



Review

Ionic liquids as electrolytes for Li-ion batteries—An overview of electrochemical studies

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ABSTRACT

The paper reviews properties of room temperature ionic liquids (RTILs) as electrolytes for lithium and lithium-ion batteries. It has been shown that the formation of the solid electrolyte interface (SEI) on the anode surface is critical to the correct operation of secondary lithium-ion batteries, including those working with ionic liquids as electrolytes. The SEI layer may be formed by electrochemical transformation of (i) a molecular additive, (ii) RTIL cations or (iii) RTIL anions. Such properties of RTIL electrolytes as viscosity, conductivity, vapour pressure and lithium-ion transport numbers are also discussed from the point of view of their influence on battery performance.

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1. Introduction

There are three basic parts of any lithium or lithium-ion battery, being the subject of extensive research: the anode, cathode and electrolyte. Cathode and anode are usually studied separately and the results are published in separate papers. Metallic lithium has a very high-energy density, amounting to 3860 mAh g^{-1} [1,2]. However, due to the instability of the Li/electrolyte interface, with the formation of dendrites forming pathways resulting in short-cuts, it

has been replaced by carbon materials, which are able to intercalate lithium with the formation of the C_6Li compound (reversible capacity of ca. 370 mAh g^{-1}). Lithium alloys, such as Li–Sn, Li–Sb, Li–Bi, Li–Cd, Li–Ga, Li–In, Li–Pb and Li–Zn have been studied [3] as alternative anodes. The lithium negative electrode may be composed of SnO_x and during the first charging-cycle the oxide is converted into an Sn–Li alloy anode and Li_2O serving as a solid electrolyte [4]. Recently, there is a growing interest in silicon (or C/Si composites) as a material for negative electrodes, due to its exceptionally high theoretical capacity, amounting to ca. 4000 mAh g^{-1} [5]. Cathodes may be of the spinel type $\text{Li}(\text{M}_2)\text{O}_4$ (for example LiTi_2O_4 , LiMn_2O_4 or LiMnCoO_4), olivine type LiMPO_4 (for example LiFePO_4 or $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$), Nasicon type $\text{Li}_2(\text{M}_2)\text{SO}_4$ or $\text{Li}_3(\text{M}_2)(\text{PO}_4)_3$ (for

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example $\text{Li}_2\text{Fe}_2(\text{SO}_4)_3$ or $\text{Li}_x\text{TiNb}(\text{PO}_4)_3$, of lamellar lattice (for example Li_xTiS_2) or of a different type [1]. This leads to a high number of possible anode–cathode combinations.

The energy is stored in electrodes however, they must work together with a lithium conducting liquid or solid electrolyte. Usually, a lithium salt (for example LiPF_6 or $\text{LiN}(\text{CF}_3\text{SO}_2)_2$) is dissolved in a mixture of organic solvents, such as cyclic carbonates [1]. Polymer electrolytes, formed by the dissolution of a lithium salt in a polymer network, or in the form of the polymer network swollen in a solution of the lithium salt in an organic solvent (gel-type polymer electrolyte) may also be used as a lithium-ion conductor [6]. Polymer electrolytes may be prepared in the form of thin foils, and therefore, they serve as a separator. The non-volatility of solvent-free polymer electrolytes is important from the point of view of battery safety. However, such solvent-free polymer electrolytes suffer from low specific conductivity. During the last decade room temperature ionic liquids (RTIL), being salts of low temperature melting points, have been studied extensively [7–10]. They may be used as solvents for many processes and as electrolytes in electrochemical devices [9]. Batteries filled with such a type of electrolytes do not contain any volatile components and therefore, they are not flammable. Room temperature ionic liquids, being usually quaternary ammonium salts, are characterized by negligible vapour pressure, which makes them inflammable. In addition, they show a broad electrochemical stability window, generally >4V, which is necessary for the application in lithium-ion batteries with high-energy cathodes. While the RTILs based on quaternary ammonium cations cannot be directly applied in any known type of primary or secondary batteries, it is possible to dissolve a lithium salt $[\text{Li}^+][\text{X}^-]$ in ionic liquids $[\text{A}^+][\text{X}^-]$, with the formation of a new ionic liquid $[\text{Li}^+]_m[\text{A}^+]_n[\text{X}^-]_{m+n}$, consisting of two cations. During the last few years there has been increasing interest in ionic liquids as electrolytes for lithium or lithium-ion batteries. Representative ionic liquids tested as components of lithium or lithium-ion batteries are shown in Table 1 together with electrodes working with the ILs. The main purpose of this paper is to discuss main problems associated with possible application of RTILs as electrolytes in lithium and lithium-ion batteries.

2. SEI formation

Passive layers formed at the surface of various materials, such as oxides formed on metals, are responsible for their stability in contact with the gas phase (for example air) or with a liquid (for example an electrolyte solution). Materials used for the Li-ion battery electrodes are not exceptions [78]. Both anode (Li and C) and cathode materials for the use in Li-ion batteries are not stable in respect to the electrolyte solutions [79]. The graphite electrode working together with ‘conventional’ solutions of lithium salts in a mixture of cyclic carbonates, usually containing propylene carbonate, may function owing to a reaction building up the Li^+ conducting film, protecting the electrolyte and electrode against their further degradation. The use of electrolyte components (solvent or salt) is one of the most effective way for the formation of the protective coating on the electrode surface, usually called the solid electrolyte interface (SEI) [80]. Spectroscopic investigations showed that SEI is composed of electrolyte decomposition products, such as e.g. Li_2CO_3 (decomposition of cyclic carbonate solvent) or LiF (decomposition of LiPF_6 salt) [81]. The SEI may be approximated by an inorganic layer (Li_2CO_3 , LiF) on the anode surface and the second porous organic layer formed on the inorganic one, both layers of the total thickness ranging from 2 nm to several tens of nanometers [82]. In the case of ionic liquids, a molecular additive may form SEI in a similar way to the classical solution. The amount of the additive is usually at the level of ca. 5–10 wt.%

[14,17,20,34,41,48,65]. During the initial charging/discharging cycles additive forms the SEI on the electrode surface and hence its concentration in the ionic liquid decreases to a lower level. However, the ionic liquid cation or anion may also be electrochemically transformed into the protective film. The intercalation of lithium from the $[\text{Li}^+]_m[\text{EtMeIm}^+]_n[\text{NTf}_2^-]_{m+n}$ electrolyte into the graphite was examined with the LiCoO_2 counter-electrode (300% excess) [14]. The reduction of the electrolyte (probably of the $[\text{EtMeIm}^+]$ cation) without intercalation of lithium into the graphite was observed. Also after an addition of 25% of EC no protective film was formed. When EC was replaced by 2% of acrylonitrile, the layer of SEI was formed which resulted in an increase of the graphite anode capacity [14]. Replacing acrylonitrile with 5% of ethylene sulphide or 10% of vinylene carbonate led to cycling curves close to those typical of standard electrolytes in cyclic carbonates [14]. Another approach is to incorporate into the ionic liquid cation or anion a functionality capable of providing the protective film. Salts with a cyano group incorporated into the cation, for example N-cyanomethyl-N,N,N-trimethylammonium bis(trifluorosulfonyl)imide ($[\text{CMMe}_3\text{N}^+][\text{NTf}_2^-]$) [36], or 1-cyanoalkyl-3-methylimidazolium ($[\text{CMMeIm}^+][\text{NTf}_2^-]$ and $[\text{CPMeIm}^+][\text{NTf}_2^-]$) [60,61], were investigated from the point of view of lithium cycling, and compared to the corresponding ionic liquid without the cyano group. The melting point of $[\text{CMMe}_3\text{N}][\text{NTf}_2^-]$ is 35.2 °C, but the salt was liquid at room temperature as a result of the supercooling effect. It has been found that the cyano group is effective in improving the interfacial properties of the lithium/IL system. Cyclic voltammograms of the $[\text{Li}^+][\text{EtMeIm}^+][\text{NTf}_2^-]$ ionic liquid (without the cyano group) did not show a lithium dissolution peak, while the modified $[\text{Li}^+][\text{CMMeIm}^+][\text{NTf}_2^-]$ or $[\text{Li}^+][\text{CPMeIm}^+][\text{NTf}_2^-]$ ionic liquids showed the lithium dissolution [60]. The protective properties may also be shown by the ionic liquid anion. A comparative study of imidazolium based ionic liquids consisting of the same cation and different anions ($[\text{EtMeIm}^+][\text{BF}_4^-]$ and $[\text{EtMeIm}^+][\text{NTf}_2^-]$) showed that the $\text{Li}_4\text{Ti}_5\text{O}_{12}/[\text{Li}^+]_m[\text{EtMeIm}^+]_n[\text{NTf}_2^-]_{m+n}/\text{LiCoO}_2$ battery delivered up to 106 mAh g^{-1} after 200 cycles, in contrast to that containing $[\text{Li}^+]_m[\text{EtMeIm}^+]_n[\text{BF}_4^-]_{m+n}$ as an electrolyte [16]. This phenomenon indicates that the imide ion is capable of forming the protective film on the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /electrolyte interface. In a study [17] a special procedure of SEI formation was used. First, the assembled cell $\text{C}/[\text{Li}^+]_m[\text{Et}_2\text{MeMeON}^+][\text{NTf}_2^-]_{m+n}/\text{LiCoO}_2$ (the ionic liquid contained VC as an additive) was charged with a small current to 4V and discharged to 3V. Then it was charged again to 4.2V and discharged to 2.7V. During these charging/discharging processes the SEI was formed under optimal conditions. In some ionic liquid systems, based on $[\text{BuMeIm}^+][\text{BF}_4^-]$ or $[\text{MePrPip}^+][\text{NTf}_2^-]$, ethylene carbonate, a molecular component of conventional Li^+ electrolytes, was found to be the best as an additive [41].

