodium batteries [165]. The research by Miao et al. [130] showed that LiFSI-LiTFSI/DOL-DME avoids the formation of dendrites in Li-metal batteries, and a highly concentrated 4 mol L^{-1} LiFSI-DME electrolyte works even better [303]. These observations prompted research to study KPF_6 salt in DME. Indeed, 0.5 mol L^{-1} KPF_6 in DME was used successfully to cycle a potassium-air battery [304]. On the other hand, 1 mol L^{-1} KPF_6 in DME did not work in a K/Cu half-cell; 1 mol L^{-1} KTFSI-DME and 0.8 mol L^{-1} KPF_6 -EC/DEC also did not work [305]. These authors, however, found improved cycle behavior by choosing the KFSI salt instead of KTFSI. The KFSI-DME electrolyte forms a uniform SEI on the surface of potassium, enabling reversible plating/stripping [305], similar to that observed with LiFSI-DME on the Li surface [303]. The K/KPB battery with highly concentrated KFSI-DME electrolyte (KFSI/DME=0.6) delivered a capacity of 65 mA h g_{KPB}^{-1} at a rate of 100 mA g_{KPB}^{-1}. But, this capacity is much smaller than the capacity (142 mAh g^{-1}) found with the organic electrolyte $KClO_4$ in PC containing 10 wt.% FEC used in Ref. [300], and the tests were limited to only 50 cycles.

Carbon electrodes can also be used. The full cell with the KPB electrode and a counter-electrode consisting of the commercially available carbon material Super P as the anode still delivered a capacity of 68.5 mAh g^{-1} at 100 mA g^{-1} and retained 93.4% capacity after 50 cycles [299]. Insertion in graphite,

as said above, is possible, provided the PVDF binder is replaced by functionalized binders that maintain the integrity of the electrode despite its 61% volume change during cycling; a capacity retention of 200-240 mAh g^{-1} is retained after 200 cycles [306-308]. Better rate capabilities were obtained with hard and soft carbon microparticles because they are low-density carbons that expand more easily [309,310]. The best results, however, were obtained with N-rich carbon nanofibers produced by electrospinning of polyacrylonitrile polymer and subsequent carbonization to yield freestanding potassium-ion anodes. The corresponding cell with a potassium counter-electrode, Whatman® glass fiber separator and 0.8 mol L^{-1} KPF_6 dissolved in 1:1 volume ratio EC:DEC electrolyte, delivered a stable capacity of 170 mAh g^{-1} after 1900 cycles at 1C rate, and the capacity was still 110 mAh g^{-1} at 10C [311]. The only drawback is the low potential (between 0 and 3 V), compared with 3.6 V obtained with $K_xMnFe(CN)_6$.

Dual-ion batteries can be constructed with potassium ions to take advantage of the insertion of K^+ ions in graphite (at contrast with Na^+ which can reversibly intercalate only with prior graphitic expansion or co-solvent molecules [306,309,312,313]), and similar to that described with Al batteries. A potassium-based dual-graphite battery (K-DGB) was constructed with commercially available synthetic flake-type graphite as both anode and cathode active materials with $Pyr_{14}TFSI$ + 0.3 mol L^{-1} KTFSI + 2 wt.% ES electrolyte [314]. The $Pyr_{14}TFSI$ + ES additive was successfully used in the Al-dual battery [286], and as noted earlier, the role of the ES additive is to avoid exfoliation of the graphene layers by insertion of the large Pyr_{14}^+ ions. Therefore, the Pyr_{14}^+ ions remain in the electrolyte because of the presence of ES. During charge, K^+ ions intercalate graphite on the anode side, while $TFSI^-$ ions intercalates graphite on the cathode side; all of these ions de-intercalate during discharge. This electrolyte with the graphite anode showed a reversible capacity of 230 mA h g^{-1}, a first cycle capacity of 442 mAh g^{-1} (with respect to the graphite cathode) even at a current of 250 mA g^{-1}; the Coulombic efficiency (CE) exceeded 99% in the potential range from 3.4 V to 5.0 V vs. K^+/K with capacity retention of 95% after 1500 cycles.

8. Prospective

Lithium-ion and lithium-metal polymer batteries are still the best choice for plug-in EVs. However, Li-S batteries are reaching the market, with some companies (Oxis, Sion power) reporting 400 Wh kg^{-1} cells [315,316]. The advantage of Li-S over Li-ion batteries is the gravimetric energy

density. However, the volumetric energy density is lower for Li-S batteries, and is expected to stay lower in the next few years. The initial application of Li-S batteries in transportation should be in electric buses because there is ample space available for batteries [317]. The cyclability of these batteries, which was a major problem due to the internal shuttle effect, is improving, and the cycling life of recent Li-S cells is typically 1000 cycles [318].

There is presently no commercial magnesium nor aluminum batteries, despite extensive efforts at the research level. Both systems have in principle solved the problems on the metallic Mg or Al electrode. $Mg(CB_{11}H_{12})_2$ offers the best performances, high conductivity and a 3.5 V stability window. All electrolytes containing Cl, lead to severe corrosion within the battery components and should be avoided despite their simplicity and lower cost. However, $[CB_{11}H_{12}]$- is complicated to synthesize and boron is a relatively rare element, being half as abundant as lithium. These anions are likely to be permanent in the environment. Aluminum can be easily plated, dendrite free from chloroaluminate melts, and the corresponding ILs would be relatively inexpensive. Chlorine again results in a very corrosive medium, and these electrolytes are to be used in a completely dry environment lest HCl will form. The biggest challenge now for these multivalent batteries is to find good positive electrode material. Mg^{++} does not diffuse at an acceptable rate on intercalation oxide, and one has to resort to sulfides (Chevrel phase, Ti_2S_4, etc.), where the host lattice is "soft" enough to allow the motion of the polarizing Mg cation. The drawback is low voltage and low gravimetric capacity. This handicap in terms of capacity could disappear if sulfur S_8 could be harnessed, as polysulfides of Mg are likely polymers with low solubility. The situation for Al is even worse, as there is nothing like an Al^{3+} diffusing in a solid electrode, aluminum being on the contrary a scaffolding element. The interesting results with a graphite positive work on the principle of anion intercalation, the end-product being $AlCl_4^-@C_{24}^+$; with an equivalent mass of 457 g/electron, this chemistry results in practice in low gravimetric energy though high power is available. Needless to say, there is no known practical solid electrolyte for Mg and Al motion, and in solvating polymers like PEO, Mg^{2+} is immobile dues to its trapping by the ether oxygens.

Huge efforts have been made on Na-ion batteries and progress has been made through the years, in terms of capacity (similar to Li-ion batteries), cyclability (still smaller with minor exceptions than that of Li-ion batteries), but they did not find a market so far. We will discuss hereunder the prospect of this chemistry, by comparing Na- and Li- batteries in the context of environmental and cost issues.

8.1. Environmental issues

Irrespective of their composition, lithium-ion batteries are considered a source of pollutants because this chemistry is classified as mildly toxic, although some of the chemistries are more toxic than others. For instance, the higher energy-density lithium-ion batteries required in some EV applications use cathodes made of lamellar compounds $Li(Ni,Mn,Co)O_2$, and cobalt is not only expensive (borderline to be a "conflict element", but also toxic). On another hand, a $LiFePO_4$ cathode is environmentally friendly. Looking at the environmental aspects for electrolytes, the carbonate solvents from the electrolyte have low toxicity and are easily disposed of. Similarly, PEO and polyethers are biodegradable and non-toxic. PF_6^- and FSI^- due to their sensitivity to hydrolysis are not permanent but bring the risk of the toxicity of released fluoride ion. Meanwhile, $TFSI^-$ with its stable CF_3 groups is permanent in the environment, though by itself only moderately irritant. It can however be recycled easily. The case of ILs is different; the IL cations are toxic for the water ecosytems, the toxicity increasing with the alkyl chain length.

Nayak et al. reported that a 60-kWh EV battery (about 350 km driving range) contains roughly 7.5 kg Li, 65 kg Ni, Co, Mn in total, 55 kg graphite, 48 kg copper and 30 kg aluminum, which points to the need for recycling [149]. All these materials are extracted from mines and purified, so that these figures allow us to understand the conclusion of the Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME) in France that the carbon footprint of EVs is not good and the gain with respect to conventional gasoline cars is small if not negligible and much dependent of the source of electricity [319]. Specific data for comparison from this reference and a discussion on these environmental aspects have been reported in Ref [320], with the conclusion that the advantage of EV cars compared to gasoline cars regarding environmental aspects was mainly a decrease in the production of fine soot particles and NO_x and should then be subsidized by government because of their potential impact on health rather than an impact on the climate. Actually, there are many reasons for EV credits, but they are more economic, and will be discussed hereunder in the section devoted to cost; health and climate are not specifically drivers for EVs.

Life-cycle assessment (LCA) of sodium-ion batteries were investigated and compared with that of Li-ion batteries [321-325]. LCA is a standardized methodology for quantifying the environmental impact that takes into account the whole life cycle, from resource extraction over production, use phase until the end-of-life handling, and recycling/disposition of waste. The conclusion of this study is that

the environmental impacts of SIBs are at the lower end of those of existing LIBs, as can be seen in Fig. 13, based on the energy capacity of 1 kWh of storage capacity, but only with an assumed cycle life as high as 2000 cycles. So far, however, such cyclability is not available for most Na chemistries, and the cycling life is the main weakness of SiBs, but progress has been recently made. The problem is not due to the anode. Sn-based anodes for SiBs have high cycle life up to 1000 cycles [326], and Bi anode in a $NaPF_6$-diglyme electrolyte has capacity retention of 94.4% after 2000 cycles [327]. Even 6000 cycles at 110 mAh g^{-1} was still obtained in a half-cell with 1 mol L^{-1} sodium triflate $NaCF_3SO_3$ (or NaTf)/tetraglyme electrolyte [164]. Therefore, the limitation of the cycle life is attributed to the cathode. Recent improvements, however, were obtained with NASICON-type cathodes. $Na_4MnV(PO_4)_3$ and $Na_3FeV(PO_4)_3$ cathodes delivered a reversible capacity of over 100 mAh g^{-1} with good capacity retention at 10 C and stable capacities over 1000 cycles [328]; and the capacity even improved by Mg doping in $Na_3V_{2-x}Mg_x(PO_4)_3$/C composites [329]. $Na_3(VOPO_4)_2F$ shows a 90% capacity retention over 1200 cycles at 2C rate [330]. $Na_3(VO)_2(PO_4)_2F$@C nanocuboïds delivered 70 mAh g^{-1} with 81% retention after 2000 cycles [331]. $NaVPO_4F$ is another promising candidate amenable to carbon coating [332]. However, resorting to vanadium compounds annihilates any advantage of SIBs, only displacing the problem of scarcity from that of cobalt to that of vanadium. From the point-of-view of cycle life, SiBs cannot compete with LIBs, but continuous progress is promising. It will be difficult however, for LIBs to compete with the $LiFePO_4$//$Li_4Ti_5O_{12}$ (LFP//LTO) Li-ion battery which has an outstanding cycleability [20], and the cycle life is a critical parameter implying that the environmental impact of the SIB will exceed that of LFP/LTO, even though the energy density of LFP/LTO is smaller than that of SIBs (and that of other LIBs), due to the lower operating voltage (1.75 V).