Comparative studies of lithium intercalation into the graphite anode from LiClO_4 solution in EC+DEC or in a quaternary ammonium ionic liquid $[\text{Me}_3\text{HexN}^+][\text{NTf}_2^-]$ showed that the latter system works properly with 20 vol.% of chloroethylene carbonate as the SEI forming additive [34]. However, the SEI formed at the electrode surface resulted in increased resistance, and hence, in poor cell performance at higher discharge rates. The graphite anode working with the piperidinium based ionic liquid $[\text{Li}^+][\text{MePrPip}^+][\text{NTf}_2^-]$ with 10 wt.% of vinylene carbonate as the additive, showed 90% of its initial capacity after 100 cycles [48].

In some cases the ionic liquid is able to form SEI by itself as it was in the case of a piece of lithium foil which was left in 0.1 mol kg⁻¹ solution of LiNTf_2 in N-butyl-N-ethylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($[\text{Li}^+][\text{BuEtPyrrol}^+][\text{NTf}_2^-]$) [59]. No significant damage of the foil surface was visually observed during the first 6 days. After 15 days a part of the foil became slightly black and totally deteriorated

Table 1
Representative electrochemical systems tested with ionic liquids as electrolytes.

Electrochemical system	Ionic liquid + additives	Ref.
Li/LiMn ₂ O ₄	[M ⁺][AlCl ₄ ⁻] (M ⁺ – sulphonyl chloride or phosphoryl chloride cations	[11]
Li/LiCoO ₂	[EtMelm ⁺][NTf ₂ ⁻], [MePrPip ⁺][NTf ₂ ⁻], [MePrPy ⁺][NTf ₂ ⁻], [Me ₃ PrN ⁺][NTf ₂ ⁻]	[12]
Li ₈ Ti ₅ O ₁₂ /LiCoO ₂	[EtMelm ⁺][BF ₄ ⁻]	[13]
C/Li ₄ Ti ₅ O ₁₂	[EtMelm ⁺][NTf ₂ ⁻] + additives (VC, AN, ES)	[14]
C/LiCoO ₂	[EtMelm ⁺][NTf ₂ ⁻] + VC	[14]
Li/Li	[CMMe ₃ N ⁺][NTf ₂ ⁻]	[15]
Li ₄ Ti ₅ O ₁₂ /LiCoO ₂	[EtMelm ⁺][NTf ₂ ⁻], [EtMelm ⁺][BF ₄ ⁻]	[16]
Li/C	[Et ₂ MeMeON ⁺][NTf ₂ ⁻], [Et ₂ MeMeON ⁺][NTf ₂ ⁻] + VC	[17]
C/LiCoO ₂	[Et ₂ MeMeON ⁺][NTf ₂ ⁻] + VC	[17]
C/Li	[BuMelm ⁺][BF ₄ ⁻] + γ-BL	[18]
Li/LiCoO ₂	[BuMelm ⁺][BF ₄ ⁻] + γ-BL	[18]
Li/Li ₄ Ti ₅ O ₁₂	[BuMelm ⁺][BF ₄ ⁻] + γ-BL	[18]
Li/S	[BuMelm ⁺][PF ₆ ⁻], [EtMelm ⁺][NPF ₂ ⁻]	[19]
Li ₄ Ti ₅ O ₁₂ /LiCoO ₂	[EtMelm ⁺][NTf ₂ ⁻] + LiPF ₆ + VC	[20]
C/Li ₄ Ti ₅ O ₁₂	[EtMelm ⁺][NTf ₂ ⁻] + LiPF ₆ + VC	[20]
C/Li	[EtMelm ⁺][NTf ₂ ⁻] + additives (AN, ES, VC)	[20]
Li/V ₂ O ₅	Composite: [BuMePyrrol ⁺][NTf ₂ ⁻] + PEO	[21]
Li/LiCoO ₂	[MePrPip ⁺], [EtMelm ⁺], [MePrPip ⁺], [TSAC ⁻], [NTf ₂ ⁻]	[22]
Li/air	[EtMelm ⁺][NTf ₂ ⁻], [EtMelm ⁺][NPF ₂ ⁻]	[23]
No cell study	Various ILS	[24]
C/LiCoO ₂	[BuMe ₂ Im ⁺][PF ₆ ⁻] + LiPF ₆ + non-defined molecular solvent	[25]
Li/air	[BuMelm ⁺][NTf ₂ ⁻], [BuMelm ⁺][PF ₆ ⁻]	[26]
No cell study	[BuMelm ⁺][BF ₄ ⁻], [BuMelm ⁺][PF ₆ ⁻], [BuMePy ⁺][BF ₄ ⁻]	[27]
Li/LiMn ₂ O ₄	[Me ₃ HexN ⁺][NTf ₂ ⁻]	[28]
Li/LiCoO ₂	[Et ₂ Me ₂ Im ⁺][NTf ₂ ⁻]	[29]
C/LiCoO ₂	[BuMe ₂ Im ⁺][PF ₆ ⁻] + PC	[30]
Li/LiCoO ₂	[Me ₃ HexN ⁺][NTf ₂ ⁻]	[31]
Li/LiCoO ₂	[MeEt ₂ MetoxyEtN ⁺][NTf ₂ ⁻]	[32]
Li/V ₂ O ₅	[MePrPyrrol ⁺][NTf ₂ ⁻] + PEO	[33]
C/Li	[Me ₃ HexN ⁺][NTf ₂ ⁻] + additives (EC, ES, Cl-EC, VC)	[34]
Li/LiCoO ₂	Various ILS	[35]
Li/LiCoO ₂	[EtMelm ⁺][NTf ₂ ⁻] + [CMMe ₃ N ⁺][NTf ₂ ⁻] or [CEMe ₃ N ⁺][NTf ₂ ⁻]	[36]
C/Li	[EtMelm ⁺][NTf ₂ ⁻], [EtMelm ⁺][Nf ₂ ⁻], [MePrPyrrol ⁺][Nf ₂ ⁻]	[37]
Li ₄ Ti ₅ O ₁₂ /LiFePO ₄	[Et ₂ MePyrroz ⁺][NTf ₂ ⁻]	[38]
Li/LiNi _{0.5} Mn _{1.5} O ₄	[EtMelm ⁺][BF ₄ ⁻], [BuMelm ⁺][BF ₄ ⁻],	[39]
Li/LiCoO ₂	[EtMelm ⁺][NTf ₂ ⁻], [MePrPip ⁺][NTf ₂ ⁻], [MePrPyrrol ⁺][NTf ₂ ⁻], [EtMelm ⁺][Nf ₂ ⁻], [MePrPip ⁺][Nf ₂ ⁻], [MePrPyrrol ⁺][Nf ₂ ⁻]	[40]
Li/LiCoO ₂	[MePrPip ⁺][NTf ₂ ⁻], [BuMelm ⁺][BF ₄ ⁻], additives (EC, ES, VA)	[41]
Li/S	[BuMePip ⁺][NTf ₂ ⁻]	[42]
Li/LiFePO ₄	Composite: [MePrPyrrol ⁺][NTf ₂ ⁻] + PEO	[43]
Li/ZrO ₂ -LiCoO ₂	[Et ₂ MeMeON ⁺][NTf ₂ ⁻]	[44]
Li/LiCoO ₂	[Et ₂ MeMeON ⁺][NTf ₂ ⁻]	[44]
Li/LiCoO ₂	[EtMelm ⁺][NTf ₂ ⁻], [Me ₂ Prlm ⁺][NTf ₂ ⁻]	[45]
Li/C	[Me ₃ HexN ⁺][NTf ₂ ⁻], [Me ₃ HexN ⁺][NTf ₂ ⁻] + Cl-EC	[46]
Li/LiMn ₂ O ₄	[Me ₃ HexN ⁺][NTf ₂ ⁻] + Cl-EC	[46]
C/LiCoO ₂	[BuMe ₂ Im ⁺][NTf ₂ ⁻]	[47]
Li/C	[MePrPip ⁺][NTf ₂ ⁻], [MePrPip ⁺][NTf ₂ ⁻] + additives (VC, EC)	[48]
Li/LiFePO ₄	Composite: [MeBulm ⁺][NTf ₂ ⁻] + PEO	[49]
No cell study	Composite: various ILS + PEO	[50]
No cell study	Composite: [R ₁ R ₂ Pyrrol ⁺][NTf ₂ ⁻] + branched PEO	[51]
Li/LiFePO ₄	Composite: [MeBulm ⁺][NTf ₂ ⁻] or [MeBulm ⁺][BF ₄ ⁻] + PVDF-HFP	[52]
Li/LiFePO ₄	Composite: [RMePyrrol ⁺][NTf ₂ ⁻] + PEO	[53]
Si/Li, Si/LiCoO ₂	[MePrPip ⁺][NTf ₂ ⁻]	[54]
Li/LiCoO ₂	[MeRlm ⁺][NTf ₂ ⁻]	[55]
Li/LiCoO ₂	[Me ₂ Prlm ⁺][NTf ₂ ⁻]	[56]
Li/LiFePO ₄	[MeEt ₂ MetoxyEtN ⁺][NTf ₂ ⁻]	[57]
C/Li	[MePrPip ⁺][NTf ₂ ⁻] + EC + DMC + EMC	[58]
Li/LiFePO ₄	[BuEtPyrrol ⁺][NTf ₂ ⁻]	[59]
Li/Li ⁺	[CMMelm ⁺][NTf ₂ ⁻], [CPMelm ⁺][NTf ₂ ⁻]	[60]
Li/Li ⁺	[EtMelm ⁺][NTf ₂ ⁻], [CMMelm ⁺][NTf ₂ ⁻], [CPMelm ⁺][NTf ₂ ⁻]	[61]
Li/O ₂	Composite: [MePrPyrrol ⁺][NTf ₂ ⁻] + PVdF-HFP	[62]
Li/LiCoO ₂	[EtMelm ⁺], [MePrPip ⁺], [Am ₄ N ⁺], [NTf ₂ ⁻], [TSAC ⁻]	[63]
Li/C, Li/LiFePO ₄	[EtMelm ⁺][Nf ₂ ⁻], [MePrPyrrol ⁺][Nf ₂ ⁻]	[64]
Li/PMT-CNT	[EtMelm ⁺][BF ₄ ⁻], [EtMelm ⁺][BF ₄ ⁻] + VC	[65]
Li/LiMn ₂ O ₄	[MePrPyrrol ⁺][NTf ₂ ⁻], [MePrPyrrol ⁺][Nf ₂ ⁻]	[66]
Al/Ni	[EtMelm ⁺][AlCl ₄ ⁻] + LiCl + SOCl ₂	[67]
Li/Li	Composite: [BuMePyrrol ⁺][NTf ₂ ⁻] + PUA	[68]
Li(?) / C + S	[EtMelm ⁺][NTf ₂ ⁻]	[69]
Li/LiMn ₂ O ₄	[Melm ⁺ -R-Me ₃ N ⁺][NTf ₂ ⁻]	[70]
Li/LiCoO ₂ (LiTi ₅ O ₁₂)	[Me ₃ HexN ⁺][NTf ₂ ⁻] + EC + DEC	[71]
Li/S	Composite: [BuMePyrrol ⁺][NTf ₂ ⁻] + PEGDME	[72]
Li/LiFePO ₄	[BuMelm ⁺][NTf ₂ ⁻] + PVdF-HFP + SiO ₂	[73]
Li/C	[EtMelm ⁺][NTf ₂ ⁻], [EtMelm ⁺][Nf ₂ ⁻]	[74]
Li/LiCoO ₂	Various ILS	[75]
Li/Li	Composite: [BuEtPyrrol ⁺][NTf ₂ ⁻] + PVdF-HFP + EC + PC	[76]
Li/LiMn _{1.5} Ni _{0.5} O ₄	Various cations, [NTf ₂ ⁻]	[77]

after 19 days. The visual observation was followed by impedance spectra investigation in the system $\text{Li}/[\text{Li}^+][\text{BuEtPyrrol}^+][\text{NTf}_2^-]/\text{Li}$ under open circuit conditions. The impedance of the system was continuously growing during the initial 240 min of contact. This was interpreted as the occurrence of a reaction between lithium metal and the ionic liquid, with the formation of the SEI layer. The interface resistance remained approximately constant (ca. 300 Ω) for 8 days. The same impedance analysis of a $\text{Li}/[\text{Li}^+][\text{BuMelm}^+][\text{NTf}_2^-]/\text{Li}$ showed a fast growth of the cell impedance from an initial 3 k Ω to several k Ω within a week of storage.

Recently, it has been shown that the addition of 0.15 mol kg⁻¹ N-methyl-N-(butyl sulfonate) pyrrolidinium zwitterions to $[\text{Li}^+][\text{PrMePyrrol}^+][\text{NTf}_2^-]$ ternary ionic liquid had a beneficial effect on SEI formation on lithium electrode surface [83]. The lithium layer was deposited galvanostatically from the electrolyte on a copper electrode. The potential versus time curve showed two sections, which were interpreted as results of two processes: SEI formation followed by lithium deposition. It has been found that the time necessary to build the SEI is shorter in the case of the electrolyte containing zwitterions. In addition, the electrodeposition of lithium from the ionic liquid containing zwitterions (with a lithium counter-electrode) occurred at lower overpotentials (ca. 100 mV) in comparison to the RTILs without the zwitterion (ca. 200 mV). It was explained by higher ohmic resistance of SEI in the latter case.

3. Viscosity

Viscosity of ionic liquids is much higher than that characteristic for water ($\eta(\text{H}_2\text{O})=0.89$ cP at 25 °C). Typically it is at the level of 30–50 cP, but in some cases much higher, even several hundreds of cP. After the addition of the $[\text{Li}^+][\text{X}^-]$ salt to the neat ionic liquid $[\text{A}^+][\text{X}^-]$, the viscosity of the resulting $[\text{Li}^+]_m[\text{A}^+]_n[\text{X}^-]_{m+n}$ system rather increases [2]. The high viscosity, characteristic for ionic liquids, causes some difficulties with their handling. Battery electrodes consist of active material mixed with an electron conductor (acetylene black) and a polymer (binder). The volume between particles should be filled with the electrolyte. In the case of viscous electrolytes and thick, quasi three-dimensional electrodes this may be difficult. The relatively low capacity of the LiCoO_2 cathode (100 mA g⁻¹), working together with 1,2-diethyl-3,4-dimethylimidazolium imide, was explained as a consequence of a poor impregnation of the electrode by the viscous electrolyte [29]. A similar effect has been observed in the case of the LiFePO_4 cathode: the Coulombic efficiency of the system depended on the manner of the electrode preparation [64]. If the electrode was soaked with the ionic liquid electrolyte under vacuum for 8 h at 60 °C, the Coulombic efficiency was higher in comparison to the same electrode filled with the same electrolyte but at ambient temperature and pressure.