The main beneficial effect of the batteries discussed in this review was focused on stationary energy storage of electricity produced by photovoltaic and wind-powered plants, since this mode of storage is competitive for such applications [2]. One critical parameter for battery applications in energy storage is the cycle life, and again the best result is obtained with LFP//LTO batteries [20].

The need for recycling is critical, and the impact was analyzed in a report [333] that claims it takes 6 to 10 times less energy to reclaim recycled metals from batteries than from mining, which further increases the negative impact on the environment. In addition, while it is possible to envision a situation where all large stationary energy storage or EV batteries will be recycled, only 20 to 40 percent of batteries in mobile phones and other consumer products are currently recycled. We also note

that Li-ion batteries command a high recycling fee due to poor metal retrieval value. This is an advantage of the lithium-metal polymer over the Li-ion technology because the recycling of lithium is much easier, but the drawback is that they contain three times more lithium than needed for electrochemical activity. We are not aware of any study on the recycling of SIBs or other batteries reported in this review, presumably because they are currently not yet on the market.

8.2. Cost issues

On a general basis, the main reason why the governments support the PHEVs and EVs is economic. Most of the developed countries do not take into consideration the energy that has been consumed to build such cars (including extraction of the metals from the mines, synthesis of the materials, assembly of the components, and so on…), especially when the extraction of the raw materials is not made in the countries where the cars are used. They only consider the gain in energy, and thus in money upon using EVs and HEVs once they have been built, and indeed this gain is significant, since the efficiency of the electric engines is much better than that of the combustion engines [334]. However, the purchase prices of these cars can be significantly higher, more or less offset by state incentives. An example of such incentives in the US is given in Ref. [335]. The overprice paid to buy EVs and HEVs mainly comes from the battery, and it is thus of interest to make a comparison between the price expected for the different chemistries is also a parameter to take into consideration in the prospect of the next generation of rechargeable batteries.

The main argument in favor of SiBs has been the lower cost with respect to Li-based batteries, even if recent comparisons between Li- and Na-ion batteries show that the new cathode and anode materials for Li-ion batteries have superior electrochemical activity and stability. However, the suitability of matching the cathode and anode with high cell performance, optimization of electrolyte and additives, and improvement of safety are still needed to insure the viability of SiBs [151]. Also, this advantage of the price in favor of SIBs should be revisited, taking into account the huge decrease in price of lithium batteries by a factor 10 in 20 years to now below 200 € per kWh, which is expected to decrease further below 100 € per kWh within the next 5-10 years [149]. As a confirmation, the French enterprise Valeo has just presented a two-seater electric car with a range of 100 km and a top speed of 100 km/h for the price of 7500 € (approximately US$ 9300) only. Therefore, it is not clear whether the substitution of Li for sodium will decrease significantly the price of the batteries despite

the abundance of Na. This abundance is sometimes also invoked as an argument in favor of the Na-base batteries, but this is often not justified as for the vanadium case for the cathode. Also, the battery management system and electronic parts (also cables) can be identified as one of the key drivers for resource depletion (Cu) for the batteries, and these drivers are independent of the chemistry of the batteries [336].

Table 2 lists the properties of three salts currently used in Li-ion and Li-polymer batteries: $LiPF_6$, LiFSI and LiTFSI for comparison, including their price. The price expected in 2023 is an estimation of Hydro-Québec. This table illustrates that LiFSI is the best salt but the most expensive. However, according to the decrease of the price expected within 5 years, LiFSI is expected to win the market, $LiPF_6$ being reduced to the role of additive to passivate the aluminum collector. The cost of the electrolyte [337] is only 6% in the total cost of the battery (Fig. 14). So, there is the margin to introduce new salts.

9. Conclusions

This review has for goal an assessment of the various salts that are in use or are considered for such in new battery systems. It is certainly impossible to separate this component from the solvent, liquid or solid which together constitute the electrolyte. In turn, each electrolyte is designed to allow a smooth operation of both electrodes with safety included, in a variety of environments and chemistries. This work reflects this complexity.

The most used salt, $LiPF_6$ in classical LIBs is produced in thousands of tons and represents 6% of the cost of the battery. This salt, with its very demanding chemistry (PCl_5, anhydrous HF) is in fact a technology marker; for instance, the emergence of China as a leader in battery production became possible when the fabrication was controlled within the country. LiTFSI on the other hand is produced by hundreds of tons only but is a critical ingredient of the Li/polymer batteries, stable enough to allow an extrusion process at high temperature. TDI is a possible outsider considering it resistance to oxidation and non-corrosiveness vs. aluminum. None on the alternative battery systems (Na, K, Mg, Ca, Al) being commercial, the production of the corresponding salts is at the lab level and likely to change as more progress is made in the corresponding electrolytes. The same criteria that apply to the availability of components in a sustainable amount are to be applied to the salts. Neither F, P or S are in a critical situation, but boron is.

References

[1] J. Rogelj, M. den Elzen, N. Höhne, T. Fransen, H. Fekete, H. Winkler, R. Schaeffer, F. Sha, K. Riahi, M. Meinshausen, Nature 534 (2016) 631.

[2] K. Zaghib, C.M. Julien, A. Mauger, Rechargeable Lithium Batteries for energy storage in smart grids, Chapter 12 in: Rechargeable Lithium Batteries, Woodhead Publishing Series in Energy number 81, Elsevier (2015).

[3] K. Xu, Chem. Rev. 104 (2004) 4303.

[4] J. B. Goodenough, Y. Kim, Chem. Mater. 22(3) (2010) 587.

[5] C.G. Barlow, Electrochem. Solid-State Lett. 2 (1999) 362.

[6] E. Zinigrad, L. Larush-Asraf, J.S. Gnanaraj, M. Sprecher, D. Aurbach, Thermochim. Acta 438 (2005) 184.

[7] H. Yang, G.V. Zhuang, P.N. Ross Jr., J. Power Sources 161 (2006) 573.

[8] A. Hammami, N. Raymond, M. Armand, Nature 424 (2003) 635.

[9] S.E. Sloop, J.K. Pugh, S. Wang, J.B. Kerr, K. Kinoshita, Electrochem. Solid-State Lett. 4 (2001) A42.

[10] C.L. Campion, W. Li, B.L. Lucht, J. Electrochem. Soc. 152 (2005) A2327.

[11] J.S. Gnanaraj, E. Zinigrad, L. Asraf, H.E. Gottlieb, M. Sprecher, M. Schmidt, W. Geissler, D. Aurbach, J. Electrochem. Soc. 150 (2003) A1533.

[12] U. Heider, R. Oesten, M. Jungnitz, J. Power Sources 81 (1999) 119.

[13] K. Tasaki, K. Kanda, S. Nakamura, M. Ue, J. Electrochem. Soc. 150 (2003) A1628.

[14] A.V. Plakhotnyk, L. Ernst, R. Schmutzler, J. Fluorine Chem. 126 (2005) 27.

[15] Y. Marcus, Ion Solvation, Wiley, New York, 1985, p. 135.

[16] S. S. Zhang, K. Xu, T. R. Jow, J. Electrochem. Soc. 149 (2002) A586.

[17] S. S. Zhang, K. Xu, J. L. Allen, T. R. Jow, J. Power Sources110 (2002) 216.

[18] S. S. Zhang, J. Power Sources 180 (2008) 586.

[19] A. Chagnes, B. Carré, P. Willmann, R. Dedryvère, D. Gonbeau, D. Lemordant, J. Electrochem. Soc. 150 (2003) A1255.

[20] K. Zaghib, M. Dontigny, A. Guerfi, J. Trottier, J. Hamel-Paquet, V. Gariepy, K. Galoutov, P. Hovington, A. Mauger, H. Groult, C. M. Julien, J. Power Sources 216 (2012) 192.

[21] K. Zaghib, K. Striebel, A. Guerfi, J. Shim, M. Armand, M. Gauthier, Electrochim. Acta 50 (2004) 263.

[22] T. Ohsaki, N. Takami, M. Kanda, M. Yamamoto, Stud. Surf. Sci. Catal. 132 (2001) 925.

[23] M. Xu, A. Xiao, W. Li, B.L. Lucht, J. Electrochem. Soc. 157 (2010) A115.

[24] M. Eberwein, A. Schmid, M. Schmidt, M. Zabel, T. Burgemeister, J. Barthel, W. Kunz, H.J. Gores, J. Electrochem. Soc. 150 (2003) A994.

[25] M. Schmidt, U. Heider, A. Kuehner, R. Oesten, M. Jungnitz, N. Ignatev, P. Sartori, J. Power Sources 97–98 (2001) 557.

[26] J.S. Gnanaraj, M.D. Levi, Y. Gofer, D. Aurbach, M. Schmidt, J. Electrochem. Soc. 150 (2003) A445.

[27] F. Kita, H. Sakata, A. Kawakami, H. Kamizori, T. Sonoda, H. Nagashima, N.V. Pavlenko, Y.L. Yagupolskii, J. Power Sources 97–98 (2001) 581.

[28] M. Handa, M. Suzuki, J. Suzuki, H. Kanematsu, Y. Sasaki, Electrochem. Solid-State Lett. 2 (1999) 60.

[29] M.B. Armand, C.E.M.F. El Kadiri, United States Patent US 4505997 (1985).

[30] L.J. Krause, W. Lamanna, J. Summerfield, M. Engle, G. Korba, R. Loch, R. Atanasoski, J. Power Sources 68 (1997) 320.

[31] F. Kita, A. Kawakami, J. Nie, T. Sonoda, H. Kobayashi, J. Power Sources 68 (1997) 307.

[32] L.A. Dominey, V.R. Koch, T.J. Blakley, Electrochim. Acta 37 (1992) 155130.

[33] J. Barthel, A. Schmid, H.J. Gores, J. Electrochem. Soc. 147 (2000) 21.

[34] Y. Sasaki, M. Handa, S. Sekiya, K. Kurashima, K. Usami, J. Power Sources 97–98 (2001) 561.

[35] H.S. Lee, X.Q. Yang, X. Sun, J. McBreen, J. Power Sources 97–98 (2001) 566.

[36] U. Wietelmann, U. Lischka, M. Wegner, United States PatentUS6506516 (2003).

[37] W. Xu, C.A. Angell, Electrochem. Solid-State Lett. 3 (2001) 366.

[38] K. Xu, S. Zhang, T.R. Jow, W. Xu, C.A. Angell, Electrochem. Solid-State Lett. 5 (2002) A26.

[39] K. Xu, S.S. Zhang, U. Lee, J.L. Allen, T.R. Jow, J. Power Sources 146 (2005) 79.

[40] H. Yamaguchi, H. Takahashi, M. Kato, J. Arai, J. Electrochem. Soc. 150 (2003) A312.

[41] T.J. Barbarich, P.F. Driscoll, Electrochem. Solid-State Lett. 6 (2003) A113.

[42] Z.-B. Zhou, M. Takeda, T. Fujii, M. Ue, J. Electrochem. Soc. 152 (2005) A351.

[43] S.S. Zhang, Electrochem. Commun. 8 (2006) 1423.

[44] J. Arai, A. Matsuo, T. Fujisaki, K. Ozawa, J. Power Sources 193 (2009) 851.

[45] M. Armand, P. Johansson, J. Power Sources 178 (2008) 821.

[46] J. Scheers, P. Johansson, P. Szczecinski, W. Wieczorek, M. Armand, P. Jacobsson, J. Power Sources 195 (2010) 6081.

[47] J. T. Dudley, D. P. Wilkinson, G. Thomas, R. LeVae, S. Woo, H. Blom, C. Horvath, M. W. Juzkow, B. Denis, P. Juric, P. Aghakian and J. R. Dahn, J. Power Sources 35 (1991) 59-82

[48] Fluorinated Materials for Energy Conversion, T. Nakajima and H. Groult, Editors, Elsevier, Amsterdam (2005).

[49] J. W. Jiang, J.R. Dahn, Electrochem. Solid State Lett. 6 (2003) A180.

[50] J.W. Jiang, J.R. Dahn, Electrochim. Acta 49 (2004) 4599.

[51] J. Dahn J. Electrochem. Soc. 151 (2004) A609.

[52] E.S. Hong, S. Okada, T. Sonoda, S. Gopukumar, J. Yamaki, J. Electrochem. Soc. 151 (2004) A1836.

[53] Z.-A. Zhang, X.-X. Zhao, B. Peng, Y.-Q. Lai, Z.-Y. Zhang, J. Li, Trans. Nonferrous Met. Soc. China 25(2015) 2260.

[54] K. Matsumoto, K. Inoue, K. Nakahara, R. Yuge, R. Noguchi, K. Utsugi, J. Power Sources 231 (2013) 234.

[55] Z. Zeng, W. I. Liang, H. G. Liao, H. L. Xin, Y. H. Chu, H. Zheng, Nano Lett. 14 (2014) 1745.

[56] https://elibama.files.wordpress.com/2014/10/ii-c-litfsi-electrolyte.pdf

[57] D. Auchbach, Y. Talyosef, B. Markovsky, E. Markevich, E. Zinigrad, L. Asraf, J. S. Gnanaraj, H. J. Kim, Electrochim. Acta 50 (2004) 247.

[58] J. S. Gnanaraj, E. Zinigrad, L. Asraf, M. Sprecher, H. E. Gottlieb, W. Geissler, M. Schmidt, D. Aurbach, Electrochem. Commun. 5(11) (2003) 946.

[59] J.S. Gnanaraj, E. Zinigrad, L. Asraf, H.E. Gottlieb, M. Sprecher, D. Aurbach, M. Schmidt, J. Power Sources 119–121 (2003) 794.

[60] K. Xu, U. Lee, S.S. Zhang, M. Wood, T.R. Jow, Electrochem. Solid-State Lett. 6 (2003) A144.

[61] K. Xu, S.S. Zhang, T.R. Jow, Electrochem. Solid-State Lett. 6 (2003) A117.

[62] K. Xu, U. Lee, S.S. Zhang, T.R. Jow, J. Electrochem. Soc. 151 (2004) A2106.

[63] K. Xu, U. Lee, S.S. Zhang, J.L. Allen, T.R. Jow, Electrochem. Solid-State Lett. 7 (2004) A273.

[64] K. Xu, S.S. Zhang, R. Jow, J. Power Sources 143 (2005) 197.

[65] G.V. Zhuang, K. Xu, T.R. Jow, P.N. Ross, Electrochem. Solid-State Lett. 7 (2004) A224.

[66] Z. Chen, W. Lu, J. Liu, K. Amine, Electrochim. Acta 51(16) (2006) 3322.

[67] L. Zhang, L. Chai, L. Zhang, M. Shen, X. Zhang, V. S. Battaglia, T. Stephenson, H. Zheng, Electrochim. Acta 127 (2014) 39.

[68] J. Barthel, R. Buestrich, E. Carl, H.J. Gores, J. Electrochem. Soc. 143 (1996) 3572.

[69] J. Barthel, R. Buestrich, H.J. Gores, M. Schmidt, M. Wuhr, J. Electrochem. Soc. 144 (1997) 3866.

[70] J. Barthel, M. Schmidt, H.J. Gores, J. Electrochem. Soc. 145 (1998) L17.

[71] C. Liao, K. S. Han, L. Baggetto, D. A. Hillesheim, R. Custelcean, E.-S. Lee, B. Guo, Z. Bi, D. Jiang and G. M. Veith, E. W. Hagaman, G. M. Brown, C. Bridges, M. B. Paranthaman, A. Manthiram, S. Sai, X.-G. Sun, Adv. Energy Mater. 4 (2014) 1301368.

[72] M. Q. Xu, L. Zhou, L. S. Hao, L. D. Xing, W. S. Li, B. L. Lucht, J. Power Sources 196 (2011) 6794.

[73] T. Schedlbauer, S. Krueger, R. Schmitz, R. W. Schmitz, C. Schreiner, H. J. Gores, S. Passerini and M. Winter, Electrochim. Acta 92 (2013) 102.

[74] J. Liu, Z. Chen, S. Busking, I. Belharouak, K. Amine, J. Power Sources 174 (2007) 852.

[75] S. Zugmann, M. Fleischmann, M. Amereller, R. M. Gschwind, H. D. Wiemhoefer, H. J. Gores, Electrochim. Acta 56 (2011) 3926.

[76] S. Zugmann, D. Moosbauer, M. Amereller, C. Schreiner, F. Wudy, R. Schmitz, R. Schmitz, P. Isken, C. Dippel, R. Mueller, M. Kunze, A. Lex-Balducci, M. Winter, H. J. Gores, J. Power Sources 196 (2011) 1417-1424.

[77] L. Niedzicki, G. Z. Zukowska, M. Bukowska, P. Szczecinski, S. Grugeon, S. Laruelle, M. Armand, S. Panero, B. Scrosati, M. Marcinek, W. Wieczorek, Electrochim. Acta 55 (2010) 1450.

[78] S. Giri, S. Behera, P. Jena, Angew. Chem., Int. Ed. 53 (2014) 13916.

[79] O. Tutusaus, R. Mohtadi, T. S. Arthur, F. Mizuno, E. G. Nelson, Y. V. Sevryugina, Angew. Chem., Int. Ed. 54 (2015) 7900.

[80] G. N. Reddy, R. Parida, S. Giri, ChemComm Chem. Commun. 53 (2017) 9942.

[81] R. Tao, D. Miyamoto, T. Aoki, T. Fujinami. J. Power Sources 135 (2004) 267.

[82] H. Shobukawa, H. Tokuda, S. Tabata, M. Watanabe, Electrochim. Acta 50 (2004) 1.

[83] T. Tamura, K. Yoshida, T. Hachida, M. Tsuchiya, M. Nakamura, Y. Kazue, N. Tachikawa, K. Dokko, M. Watanabe, Chem. Lett. 39 (2010) 753.

[84] T. Tamura, T. Hachida, K. Yoshida, N. Tachikawa, K. Dokko, M. Watanabe, J. Power Sources 195 (2010) 6095.

[85] A. Brandt and A. Balducci, J. Power Sources 250 (2014) 343.

[86] M. Shamsipur, A. K. M. Beigi, M. Teymouri, S. M. Pourmortazavi, M. Irandoust, J. Molecular Liquids 157 (2010) 43.

[87] C.-H. Wang, Y. W. Yeh, N. W. Wongittharom, Y.-C. Wang, C.-J. Tseng, S.-W. Lee, W. S. Chang, J.-K. Chang, J. Power Sources 214 (2015) 1016.

[88] M. Ue, A. Murakami, K. Omata, S. Nakamura, Book of Abstracts of the 41st Battery Symposium in Japan, 2000, p. 292.

[89] T. L. Merrigan, E. D. Bates, S. C. Dorman and J. H. Davis Jr, Chem. Commun. (2000) 2051.

[90] Y. R. Mirzaei, B. Twamley and J. N. M. Shreeve, J. Org. Chem. 67 (2002) 9340.

[91] B. Clare, A. Sirwardana, D. R. McFarlane, Synthesis, Purification and Characterization in Ionic Liquids, Topic in Current Chemistry, B. Kirchner Ed., Springer-Verlag, Berlin, Heidelberg 290 (2009) 1.