4. Conductivity

Room temperature conductivity of aprotic RTILs is within a broad range of 0.1–18 mS cm⁻¹. Conductivity at the level of 10 mS cm⁻¹ is typical of ionic liquids based on the $[\text{EtMelm}^+]$ cation (14 mS cm⁻¹ for $[\text{EtMelm}^+][\text{BF}_4^-]$), similar to that characteristic for classical electrolytes based on lithium salt solutions in mixtures of cyclic carbonates [1]. However, RTILs based on such cations as pyrrolidinium or piperidinium show lower conductivities, at the level of 1–2 mS cm⁻¹. The dissolution of the $[\text{Li}^+][\text{X}^-]$ salt in the $[\text{A}^+][\text{X}^-]$ ionic liquid leads to a ternary system $[\text{Li}^+]_m[\text{A}^+]_n[\text{X}^-]_{(m+n)}$ with increased viscosity and lower conductivity. For example, it has been shown that the conductivity of the $[\text{Li}^+][\text{BuEtPyrrol}^+][\text{NTf}_2^-]$ ternary ionic liquid exhibited a lower conductivity in comparison

to the neat $[\text{BuEtPyrrol}^+][\text{NTf}_2^-]$ ionic liquid [59]. The conductivity of the solution decreased almost linearly with increasing LiNTf_2 concentration.

5. Lithium cation transport numbers

One of the most important factors determining possible applications of $[\text{Li}^+]_m[\text{A}^+]_n[\text{X}^-]_{(m+n)}$ ionic liquids in lithium-ion batteries is the Li^+ cation contribution to the total charge transported in the electrolyte. The $[\text{Li}^+]_m[\text{A}^+]_n[\text{X}^-]_{(m+n)}$ salt consists of three ions, in contrast to the classical LiX solutions in molecular solvents. Assuming the simplest case $m = n$, the ionic liquid composition is LiAX_2 and the transport numbers of the lithium cation are:

$$t(\text{Li}^+) = \frac{Q(\text{Li}^+)}{Q(\text{Li}^+) + Q(\text{A}^+) + Q(\text{X}^-)} = \frac{u(\text{Li}^+)}{u(\text{Li}^+) + u(\text{A}^+) + 2u(\text{X}^-)}$$

while in the classical solution of the LiX salt it is given by:

$$t(\text{Li}^+) = \frac{Q(\text{Li}^+)}{Q(\text{Li}^+) + Q(\text{X}^-)} = \frac{u(\text{Li}^+)}{u(\text{Li}^+) + u(\text{X}^-)}$$

where $Q(i)$ is the charge transported by the ionic species i and $u(i)$ is the corresponding ionic mobility.

A comparison of both equations shows that the comparable mobility of all ions in the ionic liquid LiAX_2 and the classical solution of LiX in molecular solvents leads to much lower lithium transport number: $t(\text{Li}^+ \text{ in } \text{LiAX}_2) = 0.25$ for $u(\text{Li}^+) \approx u(\text{A}^+) \approx u(\text{X}^-)$, while $t(\text{Li}^+ \text{ in } \text{LiX solution}) = 0.5$ for $u(\text{Li}^+) \approx u(\text{X}^-)$.

Another problem is the determination of transference numbers. In the popular Hittorf method, transport numbers are calculated from electrolyte concentration changes in cathodic and anodic regions. This may be applied in the case of conventional electrolyte solutions in molecular solvents, where ions exist in the form of solvato-complexes, and hence, the solvent molecules move together with ions, which results in the formation of a concentration change in the cathodic and anodic compartments during the electrolysis. In the case of ionic liquids there is no solvent and therefore the passage of electric current through the cell brings about a difference in the molten salt mass in the cathodic and anodic compartments, being difficult to measure. However, transference numbers may be estimated from the diffusion coefficient of both cation and anion, according to:

$$t_+ = \frac{D_+}{D_+ + D_-} \quad \text{and} \quad t_- = \frac{D_-}{D_+ + D_-}$$

Values of self-diffusion coefficients may be estimated by using pulsed-gradient spin-echo nuclear magnetic resonance (PGSE-NMR). Measurements may be taken with ¹H (belonging to the quaternary ammonium cation), ¹⁹F (belonging to tetrafluoroborate, triflate or imide anions) or with ⁷Li. The self-diffusion coefficients estimated by this method are average coefficients of ions and their associates, as NMR detects the nucleus signal without distinguishing between ions and neutral ionic associates. The temperature dependence of the self-diffusion coefficient was studied with the NMR technique in ionic liquids based on the $[\text{BuMelm}^+]$ cation and a number of fluorinated anions [84]. The self-diffusion coefficients exhibited higher values for the cation in comparison to anions, even if its radius was larger than that characteristic for anions. Transport numbers calculated for ionic liquid ions may be comparable, as in the case of $[\text{BuPy}^+][\text{BF}_4^-]$ ($t_+ = 0.48$, $t_- = 0.52$) or differ considerably as in the case of $[\text{EtMelm}^+][\text{AlBr}_4^-]$ ($t_+ = 0.76$, $t_- = 0.24$) [9]. The Li^+ transport number, estimated from NMR diffusion coefficients in the ionic liquid based polymer electrolyte PVdF-HFP- $[\text{Li}^+]_m[\text{MePrPyrrol}^+]_n[\text{NTf}_2^-]_x$, was as low as 0.034 [62]. There are no systematic studies on transport numbers of Li^+ containing ionic liquids. There are data for solutions in molecular

solvents. For example, a $[\text{EtMeIm}^+][\text{PF}_6^-] + \text{LiPF}_6$ system was investigated in propylene carbonate [20]. However, such a system is not an ionic liquid but rather a solution of two salts in a molecular solvent.

In principle, the charge may be transported in ionic liquids by all the mobile species present in the system, such as simple ions as well as their charged combinations, e.g. Li^+ , A^+ , X^- and LiX_2^- or AX_2^- . Consequently, the description of transport properties in ILs would be more comprehensive with the use of transference numbers, defined as the charge carried by a constituent Li, A or X:

$$T_{\text{Li}} = t_{\text{Li}^+} - t_{\text{LiX}_2^-} - t_{\text{AX}_2^-}$$

It should be taken into account that transport numbers t_i are valid in the case of diluted salt solution in molecular solvents. Ionic liquids are 100% concentrated salts with strong ion–ion interactions and hence, transference numbers T_j should rather be used instead of transport numbers t_i . The net mobility of lithium in an $[\text{Li}^+][\text{EtMeIm}^+][\text{BF}_4^-]$ ionic liquid has been estimated from NMR data as a function of Li^+ concentration [85]. The lithium transference number increased linearly with the Li^+ concentration, to reach the value of ca. 0.045 at LiBF_4 mole fraction of about 1.5. The small value of the lithium transference number may lead to a concentration overpotential and hence, it is a disadvantage of ILs as electrolytes for Li-ion batteries.