[92] Electrolytes for Lithium and Lithium-Ion Batteries, R. T. Jow, K. Xu, O. Borodin, M. Ue Eds., Springer, Berlin (2014).

[93] T. Sato, G. Masuda, K. Takagi, Electrochim. Acta 49 (2004) 3606.

[94] Z. B. Zhou, H. Matsumoto, K. Tatsumi, Chem. Eur. J. 11 (2005) 752.

[95] D. R. McFarlane, P. Meakin, J. Sun, M. Amini, M. Forsyth, J. Phys. Chem. B 103 (1999) 4164.

[96] H. Matsumoto, Electronic windows of Room-Temperature Ionic Liquids, in Electrochemical Aspects of ionic Liquids, Second Edition; H. Ohno Ed., John Wiley&Sons, Hoboken, New-Jersey (2011) p. 205.

[97] H. Matsumoto, Y. Miyazaki, H. Ishikawa, Japan Patent Kokei, 297355 (1999).

[98] H. Matsumoto, Y. Yanagida, T. Tanimoto, Y. Kojima, Y. Tamiya, Y. Miyazaki, in: Molten salts XII Proceedings of the International Symposium, P.C. Trulove, H. C. De Long, G. R. Stafford, S. Deki Eds., Electrochem. Soc. Proceedings Series, The Electrochemical Society, Pennington, NJ, PV99-41 (2000) p. 186.

[99] P. C. Howlett, D. R. McFarlane, A. F. Hollenkamp, Electrochem. Solid-State Lett. 7 (2004) A97.

[100] H. Sakaebe, H. Matsumoto, in Electrochemical aspect of ionic liquids, H. Ohno, Ed., Springer, Hoboken, NJ, 2005, chapter 16.

[101] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, M. Kono, J. Power Sources 160 (2006) 1308.

[102] N. Wongittharom, C.-H. Wang, Y.-C. Wang, G. T.-K. Fey, H.-Y. Li, T.-Y. Wu, T.-C. Lee and J.-K. Chang, J. Power Sources 260 (2014) 268.

[103] K. Kubota, H. Matsumoto, J. Phys. Chem. C 117 (2013) 18829.

[104] A. Watarai, K. Kubota, M. Yamagata, T. Goto, T. Nohira, R. Hagiwara, K. Ui, N. Kubagai. J. Power Sources 183 (2008) 724.

[105] A. Vilcnik, I. Jerman, A. Surca Vuk, M. Kozelj, B. Orel, B. Tomsic, B. Simoncic and J. Kovac, Langmuir, 2009, 25 5869.

[106] S. Yamazaki, M. Torii and M. Usui, Patent JP 2010095473 (2010).

[107] M. Kozelj, A. Guerfi, K. Zaghib, J. Mater. Chem. A 2 (2014) 15964.

[108] J. Sun, M. Forsyth, D.R. MacFarlane, J. Phys. Chem. A 2 (2014) 15964.

[109] D.R. MacFarlane, J. Huang, M. Forsyth, Nature 42 (1999) 792.

[110] A. Guerfi, A. Vijh, K. Zaghib. Safe lithium rechargeable batteries based on ionic liquids. In B. Scrosati, K. M. Abraham, W. V. Schalkwijk, J. Hassoun (eds) Lithium batteries. Advanced technologies and applications. Wiley, New York (2013) p. 291.

[111] M. Holzpfel, C. Jost, P. Novak, Chem. Commun. 4 (2004) 2098.

[112] M. Holzpfel, C. Jost, A. Prodi-Schaw, F. Krumeich, A. Wursig, H. Buqa, P. Novak, Carbob 43 (2005) 1488.

[113] T. Sato, T. Maruo, S. Marukane, K. Takagi, J. Power Sources 138 (2004) 253.

[114] Y. Wang, K. Zaghib, A. Guerfi, F. F. C. Bazito, R. M. Torresi, J. R. Dahn, Electrochim. Acta 52 (2007) 6346.

[115] A. Guerfi, M. Dontigny, P. Charest, M. Petitclerc, M. Lagacé, A. Vijh, K. Zaghib, J. Power Sources 195 (2010) 845.

[116] J. Mindemark, E. Törmä, B. Sun, D. Brandell. Polymer 63 (2015) 91.

[117] Y. Tominaga, K. Yamazaki, Chem. Commun. 50 (2014) 4448.

[118] A. Mauger, M. Armand, C. M. Julien, K. Zaghib, J. Power Sources 353 (2017) 333.

[119] J. Mindemark, M. Lacey, T. Bowden, D. Brandell, Progress in Polymer Science (2018) DOI 10.1016/j.progpolymsci.2017.12.004.

[120] J.S. Lee, S. Tai Kim, R. Cao, N.S. Choi, M. Liu, K.T. Lee, J. Cho, Adv. Energy Mater. 1 (2011) 34.

[121] Y. Gofer, M. Ben-Zion, D. Aurbach, J. Power Sources 39 (1992) 163.

[122] X. Liang, Z. Wen, Y. Liu, M. Wu, J. Jin, H. Zhang, X. Wu, J. Power Sources 196 (2011) 9839.

[123] S. Xiong, K. Xie, Y. Diao, X. Hong, Electrochim. Acta 83 (2012) 78.

[124] M. Barghamadi, A. S. Best, A. J. Bhatt, A. F. Hollenkamp, P. J.Mahon, M. Musameh, R. Rüther,

J. Power Sources 295 (2015) 212.

[125] A. Jozwiuk, B. B. Berkes, T. Weiss, H. Sommer J. Janek, T. Brezesinski, Energy Environ. Sci. 9 (2016) 2603.

[126] C. Qu, Y. Chen, X. Yang, H. Zhang, X. Li, H. Zhang, Nano Energy 39 (2017) 262.

[127] UN, Recommendations on the transport of dangerous goods: model regulations, (20th revised edition), United Nations (2017).

[128] X. Zhang, H. Xie, C. S. Kim, K. Zaghib, A. Mauger, C. M. Julien, Mater. Sci. Eng. R 121 (2017) 1-29.

[129] E. L. Cooper, C. A. Angell, Solid State Ionics 18-19 (1986) 570.

[130] R. Miao, J. Yang, X. Feng, H. Jia, J. Wang, Y. Nuli, J. Power Sources 271 (2014) 291.

[131] H. F. Xiang, P. C. Shi, P. Bhattacharya, X. L. Chen, D. H. Mei, M. E. Bowden, J. M. Zheng, J. G. Zhang, W. Xu, J. Power Sources 318 (2016) 170.

[132] J. A. Seel, J. R. Dahn, J. Electrochem. Soc. 147(3) (2000) 892-898, J. A. Seel, J. R. Dahn, J. Electrochem. Soc. 147 (2000) 899.

[133] S. Rothermel, P. Meister, O. Fromm, J. Huesker, H.M. Meyer, M. Winter, T. Placke, ECS Trans. 58 (2014) 15.

[134] G. Schmuelling, T. Placke, R. Kloepsch, O. Fromm, H.M. Meyer, S. Passerini, M. Winter, J. Power Sources 239 (2013) 563.

[135] T. Placke, O. Fromm, S.F. Lux, P. Bieker, S. Rothermel, H.W. Meyer, S. Passerini, M. Winter, J. Electrochem. Soc. 159 (2012) A1755.

[136] T. Placke, O. Fromm, S. Rothermel, G. Schmuelling, P. Meister, H.W. Meyer, S. Passerini, M. Winter, ECS Trans. 50 (2013) 59.

[137] T. Placke, S. Rothermel, O. Fromm, P. Meister, S.F. Lux, J. Huesker, H.-W. Meyer, M. Winter, J. Elecrochem. Soc. 160 (2013), A1979.

[138] P. Meister, V. Siozios, J. Reiter, S. Klamor, S. Rothermal, O. Fromm, H.W. Meyer, M. Winter, T. Placke, Electrochim. Acta 130 (2014) 625.

[139] G. B. Appetecchi, M. Carewska, M. Montanino, M. Moreno, A. Mele, F. Castiglione, S. V. Meille., G. Raos, A. Famulari, *Green and Safe Electrolytes Based on Ionic Liquids in Advanced Manufacturing Processes For Low Cost Greener Li-Ion Batteries* - The White Paper of The GREENLION Project, Chapter II, Retrieved from http://www.greenlionproject.eu (2016).

[140] M. Moreno, E. Simonetti, G. B. Appetecchi, M. Carewska, M. Montanino, G.-T. Kim, N. Loeffler, S. Passerini, J. Electrochem. Soc. 164 (2017) A6026.

[141] H. Chen, M. Armand, M. Courty, M. Jiang, C. P. Grey, F. Dolhem, J.-M. Tarascon, P. Poizot, J. Am. Chem. Soc. 131 (2009) 8984.

[142] Z. Song, Y. Qian, X. Liu, T. Zhang, Y. Zhu, H. Yu, M. Otani, H. Zhou, Energy Environ. Sci. 7 (2014) 4077.

[143] Y. Liang, P. Zhang, J. Chen. Chem. Sci. 4 (2013) 1330.

[144] Y. Wang, Y. Ding, L. Pan, Y. Shi, Z. Yue, Y. Shi, G. Yu, Nano Lett. 16 (2016) 3329.

[145] V. Palomares, P. Serras, I. Villaluenga, K. B. Hueso, J. Carretero-Gonzales, T. Rojo, Energy Environ. Sci. 5 (2012) 5884.

[146] A. Ponrouch, D. Monti, A. Boschin, B. Steen, P. Johansson, M. R. Palacin, J. Mater Chem. A 3 (2015) 22.

[147] K. Vignarooban, R. Kushagra, A. Elango, P. Badami, B. E. Mellander, X. Xu, T. G. Tucker, C. Nam, A. M. Kannan, Int. J. Hydrogen Energy 41 (2016) 2829; H. Che, S. Chen, Y. Xie, H. Wang, K. Amine, X.-Z. Liao, Z.-F. Man Energy & Environ. Sci. 10 (2017) 1075.

[148] P. K. Nayak, L. Yang, W. Brehm, P. Adelhelm, Angew. Chem. Int. Ed. 56 (2017) 2.

[149] V. Palomares, M. Casas-Cabanas, E. Castillo-Martinez, M. H. Han, T. Rojo, Energy Environ. Sci. 6 (2013) 2312.

[150] Y. Li, Y. Lu, C. Zhao, Y.-S. Hu, M.-M. Titirici, H. Li, X. Huang, L. Chen, Energy Storage Mater. 7 (2017) 130.

[151] D. Kundu, E. Talaie, V. Duffort, L. F. Nazar, Angew. Chem. Int. Ed. 54 (2015) 3431.

[152] K. Kubota, S. Komaba, J. Electrochem. Soc. 162 (2015) A2538.

[153] M. Sc. B. Jache, P. Adelhelm, Angew. Chem. Int. Ed. 53(38) (2014) 10169.

[154] M. Dahbi, N. Yabuuchi, K. Kubota, K. Tokiwa, S. Komaba, Phys. Chem. Chem. Phys. 16 (2014) 15007.

[155] M. Dahbi, T. Nakano, N. Yabuuchi, T. Ishikawa, K. Kubota, M. Fukunishi, S. Shibahara, J.-Y. Sun, Y.T. Cui, H. Oji, S. Komaba, Electrochem. Commun. 44 (2014) 66.

[156] S. Aladinli, F. Bordet, K. Ahlbrecht, J. Tübke, Electrochim. Acta 231 (2017) 468.

[157] A. Bhide, J. Hofmann, A. K. Dürr, J. Jannek, P. Adelhelm, Phys. Chem. Chem. Phys. 16 (2014) 1987.

[158] A. Ponrouch, E. Marchante, M. Courty, J.-M. Trarascon, M. R. Palacin, Energy Environ. Sci. 5

(2012) 8572.
[159] M. Sheng, F. Zhang, B. Ji, X. Tong, Y. Tang, Adv. Energy Mater. 7(7) (2017) 1601963.
[160] B. Jache, J. O. Binder, T. Abe, P. Adelhelm, Phys. Chem. Chem. Phys. 18 (2016) 14299.
[161] H. Kim, J. Hong, G. Yoon, H. Kim, K.-Y. Park, M.-S. Park, W.-S. Yoon, K. Kang, Energy Environ. Sci. 8 (2015) 2963.
[162] H. Kim, J. Hong, Y. U. Park, J. Kim, I. Hwang, K. Kang, Adv. Func. Mater. 25 (2015) 534.
[163] Z. Zhu, F. Cheng, Z. Hu, Z. Niu, J. Chen, J. Power Sources 293 (2015) 626.
[164] Z. W. Seh, J. Sun, Y. Sun, Y. Cui, ACS Cent. Sci. 1 (2015) 449.
[165] E. Castillo-Martinez, J. Carreterao-Gonzalez, M. Armand, Angw. Chem. Int. Ed. 53 (2014) 5341.
[166] Z. Zeng, X. Jiang, R. li, D. Yuan, X. Ai, H. Yang, Y. Cao, Adv. Sci. 3 (2016) 1600066.
[167] L. S. Plashnitsa, E. Kobayashi, Y. Noguchi, S. Okada and J. Yamaki, J. Electrochem. Soc. 157 (2010) A536.
[168] D. Monti, E. Jonsson, M. R. Palacin, P. Johansson, J. Power Sources 245 (2014) 630.
[169] F. Wu, N. Zhu, Y. Bai, L. Liu, H. Zhou, C. Wu, ACS Appl. Mater. Interfaces 8 (2016) 21381.
[170] C. Ding, T. Nohira, K. Kuroda, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta and S. Inazawa, J. Power Sources 238 (2013) 296.
[171] C. Ding, T. Nohira, R.Hagiwara, K.Matsumoto, Y. Okamoto, A. Fukunaga, S. Sakai, K. Nitta and S. Inazawa, J. Power Sources 269 (2014) 124.
[172] C.-Y. Chen, K. Matsumoto, T. Nohira and R. Hagiwara, Electrochem. Commun. 45 (2014) 63.
[173] A. Fukunaga, T. Nohira, R. Hagiwara, K. Numata, E. Itani, S. Sakai, K. Nitta and S. Inazawa, J. Power Sources 246 (2014) 387.
[174] C. H. Wang, C. H. Yang and J. K. Chang, Chem. Commun. 52 (2016) 10890.
[175] T. Carstens, A. Lahiri, N. Borisenka, F. Endres, J. Phys. Chem. C 120(27) (2016) 14736.
[176] H. Matsumoto, H. Sakaebe, K. Tatsumi, J. Power Sources 146 (2005) 45.
[177] S. A. Mohd Noor, P. C. Howlett, D. R. MacFarlane and M. Forsyth, Electrochim. Acta 114 (2013) 766.
[178] J. Serra Moreno, G. Maresca, S. Panero, B. Scrosati, G.B. Appetecchi, Electrochem. Commun. 43 (2014) 1.
[179] N. Wongittharom, T. C. Lee, C. H. Wang, Y. C. Wang and J. K. Chang, J. Mater. Chem. A 2 (2014) 5655.
[180] I. Hasa, S. Passerini and J. Hassoun, J. Power Sources 303 (2016) 203.

[181] C.Y. Chen, K. Matsumoto, T. Nohira, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, S. Inazawa, J. Power Sources 237 (2013) 52-57.

[182] T. Yamamoto, T. Nohira, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, S. Inazawa, J. Power Sources 217 (2012) 479.

[183] C.Y. Chen, K. Matsumoto, T. Nohira, R. Hagiwara, A. Fukunaga, S. Sakai, K. Nitta, S. Inazawa, J. Power Sources 246 (2014) 758.

[184] K. Matsumoto, T. Hosokawa, T. Nohira, R. Hagiwara, A. Fukunaga, K. Numata, E. Itani, S. Sakai, K. Nitta, S. Inazawa, J. Power Sources 265 (2014) 36.

[185] K. West, B. Zachau-Christiansen, T. Jacobsen, E. Hiort-Lorenzen, S. Skaarup, Br. Polym. J., 20 (1988) 243.

[186] S. A. Hashmi, S. Chandra, Mater. Sci. Eng. B 34 (1995) 18.

[187] R. Chandrasekaran, S. Selladurai, J. Solid-State Electrochem. 5 (2001) 355.

[188] V. M. Mohan, V. Raja, P. B. Bhargav, A. K. Sharma and V. V. R. N. Rao, J. Polym. Res. 14 (2007) 283.

[189] A. Boschin and P. Johansson, Electrochim. Acta 175 (2015) 124.

[190] I. Villaluenga, X. Bogle, S. Greenbaum, I. Gil de Muro, T. Rojo, M. Armand, J. Mater. Chem. A 1 (2013) 8348.

[191] Y. L. Ni'mah, M.-Y. Cheng, J. H. Cheng, J. Rick, B. J. Hwang, J. Power Sources, 278 (2015) 375.

[192] P. B. Bhargav, V. M. Mohan, A. K. Sharma, V. V. R. N. Rao, J. Appl. Polym. Sci. 108 (2008) 510.

[193] K. N. Kumar, T. Sreekanth, M. Jaipal Reddy, U. V. Subba Rao, J. Power Sources 101 (2001) 130.

[194] C. V. Subba Reddy, A. P. Jin, Q. Y. Zhu, L. Q. Mai, W. Chen, Eur. Phys. J. E: Soft Matter Biol. Phys. 19 (2006) 471.

[195] K. Kiran Kumar, M. Ravi, Y. Pavani, S. Bhavani, A. K. Sharma, V.V. R. Narasimha Rao, Physica B 406 (2011) 1706.

[196] Z. Osman, K. B. Md Isa, A. Ahmad, L. Othman, Ionics 16 (2010) 431.

[197] J. K. Kim, Y. J. Lim, H. Kim, G.-B. Cho, Y. Kim, Energy Environ. Sci. 8 (2015) 3589.

[198] D. Kumar, S. A. Hashmi, Solid State Ionics 181 (2010) 416.

[199] D. Kumar, S. A. Hashmi, J. Power Sources 195 (2010) 5101.

[200] H. Gao, W. Zhou, K. Park, J. B. Goodenough, Adv. Energy Mater. 6 (2016) 1600467.

[201] Y. Q. Yang, Z. Chang, M. X. Li, X. W. Wang, Y. P. Wu, Solid State Ionics 269 (2015) 1.

[202] H. Gao, B. Guo, J. Song, K. Park, J. B. Goodenough, Adv. Energy Mater. 5 (2015) 1402235.

[203] A. Rudola, K. Du, P. Balaya, J. Electrochem. Soc. 164 (2017) A1098.

[204] M. Matsui, J. Power Sources 196 (2011) 7048.

[205] J. Muldoon, C. B. Bucur, A. G. Oliver, T. Sugimoto, M. Matsui, H. S. Kim, G. D. Allred, J. Jacicek, Y. Kotani, Energy Environ. Sci. 5 (2012) 5941.

[206] T. D. Gregory, R. J. Hoffman, R. C. Winterton, J. Electrochem. Soc. 137 (1990) 775.

[207] Z. Lu, A. Schechter, M. Moshkovich, D. Aurbach, J. Electroanal. Chem. 466 (1999) 203.

[208] L. P. Lossius, F. Emmenegger, Electrochim. Acta 41 (1996) 445.

[209] E. Peled, J. Electrochem. Soc. 126 (1979) 2047.

[210] D. Aurbach, Z. Lu, A. Schechter, Y. Gofer, H. Gizbar, R. Turgeman, Y. Cohen, M. Moshkovich, E. Levi, Nature 407 (2000) 724.

[211] D. Aurbach, H. Gizbar, A. Schechter, O. Chusid, H. E. Gottlieb, Y. Gofer, I. Goldberg, J. Electrochem. Soc. 149 (2002) A115.

[212] Y. Guo, F. Zhang, J. Yang, F. Wang, Y. NuLi, S. Hirano, Energy Environ. Sci. 5 (2012) 9100.

[213] Z. Zhao-Karger, X. Zhao, O. Fuhr, M. Fichtner, RSC Adv. 3 (2013) 16330.