6. Electrochemical stability

The stability range of the Li^+ conducting electrolyte of above 4V is necessary in practical applications to Li-ion batteries. The electrochemical stability of liquid aprotic quaternary ammonium salts, determined usually at glassy carbon (GC) or platinum electrodes, is within a wide range of 4–6V [9]. Popular imidazolium salts show stability of ca. 4V, while piperidinium and pyrrolidinium salts, especially based on imide anions, show stability of ca. 6V. Symmetrical tetraalkylammonium cations (e.g. tetraethylammonium tetrafluoroborate) have been used for a long time as supporting electrolytes in organic solvents, due to their good stability. Asymmetric aliphatic tetraalkylammonium salts show lower melting points, and may be liquid at room temperature. Such ionic liquids also show very high electrochemical stability at the level of ca. 6V [9]. Moreover, the cathodic stability limit is shifted to more negative potentials than that characteristic for the Li/Li^+ couple in this medium. In general, the cathodic stability limit is determined by the cation while the anodic limit by the anion however, the type of anion may influence the cathodic stability limit [22]. It may be difficult to compare stability limits since the voltammetry curves, showing the stability range, are recorded on different materials (GC, Pt, Au, W) and against different references (ferrocene, Ag/Ag^+ , Li/Li^+ , I_3^-/I^-), in some cases not electrochemically defined (pseudo-references such as Pt, Al or Ag wires immersed in the solution under study) [9].

7. Thermal stability

Thermal stability of different RTILs may be estimated from DSC experiments. Classical solutions in molecular solvents (cyclic carbonates) show a decrease in weight due to solvent evaporation at increased temperatures. For example, the solution of LiBF_4 in $\gamma\text{-BL} + \text{EC}$ shows a decrease in weight at around 90–200°C [13]. The weight loss reached 88% at 200°C with the decomposition of the residual of 12% between 200 and 250°C (decomposition of the salt) [13]. The DSC analysis of the decomposition of the $[\text{Li}^+]_m[\text{EtMeIm}^+]_n[\text{BF}_4^-]_{m+n}$ ionic liquid showed two exothermic peaks around 300–350°C [13]. One of the main difference between

solutions in molecular solvents and ionic liquids is the lack of the solvent evaporation before RTILs thermal decomposition.

The main cause of thermal instability of lithium-ion batteries is a vigorous and exothermic reaction between the electrolyte and the charged (delithiated) LiCoO_2 cathode. Studies have been published on the modification of the cathode during its preparation, by an addition of 3% of butyldimethylimidazolium hexafluorophosphate to a slurry containing LiCoO_2 , acetylene black and PVdF [25]. The existence of the ionic liquid in the prepared cathode was confirmed by NMR. The modified cathode was composed of the graphite anode, a polyolefin separator and a 1 M LiPF_6 based electrolyte (not strictly defined). It was found that the small amount of the ionic liquid in the cathode active mass improved the thermal stability of the system [25]. However, it is not clear why the ionic liquid did not diffuse from the cathode to the separator.

A Li-ion battery $\text{C}/\text{LiPF}_6 + [\text{MePrPip}^+][\text{NTf}_2^-]$ (50 wt.%) + EC + DMC + EMC/ LiCoO_2 was examined from the point of view of its performance, as well as electrolyte inflammability [58]. In principle, the electrolyte was not an ionic liquid but a solution of two salts (LiPF_6 and $[\text{MePrPip}^+][\text{NTf}_2^-]$) in a volatile mixed molecular solvent (EC + DMC + EMC, 1:1:1). The system showed good discharge capacity, equivalent to that obtained with conventional electrolytes. Instead of the ‘nail test’ of the cell, flammability of the electrolyte was examined. A glass filter soaked with the electrolyte was exposed to a flame for 10s. The high amounts (40 wt.%, or more) of the contained $[\text{MePrPip}^+][\text{NTf}_2^-]$ salt resulted in the non-flammability of the electrolyte. Neat carbonates, being molecular solvents for lithium classical electrolytes, have a low flash point (16°C for DMC and 24°C for EMC) [58]. However, the fact that the $[\text{MePrPip}^+][\text{NTf}_2^-]$ salt was liquid before its dissolution in the mixture should not have any influence on the properties of the resulting solution. This rather suggests that the dissolution of a salt, liquid or solid at room temperature may lead to a kind of a ‘solvent in salt’ solution, of a reduced vapour pressure of molecular components and hence, being practically non-flammable. The most important is probably the low molar mass and high solvation number of the salt, to coordinate the solvent molecules in ion solvation shells.

Thermal stability of a solvent-free electrolyte (RTIL) may be increased by the dissolution of a solid lithium salt. For example, the neat $[\text{BuEtPyrrol}^+][\text{NTf}_2^-]$ ionic liquid has high thermal stability amounting to ca. 368°C with the 10 wt.% mass loss (detected from the DSC experiment), while the stability of the LiNTf_2 solution in this ionic liquid ($[\text{Li}^+][\text{BuEtPyrrol}^+][\text{NTf}_2^-]$) was even higher [59].

8. Cyclability and capacity

The number of possible charging/discharging cycles is one of the most important factors characterizing any energy storage device. Lithium-ion batteries working with classical electrolytes show the cycle life of ca. 500–1000. In the case of studies on ionic liquid electrolytes, usually 10–100 cycles are reported. Also the capacity loss may be higher when ionic liquids are used as electrolytes. For example, the $\text{Li}_x\text{Ti}_y\text{O}_z/[\text{Li}^+]_m[\text{EtMeIm}^+]_n[\text{BF}_4^-]_{m+n}/\text{LiCoO}_2$ cell showed good cyclability, comparable to that characteristic for the cell with a ‘classical’ LiBF_4 in $\gamma\text{-BL} + \text{EC}$ solution, but the capacity of the system with an ionic liquid was 94% of that working with the LiBF_4 in $\gamma\text{-BL} + \text{EC}$ solution [13]. In addition, the potential of the $\text{Li}_x\text{Ti}_y\text{O}_z$ electrode is ca. 1.5V versus metallic lithium and therefore the voltage of the cell was only ca. 2.5V [13]. Temperature may also influence the capacity. For example, temperature has an effect on the performance of the LiCoO_2 cathode working with trimethyl-n-hexylammonium bis(trifluoromethanesulfone)imide and LiNTf_2 [31]. Specific cathode capacity obtained during cycling

of Li/electrolyte/LiCoO₂ at 20 °C was 108.9 mAh g⁻¹ while at a temperature increased to 35 °C the specific capacity was 128.2 mAh g⁻¹ [31]. This effect may be due to the reduced IL viscosity and hence, enhanced penetration of the electrode pores by the electrolyte. Very good performance of the LiCoO₂ cathode was found in a liquid tetraalkylammonium salt N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium imide [32]. The initial capacity of the cathode was 145 mAh g⁻¹, and after the 100th cycle it was still 118 mAh g⁻¹.

9. Cathodes

Metal–air primary batteries do not contain cathode active material, which is absorbed from the environment, leading to a high specific energy density. One of the main problems in metal–air primary batteries is electrolyte evaporation, as the system must be open to the air. Hence, many ionic liquids seem to be good candidates as media for such batteries due to their negligible vapour pressure. A lithium–air battery with a lithium metal anode, [Li⁺]_m[EtMelm⁺]_n[NTf₂⁻]_x electrolyte, and a carbon–air cathode worked for 56 days in air [23]. The capacity of the cathode, expressed versus the mass of carbon was 5360 mAh g⁻¹ [23]. The Li/air battery was also assembled with a polymer electrolyte, based on the PVdF–HFP co-polymer and [Li⁺]_m[MePrPyrrol⁺]_n[NTf₂⁻]_x ionic liquid [62]. The addition of small amounts of propylene carbonate to the polymer electrolyte dramatically improved the membrane ionic conductivity. The air cathode consisted of ca. 83 wt.% of carbon black, 2 wt.% of cobaltphthalocyanine and 15 wt.% of PTFE as a binder, all deposited by the spray technique on a carbon paper. The cathode specific discharge capacity, expressed versus carbon and catalyst mass, was 900 mAh g⁻¹ at the first discharge.

A ternary ionic liquid: [EtMelm⁺][NTf₂⁻] + [CEMe₃N⁺][NTf₂⁻] + LiNTf₂ (where [CEMe₃N⁺] is N,N,N,N,cyanoethyltrimethylammonium cation) showed good compatibility with the LiCoO₂ cathode, which exhibited discharge capacity close to the theoretical value [36]. The additional advantage of the electrolyte was its good thermal stability, determined with the use of the DSC technique. The DSC profiles of delithiated Li_{0.46}CoO₂ coexisting with a classical LiPF₆ in the EC + DMC electrolyte, indicated endothermic peaks around 190–210 °C and 250 °C. The first peak was attributed to the oxidation of the electrolyte solution in molecular solvents (EC + DMC) by oxygen released from the cathode and the second peak to the electrolyte self-decomposition. However, the ternary ionic liquid electrolyte was stable (no DSC peaks) at temperatures lower than 260 °C [36]. The potential of the cathode (expressed against the Li/Li⁺ reference) may depend on the electrolyte. The LiNi_{0.5}Mn_{1.5}O₄ spinel, working together with [Li⁺][EtMelm⁺][BF₄⁻] or [Li⁺][BuMelm⁺][BF₄⁻] ionic liquids, showed reversible charging/discharging characteristics with a high 4.8 V potential versus the Li/Li⁺ couple [39].

The performance of the cathode at higher current densities depends on the ionic liquid viscosity/conductivity. For example, fast cycling of the Li/LiCoO₂ system at 4C current rate showed the retention of 70% of the discharge capacity for the [Li⁺][EtMelm⁺][Nf₂⁻] ionic liquid as the electrolyte, while the use of the [Li⁺][MePrPip⁺][Nf₂⁻] or [Li⁺][MePrPyrrol⁺][Nf₂⁻] ionic liquids limited the operation rate to 2C or 1C current rates [40]. This is probably due to the relatively poor conductivity of pyrrolidinium or piperidinium salts, lower than that characteristic for the imidazolium salt. The performance of the LiCoO₂ cathode tested in a series of imidazolium based ionic liquids, [Li⁺][MeRIm⁺][NTf₂⁻], has been improved with the extension of the alkyl chain length, especially if the R is longer than the butyl group [55]. The surface of the LiCoO₂ electrode may be modified by coating it with ZrO₂, prepared by the spray-coating technique [44]. In the first cycle,

both the LiCoO₂ and LiCoO₂–ZrO₂ electrodes, working together with N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium imide ionic liquid, [Et₂MeMeON⁺][NTf₂⁻], showed a discharge capacity of ca. 180 mAh g⁻¹, close to the theoretical value. In the case of the non-coated electrode, the capacity showed a gradual decrease on cycling, amounting to ca. 85 mAh g⁻¹ after the 30-th cycle, while the coated electrode capacity was 150 mAh g⁻¹ [44]. The performance of the LiCoO₂ cathode in imidazolium based ionic liquid [Li⁺][Me₂PrIm⁺][NTf₂⁻] showed a high charge/discharge reversibility for more than 100 cycles, without SEI forming additions [56]. It was also suggested that there exists an optimal concentration of lithium in the ternary ionic liquid, for high-rate performance of the system [56].

The LiFePO₄ cathode may work together with the ionic liquid based polymer electrolyte PEO + [MePrPyrrol⁺][NTf₂⁻] + LiNTf₂ [43]. The cathode retained 96% of its theoretical capacity after the first cycle and 85.7% after the 240th cycle. The same cathode working with PEO + [BuMelm⁺][NTf₂⁻] + LiNTf₂ polymer electrolyte showed stable electrochemical properties and the discharge capacity (at 40 °C) of ca. 82% of the theoretical value [49]. A PEO based polymer electrolyte PEO + [MeRPyrrrol⁺][NTf₂⁻] + LiNTf₂ was tested with the LiFePO₄ cathode [53]. The cathode capacity of 125 mAh g⁻¹ and a stable interfacial resistance of the system were recorded. The LiFePO₄ cathode assembled together with the PVdF–HFP membrane impregnated with the [BuMelm⁺][NTf₂⁻] + LiNTf₂ ionic liquid showed the discharge capacity of 149 mAh g⁻¹ at the 0.1C rate and 132 mAh g⁻¹ at the 0.5C rate, but the performance decreased at higher rates (>1C rate) [52].

Ionic liquid based on the piperidinium cation, [BuMePip⁺][NTf₂⁻], was tested as an electrolyte working with the sulfur cathode, which achieved an initial capacity of 1055 mAh g⁻¹ and the reversible capacity of ca. 750 mAh g⁻¹ [42]. The charging/discharging curves showed only one discharge plateau, in contrast to the system working with classical Li⁺ solutions in molecular liquids, where two plateaus may be seen, corresponding to two different types of electrode reactions taking place at the electrode: reduction of elementary sulfur to polysulfides S_x²⁻ and then their further reduction to sulfides S²⁻. An electronically conducting polymer, poly(3-methylthiophene), PMT, was also investigated as a possible cathode material for Li-ion batteries [65]. The conducting polymer was deposited on carbon nanotubes and the electrolyte was [EtMelm⁺][BF₄⁻]. The initial capacity, expressed versus the PMT mass, was 96 mAh g⁻¹. An addition of vinylene carbonate to the electrolyte increases the capacity after cycling. After 100 cycles, the VC containing system showed the capacity loss to 62 mAh g⁻¹. Inspection of Table 1 indicates that the most frequently studied cathode material has been the LiCoO₂ spinel.

10. Anodes

Graphite is usually used as an anode for the Li-ion secondary batteries with different types of electrolytes, including ionic liquids. In the case of the primary battery, metallic lithium may be used due to its high specific energy. The anion [X⁻] of the ionic liquid [Li⁺][A⁺][X⁻] is important from the point of view of the graphite electrode performance. The bis(trifluoromethanesulfonyl)imide anion seems to be the most popular component of ionic liquids applied as electrolytes in Li-ion batteries (Table 1) However, the graphite anode requires the presence of a SEI forming additive. It has been found that replacing the bis(trifluoromethanesulfonyl)imide anion ([N(CF₃SO₂)₂⁻] or [NTf₂⁻]) by bis(fluorosulfonyl)imide anion ([N(F₂SO₂)₂⁻] or [Nf₂⁻]) may prevent the irreversible Li⁺ intercalation into graphite [37]. The influence of the anion ([NTf₂⁻] or [Nf₂⁻]) on cycling performance of the Li/LiCoO₂ cell filled with the

[MePrPip⁺] based ionic liquid was examined [40]. The initial capacity of the cell containing [MePrPip⁺][NTf₂⁻] was slightly lower than that containing [MePrPip⁺][Nf₂⁻]. Capacity retention at the next cycle (at 0.1C rate) was 90% in the case of the [MePrPip⁺][Nf₂⁻] containing cell, while the cell containing [MePrPip⁺][NTf₂⁻] showed only 50% efficiency [40]. The influence of the [Nf₂⁻] anion on the reversible anode capacity has also been shown in the case of a number of other ILs [66,74].

High lithiation capacity and good safety characteristics of amorphous silicon makes it a good candidate for the anode material in Li-ion batteries. A thin film Si anode in [Li⁺][MePrPip⁺][NTf₂⁻] ionic liquid electrolyte showed a capacity of the order of 3000 mAh g⁻¹, with a small decrease in performance during 35 cycles [54].

11. Lithium/IL/water system

The reactivity of lithium with water excludes this metal as an anode for seawater batteries. However, hydrophobic ionic liquids, [BuMelm⁺][NTf₂⁻] and [BuMelm⁺][PF₆⁻] were used to separate the lithium anode surface from water [26]. A 25 μm thick, microporous membrane with a low electric resistance was used to keep the ionic liquid in place. The electrolyte was 3% aqueous solution and a nickel wire served as a cathode. The ionic liquid layer enabled the Li/IL/3% aq. KCl anode system to output current density at the level of 0.2 mA cm⁻² with 100% efficiency [26].