[214] R. Mohtadi, F. Mizuno, Beilstein J. Nanotech. 5 (2014) 1291.

[215] J. Muldoon, C. B. Bucur, T. Gregory, Angew. Chem. Int. Ed. 56 (2017) 2.

[216] D. Aurbach, Y. Gofer, Z. Lu, A. Schechter, O. Chusid, H. Gizbar, Y. Cohen, V. Ashkenazi, M. Moshkovich, R.Turgeman, E. Levi, J. Power Sources 97–98 (2001) 28.

[217] D. Aurbach, G. S. Suresh, E. Levi, A. Mitelman, O. Mizrahi, O. Chusid, M. Brunelli, Adv. Mater. 19 (2007) 4260.

[218] H. S. Kim, T. S. Arthur, G. D. Allred, J. Zajicek, J. G. Newman, A. E. Rodnyansky, A. G. Oliver, W. C. Boggess, J. Muldoon, Nat. Commun. 2 (2011) 427.

[219] J. T. Herb, C. A. Nist-Lund, C. B. Arnold, ACS Energy Lett. 1 (2016) 1227.

[220] Z. Zhang, Z. Cui, L. Qiao, J. Guan, H. Xu, X. Wang, P. Hu, H. Du, S. Li, X. Zhou, S. Dong, Z. Liu, G. Cui, L. Chen, Adv. Energy Mater. 7(11) 2017, DOI: 10.1002/aenm.201602055.

[221] R. E. Doe, R. Han, J. Hwang, A. J. Gmitter, I. Shterenberg, H. D. Yoo, N. Pour, D. Aurbach, Chem. Commun. 50 (2014) 243.

[222] T. Liu, Y. Shao, G. Li, M. Gu, J. Hu, S. Xu, Z. Nie, X. Chen, C. Wang and J. Liu, J. Mater.

Chem. A 2 (2014) 3430.

[223] C. J. Barile, R. Spatney, K. R. Zavadil, A. A. Gewirth, J. Phys. Chem. C 118 (2014) 10694.

[224] K. A. See, K. W. Chapman, L. Zhu, K. M. Wiaderek, O. J.Borkiewicz, C. J. Barile, P. J. Chupas, A. A. Gewirth, J. Am. Chem. Soc. 138 (2016) 328.

[225] J. H. Ha, B. Adams, J.-H. Cho, V. Duffort,c J. H. Kim, K. Y. Chung, B. W. Cho, L. F. Nazar, S. H. Oh, J. Mat. Chem. A 4 (2016) 7160.

[226] H.-D. Yoo, I. Shterenberg, Y. Gofer, G. Gershinsky, N. Pour, D. Aurbach, Energy Environ. Sci. 6 (2013) 2265.

[227] A. L. Lipson, S.-D. Han, B. Pan, K. A. See, A. A. Gewirth, C. Liao, J. T. Vaughey, B. J. Ingram, J. Electrochem. Soc. 163 (2016) A2253.

[228] F.-F. Wang, Y.-S. Guo, J. Yang, Y. Nuli and S.-I. Hirano, Chem. Commun. 48 (2012) 10763.

[229] C. Liao, B. Guo, D. Jiang, R. Custelcean, S. M. Mahurin, X.-G. Sun, S. Dai, J. Mater. Chem. A 2 (2014) 581.

[230] E. G. Nelson, J. W. Kampf and B. M. Bartlett, Chem. Commun. 50 (2014) 5193.

[231] B. Pan, J. Huang, N. Sa, S. M. Brombosz, J. T. Vaughey, L. Zhang, A. K. Burrell, Z. Zhang and C. Liao, J. Electrochem. Soc. 163 (2016) A1672.

[232] R. Mohtadi, M. Matsui, T. S. Arthur, S.-J. Hwang Angew. Chem. Int. Ed. 51 (2012) 9780.

[233] O. Zavorotynska, A. El-Kharbachi, S. Deledda, B. C. Hauback, Int. J. Hydrogen Energy 41 (2016) 14387.

[234] Y. Shao, T. Liu, G. Li, M. Gu, Z. Nie, M. Engelhard, J. Xiao, D. Lv, C. Wang, J.-G. Zhang, J. Liu, Sci. Reports 3 (2013) 03130.

[235] J. Chang, R.T. Haasch, J. Kim, T. Spila, P.V. Braun, A.A. Gewirth, ACS Appl. Mater. Interfaces, 7 (2015) 2494.

[236] F. Tuerxun, Y. Abulizi, Y. NuLi, S. Su, J. Yang, J. Wang, J. Power Sources 276 (2015) 255.

[237] C. Liao, N. Sa, B. Key, A. K. Burrell, L. Cheng, L. A. Curtiss, J. T. Vaughey, J.-J. Woo, L. Hu, B. Pan, Z. Zhang, J. Mater. Chem. A 3 (2015) 6082.

[238] I. Shterenberg, M. Salama, H. D. Yoo, Y. Gofer, J.-B. Park, Y.-K. Sun and D. Aurbach, J. Electrochem. Soc. 162 (2015) A7118.

[239] Y. Cheng, R. M. Stolley, K. S. Han, Y. Shao, B. W. Arey, N. M. Washton, K. T. Mueller, M. L. Helm, V. L. Sprenkle, J. Liu and G. Li, Phys. Chem. Chem. Phys. 17 (2015) 13307.

[240] T. Mandai, Y. Akita, S. Yagi, M. Egashira, H. Munakata, K. Kanamura, J. Mater. Chem. A 5

(2017) 3152.
[241] Y. Viestfrid, M. D. Levi, Y. Gofer, D. Aurbach, J. Electroanal. Chem. 576 (2005) 183.
[242] L. W. F. Wan, D. Prendergast, J. Am. Chem. Soc. 136 (2014) 14456.
[243] F. Mizuno, N. Singh, T. S. Arthur, P. T. Fanson, M. Ramanathan, A. Benmayza, J. Prakash, Y.-S. Liu, P. A. Glans, J. Guo, Front. Energy Res. 2 (2014) 46. https://doi.org/10.3389/fenrg.2014.00046
[244] P. Canepa, G. S. Gautam, R. Malik, S. Jayaraman, Z. Rong, K. R. Zavadil, K. Persson, G. Ceder, Chem. Mater. 27 (2015) 3317.
[245] T. Liu, J. T. Cox, D. Hu, X. Deng, J. Hu, M. Y. Hu, J. Xiao, Y. Shao, K. Tang, J. Liu, Chem. Commun. 51 (2015) 2312.
[246] L. F. Wan, B. R. Perdue, C. A. Apblett, D. Prendergast, Chem. Mater. 27 (2015) 5932.
[247] P. Canepa, S. Jayaraman, L. Cheng, N. N. Rajput, W. D. Richards, G. S. Gautam, L. A. Curtiss, K. A. Persson, G. Ceder, Energy Environ. Sci. 8 (2015) 3718.
[248] E. V. Brouillet, et al. Exposing elusive cationic magnesium-chloro aggregates in aluminate complexes through donor control. Dalton Trans. 45 (2016) 5590.
[249] T. J. Carter, R. Mohtadi, T. S. Arthur, F. Mizuno, R. Zhang, S. Shirai, J. W. Kampf, Angew. Chem., Int. Ed. 5 (2014) 3173.
[250] H. D. Yoo et al. Nature Commun. 8 (2017) 339.
[251] Y. NuLi, J. Yang, R. Wu, Electrochem. Commun. 7 (2005) 1105.
[252] N. Amir, Y. Vestfrid, O. Chusid, Y. Gofer, D. Aurbach, J. Power Sources 174 (2007) 1234.
[253] G. T. Cheek, W. E. O'Grady, S. Z. El Abedin, E. Moustafa, F. Endres, J. Electrochem. Soc. 155 (2008) D91.
[254] T. Ramnial, S. A. Taylor, J. A. C. Clyburne, C. J. Walsby, Ckem. Commun. 20 (2007) 2066
[255] N. Yoshimoto, M. Matsumoto, M. Egashia, M. Morita, J. Power Sources 195 (2010) 2096.
[256] N. Yoshimoto, M. Matsumoto, M. Egashira, M. Morita, 2nd International Congress on Ionic Liquids 2P07-070 (2007) p. 286.
[257] F. Bertasi, C. Hettige, F. Sepehr, X. Bogle, G. Pagot, K. Vezzu, E. Negra, S. HJ. Paddison, S. G. Greenbaum, M. Vittadello, et al. ChemSucChem 8 (2015) 3069.
[258] W. Li, S. Cheng, J.Wang, Y. Qiu, Z. Zheng, H. Lin, S. Nanda, Q. Ma, Y. Xu, F. Ye, Angew. Chem. Int. Ed. 55 (2016) 6406.
[259] C. J. Barile, E. C. Barile, K. R. Zavadil, R. G. Nuzzo, A. A. Gewirth, J. Phys. Chem. C 118 (2014) 27623.

[260] T. Watkins, A. Kumar, D. A. Buttry, J. Am. Chem. Soc. 138 (2016) 641.

[261] S. Ikeda, M. Takahashi, J. Ishikawa, K. Ito, Solid State Ionics 23 (1987) 125.

[262] J. Kawamura, K. Morota, N. Kuwata, Y. Nakamura, H. Maekawa, T. Hattori, N. Imanaka, Y. Okazaki, G.-Y. Adachi, Solid State Commun. 120 (2001) 295.

[263] M. Matsuo, H. Oguchi, T. Sato, H. Takamura, E. Tsuchida, T. Ikeshoji, S. Orimo, J. Alloys Compd. 580 (2013) S98.

[264] A. Unemoto, M. Matsuo, S.-I. Orimo, Adv. Funct. Mater. 24 (2014) 2267.

[265] K. Makino, Y. Katayama, T. Miura, T. Kishi, J. Power Sources 97–98 (2001) 512.

[266] O. Chusid, Y. Gofer, H. Gizbar, Y. Vestfrid, E. Levi, D. Aurbach, I. Riech, Adv. Mater. 15 (2003) 627

[267] G. G. Kumar, N. Munichandraiah, Electrochim. Acta 44 (1999) 2663.

[268] M. Morita, N. Yoshimoto, S. Yakushiji, M. Ishikawa, Electrochem. Solid-State Lett. 4 (2001) A177.