12. Test counter electrode

In laboratory tests of a cathode or anode for lithium or Li-ion batteries, a lithium–metal foil counter electrode is typically used. The mass and capacity of lithium is much higher in comparison to the tested electrode, and hence, even after a strong gradual degradation of the lithium counter-electrode during cell cycling, its capacity is still much higher than that characteristic for the tested one. Laboratory cells usually contain a small amount of the tested active material, at the level of several mg. The counter electrode is lithium foil hundreds of μm in thickness and with the surface area of ca. 1 cm². In such a case there is an excess of the counter electrode capacity. Typically, the ratio of the tested and counter electrode mass (or capacity) is not given. In some papers it is clearly indicated, e.g. as Li/LiCoO₂ mass ratio of 3/1, and the molecular ratio of 45/1 [45]. The lithium–metal counter electrode also serves as a commonly accepted reference electrode. It is usually assumed that the system with lithium–metal counter/reference electrode shows the potential of the tested electrode in the Li/Li⁺ scale. Moreover, the zero value of the Li/Li⁺ scale in different solutions in molecular liquids and in ionic liquids is commonly compared. However, due to the SEI formation the reference system is rather Li/SEI/Li⁺ than simply Li/Li⁺. The composition of the passivation layer (SEI) is not exactly known, and therefore the corrosion potentials of such references are not strictly defined. The nature of the Li⁺ conducting SEI as well as that of the electrolyte (ionic liquid) may influence the potential of the system. However, in general, all types of electrode materials, being in excess in respect to the tested electrode, may be used (e.g. Li₄Ti₅O₁₂ [38]).

13. Conclusions

1. The formation of the SEI on the anode surface is critical to the correct operation of secondary lithium-ion batteries, including those working with ionic liquids as electrolytes. The use of a molecular additive to ionic liquid is one of the most effective ways for the formation of the protective coating on the electrode surface. However, the SEI may also be formed by an electrochemical reaction of the ionic liquid cation or anion. Consequently, each

new electrolyte, based on RTILs or a polymer electrolyte with RTIL as a plasticizer, should be characterized from the point of view of its ability to form SEI.

2. RTILs used as electrolyte components in Li-ion batteries are quaternary ammonium salts, such as tetraalkylammonium [R₄N⁺] or based on cyclic amines, both aromatic (pyridinium, imidazolium) and saturated (piperidinium, pyrrolidinium). Most RTILs consist of a limited number of inorganic anions, such as [BF₄⁻], [PF₆⁻], [AsF₆⁻] and organic, such as triflate [CF₃SO₃⁻] or imide [N(CF₃SO₂)₂⁻], [N(F₂SO₂)₂⁻]. The latter imide anion ([N(F₂SO₂)₂⁻]) seems to be effective in SEI formation.
3. Ionic liquids are structurally composed of ions, which interact with each other with strong Coulombic forces. Consequently, they are typically very viscous, show low vapour pressure and a strong tendency for supercooling. Low vapour pressure makes them practically non-flammable, which is the main reason for the interest in such a type of electrolytes for Li-ion systems. However, the high viscosity may cause some difficulties with RTIL handling.
4. Room temperature conductivity of aprotic RTILs is within a broad range of 0.1–18 mS cm⁻¹. Conductivity at the level of 10 mS cm⁻¹ is typical of ionic liquids based on the [EtMelm⁺] cation (14 mS cm⁻¹ for [EtMelm⁺][BF₄⁻]), similar to that characteristic for classical electrolytes based on lithium salt solutions in mixtures of cyclic carbonates. However, RTILs based on such cations as pyrrolidinium or piperidinium show lower conductivities, at the level of 1–2 mS cm⁻¹. The dissolution of the LiX salt in the AX ionic liquid leads to a lithium containing electrolyte [Li⁺]_m[A⁺]_n[X⁻]_(m+n) of increased viscosity and lower conductivity.
5. The electrochemical stability of liquid aprotic quaternary ammonium salts is within a wide range of 4–6 V. Liquid imidazolium salts show stability of ca. 4 V, while piperidinium and pyrrolidinium or tetraalkylammonium salts, especially based on the imide anion, show stability at the level of ca. 6 V. Such a stability is sufficient to use RTILs as electrolytes in Li-ion batteries.
6. There are no systematic studies on transport numbers *t*_i of Li⁺ containing ionic liquids. In addition, it should be taken into account that transport numbers *t*_i are valid in the case of diluted salt solutions in molecular solvents, while ionic liquids are 100% concentrated salts with strong ion–ion interactions. Hence, the interpretation of published transport numbers for Li⁺ ion is difficult. However, low values of lithium transportation numbers may lead to a concentration polarization of the Li-ion battery with the RTIL as an electrolyte.
7. Lithium–metal serves usually as both a counter electrode and a commonly accepted Li/Li⁺ reference electrode in test cells. However, due to the SEI formation the reference system is rather Li/SEI/Li⁺ than simply Li/Li⁺. The zero value of the Li/Li⁺ scale in different solutions in molecular liquids and ionic liquids is commonly compared, neglecting the possible potential differences in different media.

List of abbreviations

CNT	Carbon nanotube
IL	Ionic liquid
RTIL	Room temperature ionic liquid

Molecular liquids

VC	Vinylene carbonate
VA	Vinylene acetate
PC	Propylene carbonate
ES	Ethylene sulphide
EC	Ethylene carbonate
Cl-EC	Chloroethylenene carbonate

DEC	Diethyl carbonate
DMC	Dimethyl carbonate
EMC	Ethylmethyl carbonate
γ -BL	γ -Butyrolactone

Polymers

PVdF	Poly(vinylidene fluoride)
PVDF-HFP	Poly(vinylidene fluoride-co-hexafluoropropylene)
PEO	Poly(ethylene oxide)
PMT	Poly(3-methyl thiophene)
PTFE	Poly(tetrafluoroethylene)
PUA	Poly(urethane acrylate)
PEGDME	Poly(ethylene glycol–dimethyl ether)

Imidazolium cations (RRIm⁺)

[EtMeIm ⁺]	1-Ethyl-3-methylimidazolium cation
[BuMeIm ⁺]	1-Butyl-3-methylimidazolium cation
[Me ₂ PrIm ⁺]	1,2-Dimethyl-3-propylimidazolium cation
[Et ₂ Me ₂ Im ⁺]	1,2-Diethyl-3,4-dimethylimidazolium cation
[MeRIm ⁺]	1-Methyl-3-alkylimidazolium cation
[BuMe ₂ Im ⁺]	1,2-Dimethyl-3-butylimidazolium cation
[CMMeIm ⁺]	1-Cyanomethyl-3-methylimidazolium cation
[CPMeIm ⁺]	1-Cyanopropyl-3-methylimidazolium cation

Pyridinium cations (RRPy⁺)

[BuMePy ⁺]	N-butyl-4-methylpyridinium cation
[MePrPy ⁺]	N-methyl-N-propylpyridinium cation
[BuPy ⁺]	N-butylpyridinium cation

Tetraalkylammonium cations (RRRRN⁺)

[Et ₂ MeMeON ⁺]	N,N,-diethyl-N-methyl-N-(2-methoxyethyl)ammonium cation
[Me ₃ HexN ⁺]	Trimethylhexylammonium cation
[CMMe ₃ N ⁺]	N-cyanomethyl-N,N,N-trimethylammonium cation
[CEMe ₃ N ⁺]	N-cyanoethyl-N,N,N-trimethylammonium cation
[Me ₃ PrN ⁺]	Trimethylpropylammonium cation
[MeEt ₂ MetoxyEtN ⁺]	N-methyl-N,N-diethyl-N-(methoxyethylene)ammonium cation
[Am ₄ N ⁺]	Tetraamylammonium cation

Pyrazolium cations (RRRPyrraz⁺)

[Et ₂ MePyrraz ⁺]	N,N,-diethyl-3-methylpyrazolium cation
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Pyrrolidinium cations (RRPyrrol⁺)

[MePrPyrrol ⁺]	N-methyl-N-propylpyrrolidinium cation
[BuEtPyrrol ⁺]	N-n-butyl-N-ethylpyrrolidinium cation
[BuMePyrrol ⁺]	N-n-butyl-N-methylpyrrolidinium cation

Piperidinium cations (RRPip⁺)

[MePrPip ⁺]	N-methyl-N-propylpiperidinium cation
[BuMePip ⁺]	N-butyl-N-methylpiperidinium cation

Dicationic species

[MeIm ⁺ -R-Me ₃ N ⁺]	1-(3-Methylimidazolium-1-alkyl-(trimethylammonium) cation
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Anions