[269] G. P. Pandey, R. C. Agrawal, S. A. Hashmi, J. Solid State Electrochem. 15 (2011) 2253.

[270] M. L. Aubrey, R. Ameloot, B. M. Wiers, J. R. Long, Energy Environ. Sci. 7 (2014) 667.

[271] S.-Y. Ha, Y.-W. Lee, S. W. Woo, B. Koo, J.-S. Kim, J. Cho, K. T. Lee, N.-S. Choi, ACS Appl. Mater. Interfaces 6 (2014) 4063.

[272] S. Hebié, H. P. K. Ngo, J.-C. Leprêtre, C. Iojoiu, L. Cointeaux, R. Berthelot, F. Alloin, ACS Appl. Mater. Interfaces 9 (2017) 28377.

[273] N. Sa, B. Pan, A. Saha-Shah, A. A. Hubaud, J. T. Vaughey, L. A. Baker, C. Liao,A. K. Burrell, ACS Appl. Mater. Interfaces 8 (2016) 16002.

[274] M. Salama, I. Shterenberg, H. Gizbar, N. N. Eliaz, M. Kosa, K. Keinan-Adamsky, M. Afri, L. J.W. Shimon, H. E. Gottlieb, D. T. Major, et al., J. Phys. Chem. C 120 (2016) 19586.

[275] P. Canepa, S-H. Bo, G.S. Gautam, B Key, W. D. Richards, T Shi, Y. Tian, Y. Wang, J. Li, G. Ceder, Nature Commun. 8 (2017) 1759.

[276] T. Jiang, M. J. Chollier Brym, G. Dubé, A. Lasia, G. M. Brisard, Surf. Coat. Technol., 201 (2006) 1.

[277] M. P. Paranthaman, G. M. Brown, X. Sun, J. Nanda, A. Manthiram and A. Manivannan, Abstract #314, 218th ECS Meeting (2010).

[278] S. K. Das, L.A. Archer, The Rechargeable Aluminum-ion battery, Cornell University Invention Disclosure, Docket #5506.

[279] N. Jayaprakash, S. K. Das, L.A. Archer, Chem. Commun. 47 (2011) 12610.

[280] M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Agell, C. Chen, J. Yang, B.-J. Hwang, H. Dai, Nature Lett. 520 (2015) 324.

[281] H. Sun, W. Wang, Z. Yu, Y. Yuan, S. Wang and S. Jiao, Chem. Commun. 51 (2015) 11892.

[282] Y. Song, S. Jiao, J. Tu, J. Wang, Y. Liu, H. Jiao, X. Mao, Z. Guo, D. J. Frey, J. Mater. Chem. A 5 (2017) 1282.

[283] M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang, H. Dai. Nature 520 (2015) 325.

[284] Y. Wu, M. Gong, M.-C. Lin, C. Yuan, M. Angell, L. Huang, D.-Y. Wang, X. Zhang J. Yang, B.-J. Hwang, H. Dai (2016) 3D graphitic foams derived from chloroaluminate anion intercalation for ultrafast aluminum-ion battery. Adv Mater 28(41):9218–9222

[285] M. Angell, C.-J. Pan, Y. Rong, C. Yuan, M.-C. Lin, B.-J. Hwang, H. Dai. Proceedings of the Academy os Science 114(5) (2017) 834.

[286] S. Rothermel, P. Meister, G. Schmuelling, O. Fromm, H.-W. Meyer, S. Nowak, M. Winter, T. Placke, Energy Environ. Sci. 7 (2014) 3412.

[287] J. A. Read, A. V. Cresce, M. H. Ervin, K. Xu, Energy Environ. Sci. 7 (2014) 617.

[288] H. Wang, M. Yoshio, Chem. Commun. 46 (2010) 1544.

[289] X. Zhang, Y. Tang, F. Zhang, C.-S. Lee, Adv. Energy Mater. 6 (2016) 1502588.

[290] F. Zhang, B. Ji, X. Tong, M. Sheng, X. Zhang, C.-S. Lee, Y. Tang, Adv. Mater. Interfaces 3 (2016) 1600605.

[291] X. Tong, F. Zhang, B. Ji, M. Sheng, Y. Tang, Adv. Mater. 28 (2016) 9979.

[292] A. Ponrouch, C. Frontera, F. Bardé, M. R. Palacin, Nature Mater. 15 (2016) 169.

[293] A. Nelson, D.L. Barney, R.K. Steunenberg, A.A. Chilenskas, E.C. Gay, J.E. Battles, A. Nelson, D.L. Barney, R.K. Steunenberg, A.A. Chilenskas, E.C. Gay, J.E. Battles, F. Hornstra, W.E. Miller, M.F. Roche, H. Shimotake, R. Hudson, R.J. Rubischko, S. Sudar, High-performance Batteries for Electric-vehicle Propulsion and Stationary, Energy Storage. ANL-78-94, Argonne National Laboratory, Chicago, 1978.

[294] P.A.Nelson, D.L.Barney,R.K.Steunenberg,A.A.Chilenskas,E.C.Gay, J.E.Battles, F. Hornstra, W.E. Miller, D.R. Vissers, M.F. Roche, H. Shimotake, R. Hudson, R.J. Rubischko, S. Sudar, High-performance Batteries for Electric-vehicle Propulsion and Stationary Energy Storage. ANL-79-39, Argonne National Laboratory, Chicago, 1979.

[295] D.L. Barney, M.F. Roche, S.K. Preto, L.E. Ross, N.C. Otto, F.J. Martino, Calcium/Metal Sulfide Battery Development Program. ANL-81-14, Argonne National Laboratory, Chicago, 1981.

[296] H. Kim, D.A. Boysen, J.M. Newhouse, B.L. Spatocco, B. Chung, P.J. Burke, D.J. Bradwell, K. Jiang, A.A. Tomaszowska, K. Wang, W. Wei, L.A. Ortiz, S.A. Barriga, S.M. Poizeau, D.R. Sadoway, Chem. Rev. 113 (2013) 2075.

[297] H. Kim, D. A. Boysen, T. Ouchi and D. R. Sadoway, J. Power Sources, 241 (2013) 239.

[298] X. Ren, M. He, N. Xiao, W. D. Mcculloch, Y. Wu, Adv. EnergyMater. 7(1) (2017) DOI: 10.1002/aenm.201601080.

[299] C. Zhang, Y. Xu, M. Zhou, L. Liang, H. Dong, M. Wu, Y. Yang, Y. Lei, Adv. Funct. Mater. 27 (2017) 1604307.

[300] L. Xue, Y. Li, H. Gao, W. Zhou, X. Lu, W. Kaveevivitchai, A. Manthiram, J. B. Goodenough, J. Am. Chem. Soc. 139 (2017) 2164.

[301] N. Xiao, X. Ren, M. He, W. D. McCulloch, Y. Wu, ACS Appl. Mater. Interfaces 9 (2017) 4301.

[302] W. D. McCulloch, X. Ren, M. Yu, Z. Huang, Y. Wu, Y. ACS Appl. Mater. Interfaces 7 (2015) 26158.

[303] J. Qian, W. A. Henderson, W.Xu, P. Bhattacharya, M. Engelhard, O. Borodin, J.-G. Zhang, Nature Comun. 6 (2015) 6362.

[304] X. Ren, Y. Wu, J. Am. Chem. Soc. 135 (2013) 2923.

[305] N. Xiao, W. McCulloch, Y. Wu, J. Am. Chem. Soc. 139 (2017) 9475.

[306] N. Yabuuchi, K. Kubota, M. Dahbi, S. Komaba, Chem. Rev. 114 (2014) 11636.

[307] J. Zhao, X. Zou, Y. Zhu, Y. Xu, C. Wang, Adv. Funct. Mater. 26 (2016) 8103.

[308] S. Komaba, T. Hasegawa, M. Dahbi, K. Kubota, Electrochem. Commun. 60 (2015) 172.

[309] Z. Jian, W. Luo, X. Ji, J. Am. Chem. Soc. 137 (2015) 11566.

[310] Z. Jian, Z. Xing, C. Bommier, Z. Li, X. Ji, Adv. Energy Mater. 6 (2016) 1501874.

[311] R. A. Adams, J.-M. Syu, Y. Zhao, C.-T. Lo, A. Varma, V. G. Pol, ACS Appl. Mater. Interfaces 9 (2017) 17872.

[312] Y. Wen, K. He, Y. Zhu, F. Han, Y. Xu, I. Matsuda, I. Ishii, J. Cumings, C. Wang, Nat. Commun. 5 (2014) 4033.

[313] Z. Xu, X. Lv, J. Chen, L. Jiang, Y. Lai, J. Li, Carbon 107 (2016) 885.

[314] K. Beltrop, S. Beuker, A. Heckmann, M. Winter, T. Placke, Energy Environ. Sci. 10 (2017) 2090.

[315] Oxis Energy (2016) https://oxisenergy.com/oxis-energy-advances-lithium-sulfur-li-s-cell-technology-400whkg/. Accessed 21 July 2017.

[316] Sion Power (2016) http://sionpower.com/media-center.php?code=sion-power-delivers-next-generation-battery-prefor. Accessed 21 july 2017

[317] T. Cleaver, P. Kovacik, M. Marinescu, T. Zhang, G. Offer, J. Electrochem. Soc. 165 (2018) A6029-A6033.

[318] X. Zhang, H. Xie, C.-S. Kim, K. Zaghib, A. Mauger, C. M. Julien, Mater. Sci. Eng. R 121 (2017) 1.

[319] http//www.ademe.fr/sites/default/files/assets/documents/90511_acv-comparative-ve-vt-rapport.pdf.

[320] A. Mauger, C. M. Julien, Ionics 23 (2017) 1933.

[321] J. Peters, D.Buchholz, S. Passerini, M. Weil, Energy Environ. Sci. 9 (2016) 1744.

[322] G. Majeau-Bettez, T.R. Hawkins, A.H. Stromman, Environ. Sci. Technol. 45 (2011) 4548.

[323] M. Zackrisson, L. Avellán, J. Orlenius, J. Cleaner Prod. 18 (2010) 1519.

[324] C. Bauer, Paul Scherrer Inst. LEA Villigen Switzerland (2010).

[325] D. A. Notter, M. Gauch, R. Widmer, P. Wäger, A. Stamp, R. Zah, H.-J. Althaus, Environ. Sci. Technol. 44 (2010) 6550.

[326] S. Q. Chen, Z. M. Ao, B. Su, X. Q. Xie, G. X. Wang, Energy Storage Mater. 5 (2016) 180.

[327] C. Wang, L. Wang, F. Li, F. Cheng, J. Chen, Adv. Mater. 29 (2017) 1702212.

[328] W. D. Zhou, L. G. Xue, X. J. Lu, H. C. Gao, Y. T. Li, S. Xin, G. T. Fu, Z. M. Cui, Y. Zhu, J. B. Goodenough, Nano Lett. 16 (2016) 7836.

[329] H. Li, X. Q. Yu, Y. Bai, F. Wu, C. Wu, L. Y. Liu, X. Q. Yang, J. Mater. Chem. A 3 (2015) 9578.

[330] Y. R. Qi, L. Q. Mu, J. M. Zhao, Y.-S. Hu, H. Z. Liu, S. Dai, J. Mater. Chem. A 4 (2016) 7178.

[331] G. Deng, D. L. Chao, Y. W. Guo, Z. Chen, H. H. Wang, S. V. Savilov, J. Y. Lin, Z. X. Shen, Energy Storage Mater. 5 (2016) 198.

[332] Y. Lu, S. Zhang, Y. Li, L. Xue, G. Xu, X. Zhang, J. Power Sources 247 (2014) 770.

[333] http://batteryuniversity.com/learn/article/recycling_batteries. Accessed 22 sept. 2017.

[334] *https://www.afdc.energy.gov/fuels/electricity_benefits.html.*

[335] *https://www.afdc.energy.gov/laws/state*.

[336] J. F. Peters, M. Weil, Resources 5 (2016) 46.

[337] X. Zhang, Consulting 2017, SynPLi Consulting, 17300 Rochefort, France.

Figure captions

Fig.1. Inverse modified Peukert plots at 60 °C of the C-LTO//C-LFP cell with different electrolytes. Reproduced from Ref. [19].

Fig. 2. The most stable lithium ion pair configuration for each anion reproduced from [45]: 4,5-dicyano-2-trifluoromethylimidazolide (TDI), 4,5-dicyano-2-pentafluoroethylimidazolide (PDI), 2,4,5-tricyanoimidazolide (CDI), 5,6-dicyano-2-trifluoromethylbenzimidazolide (TDB_{56}), 5,6-dicyano-2-pentafluoroethylbenzimidazolide (PDB_{56}), 2,5,6-tricyanobenzimidazolide (CDB_{56}), 4,7-dicyano-2-trifluoromethylbenzimidazolide (TDB_{47}), 4,7-dicyano-2-pentafluoroethylbenzimidazolide (PDB_{47}), 2,4,7-tricyanobenzimidazolide (CDB_{47}), 4,5,6,7-tetracyano-2-trifluoromethylbenzimidazolide (TTB), 4,5,6,7-tetracyano-2-pentafluoroethylbenzimidazolide (PTB), and 2,4,5,6,7-pentacyano-benzimidazolide (CTB). The 2-position substituent is changed along each row in the horizontal direction, from $–CF_3$, $–C_2F_5$ to –CN. In the vertical direction the number and position of the remaining cyano groups are varied. Li^+ in each ball and stick representation appear without a stick attached to it.

Fig. 3. Rate performance of the graphite anode in the electrolytes containing different Li salt compositions. The very poor rate capability of the graphite anode in 1 mol L^{-1} $LiPF_6$/0.2 mol L^{-1} LiBOB is shown in the inset. LiFSI helps to suppress the high electrode impedance resulting from the addition of LiBOB, while LiBOB is useful to form a stable passivation film on the Al surface. This figure is reproduced from Ref. [66].

Fig. 4. (a) Charge–discharge curves at 0.1 °C and (b) capacity retained ratios at various charge-discharge rates compared to that obtained at 0.1 °C of Li/$LiFePO_4$ cells incorporating a conventional organic electrolyte and IL electrolytes without and with 5 wt.% VC, γ-butyrolactone, and PC, respectively, at 25 °C. Reproduced from [101].

Fig. 5. Conductivity and viscosity of EC–DEC–VC–1 mol L^{-1} $LiPF_6$ with EMI-TFSI. Reproduced from [112].

Fig. 6. a) Discharge capacity and b) Coulombic efficiency (discharge capacity/charge capacity) of Li–S

battery with different electrolytes: El_{1a}: DME:DOL (1:1, v/v) + 1 mol kg^{-1} LiTFSI, El_1: DME:DOL (1:1, v/v) + 1 mol kg^{-1} LiTFSI + 0.1 mol kg^{-1} $LiNO_3$, El_{2a}: TEGDME:C_4mpyr-TFSI (1:1, v/v) + 1 mol kg^{-1} LiTFSI and El_2: TEGDME:C4mpyr-TFSI (1:1, v/v) + 1 mol kg^{-1}LiTFSI + 0.1 mol kg^{-1} $LiNO_3$. Reproduced from Ref. [119].

Fig. 7. Constant current discharge cycling (a) and coulombic efficiency (b) of metallic lithium-KS6L graphite dual-ion cells at a charge/discharge current of 50 mA kg^{-1} of the first 50 cycles with charging end potentials varying from 4.8 V vs. Li^+/Li to 5.2 V vs. Li^+/Li (lower cut-off potential: 3.4 V vs. Li^+/Li). Reproduced from [137].

Fig. 8. Charge–discharge curves of tin-graphite (Sn-G) dual-ion battery (DIB) based on sodium-ion electrolyte. (a) Sn-G DIB at various current rates from 1 to 5 C. (b) Charge/discharge capacities and corresponding Coulombic efficiencies of the Sn-G DIB at various current rates. (c) Long-term cycling stability of the Sn-G DIB at 2C for4 00 cycles. Reproduced form [151].

Fig. 9. Electrochemical properties of a sodium-ion cell with $NaNi_{0.35}Mn_{0.35}Fe_{0.3}O_2$ cathode and Sb-based alloy anode in different electrolytes coupled with: (a) Initial charge/discharge curves. (b) Cycling performance in the 0.8 mol L^{-1} $NaPF_6$/nonflammable phosphate (trimethyl phosphate, TMP) electrolyte with or without 10 vol.% fluoroethylene carbonate (FEC), and in carbonate electrolyte. (c) Rate capability in the 0.8 mol L^{-1} $NaPF_6$/TMP + 10 vol.% FEC electrolyte. Reproduced from [158].

Fig. 10. The cycling curves (a), a typical curve (b), and cycling efficiency (c) of Mg deposition–dissolution on stainless steel substrate from 0.5 mol L^{-1} heated Mg(BH4)2/TG solution. Reported from [258].

Fig. 11. (a) Charge–discharge curves of the aluminum–graphite dual-ion battery (AGDIB) under 0.5, 1, 2, 3, and 5C current rate (1C corresponding to 100 mA g^{-1}). (b) Rate capacities and corresponding coulombic efficiencies of the AGDIB. (c) Long term cycle test result of the AGDIB at a current rate of 2C. (d) Performance comparison of the AGDIB with conventional electrochemical energy storage devices and several recently reported advanced energy storage devices, where DGB represents dual-graphite battery. Reproduced from [278].

Fig. 12. (a) Rate capabilities and (b) cycling performance at 1C rate for a cell assembled with $K_{1.89}Mn[Fe(CN)_6]_{0.6}\cdot 0.75H_2O$ (KMHCF) powder as the cathode, a liquid K–Na anode, and a saturated KClO4 in PC containing 10 wt.% FEC as electrolyte. (c) Charge/discharge curves and (b) cycling performance of NI-KMHCF powder at 1C. Reproduced from [289].

Fig. 13. Relative contribution to environmental impacts per kW h of storage capacity in each assessed category. LFP = lithium iron phosphate, LTO = lithium titanate, LMO = lithium manganese oxide spinel, NCA = layered lithium nickel cobalt aluminium oxide, NCM = layered lithium nickel cobalt manganese oxide, C = graphite. M-B = inventory data from Majeau-Bettez et al. [312], Zak = inventory data from Zackrisson et al. [313], Bau = inventory data from Bauer [314], Not = inventory data from Notter et al. [315]. GWP = global warming potential, FDP = fossil depletion potential, MEP = marine eutrophication potential, FEP = freshwater eutrophication potential, HTP = human toxicity potential, TAP = terrestrial acidification potential. Reproduced from [315].

Fig. 14. Average cost structure of Li-ion cell in 2016. Reproduced from [331].

Table 1. Comparison between salts for lithium batteries (reproduced from Ref. [13]).

Properties	**Fom best → to worst**					
Ion mobility	$LiBF_4$	$LiClO_4$	$LiPF_6$	$LiAsF_6$	LiTf	LiTFSI
Ion pair dissociation	LiTFSI	$LiAsF_6$	$LiPF_6$	$LiClO_4$	$LiBF_4$	LiTf
Solubility	LiTFSI	$LiPF_6$	$LiAsF_6$	$LiBF_4$	LiTf	
Thermal stability	LiTFSI	LiTf	$LiAsF_6$	$LiBF_4$	$LiPF_6$	
Chem. inertness	LiTf	LiTFSI	$LiAsF_6$	$LiBF_4$	$LiPF_6$	
SEI formation	$LiPF_6$	$LiAsF_6$	LiTFSI	$LiBF_4$		
Al corrosion	$LiAsF_6$	$LiPF_6$	$LiBF_4$	$LiClO_4$	LiTf	LiTFSI

Table 2. Properties of lithium salts for Li-ion batteries.

Properties	$LiPF_6$	LiFSI	LiTFSI
Molecular weight (g mol^{-1})	152	187	287
Solubility (wt.%)	38	64	59
Conductivity (mS cm^{-1}) IM	7.9	9.9	6.9
Viscosity (mPa s) IM	3.5	3.3	3.6
Price 2018 (US$ kg^{-1})	25	100	100
Price 2023 (US$ kg^{-1})	20	45	50