[BF ₄ ⁻]	Tetrafluoroborate anion
[PF ₆ ⁻]	Hexafluorophosphate anion
[Nf ₂ ⁻]; [N(F ₂ SO ₂) ₂ ⁻]	Bis(fluorosulfonyl)imide anion
[NPF ₂ ⁻]; [N(C ₂ F ₅ SO ₂) ₂ ⁻]	Bis(perfluoroethylsulfonyl)imide anion
[NTF ₂ ⁻]; [N(CF ₃ SO ₂) ₂ ⁻]	Bis(trifluoromethanesulfonyl)imide anion
[OTf ⁻]; [CF ₃ SO ₃ ⁻]	Triflate anion
[AlCl ₄ ⁻]	Tetrachloroaluminate anion
[TSAC ⁻]	2,2,2-Trifluoro-N-(trifluoromethylsulfonyl)acetamide

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References

- [1] M. Wakihara, O. Yamamoto (Eds.), *Lithium Ion Batteries*, Wiley-VCH, 1998.
- [2] C.A. Vincent, B. Scrosati, *Modern Batteries*, Wiley, 1997.
- [3] R.A. Huggins, *J. Power Sources* 81–82 (1999) 13.
- [4] Y. Idota, Kubota, A. Matsufuji, Y. Maekawa, T. Miyasaka, *Science* 276 (1997) 1395.
- [5] S.H. Ng, J. Wang, D. Wexler, S.Y. Chew, H.K. Liu, *J. Phys. Chem. C* 111 (2007) 11131.
- [6] F.M. Gray, *Solid Polymer Electrolytes*, VCH, 1991.
- [7] T. Welton, *Chem. Rev.* 99 (1999) 2071.
- [8] R.D. Rogers, K. Seddon (Eds.), *Ionic Liquids: Industrial Applications to Green Chemistry*, ACS Symposium Series 818 (2002).
- [9] M. Galiński, A. Lewandowski, I. Stępnik, *Electrochim. Acta* 51 (2006) 5567.
- [10] S. Zhang, N. Sung, X. He, X. Lu, X. Zhang, *J. Phys. Chem. Ref. Data* 35 (2006) 1475.
- [11] K. Xu, S. Zhang, C.A. Angell, *J. Electrochem. Soc.* 143 (1996) 3548.
- [12] H. Sakaebe, H. Matsumoto, *Electrochem. Commun.* 5 (2003) 594.
- [13] H. Nakagawa, S. Izuchi, K. Kuwana, T. Nukuda, Y. Aihara, *J. Electrochem. Soc.* 150 (2003) A695.
- [14] M. Holzapfel, C. Jost, P. Novak, *Chem. Commun.* (2004) 2098.
- [15] M. Egashira, S. Okada, J.-I. Yamaki, D.A. Dri, F. Bonadies, B. Scrosati, *J. Power Sources* 138 (2004) 240.
- [16] B. Garcia, S. Lavallee, G. Perron, C. Michot, M. Armand, *Electrochim. Acta* 49 (2004) 4583.
- [17] T. Sato, T. Maruo, S. Marukane, K. Takagi, *J. Power Sources* 138 (2005) 253.
- [18] A. Chagnes, M. Diaw, B. Carre, P. Willmann, D. Lemordant, *J. Power Sources* 145 (2005) 82.
- [19] S. Kim, Y. Jung, S.-J. Park, *J. Power Sources* 152 (2005) 272.
- [20] M. Holzapfel, C. Jost, A. Prodi-Schwab, F. Krumeich, A. Wursig, H. Buqa, P. Novak, *Carbon* 43 (2005) 1488.
- [21] J.-H. Shin, W.A. Henderson, G.B. Appetecchi, F. Alessandrini, S. Passerini, *Electrochim. Acta* 50 (2005) 3859.
- [22] H. Sakaebe, H. Matsumoto, K. Tatsumi, *J. Power Sources* 146 (2005) 693.
- [23] T. Kuboki, T. Okuyama, T. Ohsaki, N. Takami, *J. Power Sources* 146 (2005) 766.
- [24] H. Matsumoto, H. Sakaebe, K. Tatsumi, *J. Power Sources* 146 (2005) 45.
- [25] S.-Y. Lee, H.H. Yong, S.K. Kim, Y.J. Kim, S. Ahn, *J. Power Sources* 146 (2005) 732.
- [26] Y. Zhang, M. Urquidi-Macdonald, *J. Power Sources* 144 (2005) 191.
- [27] M. Diaw, A. Chagnes, B. Carre, P. Willmann, D. Lemordant, *J. Power Sources* 146 (2005) 682.
- [28] H. Zheng, H. Zhang, Y. Fu, T. Abe, Z. Ogumi, *J. Phys. Chem. B* 109 (2005) 13676.
- [29] K. Hayashi, Y. Nemoto, K. Akuto, Y. Sakurai, *J. Power Sources* 146 (2005) 689.
- [30] S.-Y. Lee, H.H. Yong, Y.J. Lee, S.K. Kim, S. Ahn, *J. Phys. Chem. B* 109 (2005) 13663.
- [31] H. Zheng, J. Qin, Y. Zhao, T. Abe, Z. Ogumi, *Solid State Ionics* 176 (2005) 2219.
- [32] S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, Y. Mita, A. Usami, N. Terada, M. Watanabe, *Electrochem. Solid-State Lett.* 8 (2005) A577.
- [33] J.-H. Shin, W.A. Henderson, S. Passerini, *J. Electrochem. Soc.* 152 (2005) A978.
- [34] H. Zheng, K. Jiang, T. Abe, Z. Ogumi, *Carbon* 44 (2006) 203.
- [35] J.S. Lee, N.D. Quan, J.M. Hwang, J.Y. Bae, H. Kim, B.W. Cho, H.S. Kim, H. Lee, *Electrochem. Commun.* 8 (2006) 460.
- [36] M. Egashira, M. Tanaka-Nakagawa, I. Watanabe, S. Okada, J.-I. Yamaki, *J. Power Sources* 160 (2006) 1387.
- [37] M. Ishikawa, T. Sugimoto, M. Kikuta, E. Ishiko, M. Kono, *J. Power Sources* 162 (2006) 658.
- [38] Y. Abu-Lebdeh, A. Abouimrane, P.-J. Alarco, M. Armand, *J. Power Sources* 154 (2006) 255.
- [39] E. Markevich, V. Baranchugov, D. Aurbach, *Electrochem. Commun.* 8 (2006) 1331.
- [40] H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, M. Kono, *J. Power Sources* 160 (2006) 1308.
- [41] J. Xu, J. Yang, Y. NuLi, J. Wang, Z. Zhang, *J. Power Sources* 160 (2006) 621.
- [42] L.X. Yuan, J.K. Feng, X.P. Ai, Y.L. Cao, S.L. Chen, H.X. Yang, *Electrochem. Commun.* 8 (2006) 610.
- [43] J.-H. Shin, W.A. Henderson, S. Scaccia, P.P. Prosini, S. Passerini, *J. Power Sources* 156 (2006) 560.
- [44] S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, A. Usami, Y. Mita, M. Watanabe, N. Terada, *Chem. Commun.* (2006) 544.
- [45] S. Seki, Y. Kobayashi, H. Miyashiro, Y. Ohno, A. Usami, Y. Mita, N. Kihira, M. Watanabe, N. Terada, *J. Phys. Chem. B* 110 (2006) 10228.
- [46] H. Zheng, B. Li, Y. Fu, T. Abe, Z. Ogumi, *Electrochim. Acta* 52 (2006) 1556.
- [47] T.E. Sutto, M. Ollinger, H. Kim, C.B. Arnold, A. Pique, *Electrochem. Solid-State Lett.* 9 (2006) A69.
- [48] A. Lewandowski, A. Świdzka-Mocek, *J. Power Sources* 171 (2007) 938.
- [49] J.-W. Choi, G. Cheruvally, Y.H. Kim, J.-K. Kim, J. Manuel, P. Raghavan, J.-H. Ahn, K.-W. Kim, H.-J. Ahn, D.S. Choi, C.E. Song, *Solid State Ionics* 178 (2007) 1235.
- [50] Y.-H. Kim, G. Cheruvally, J.W. Choi, J.H. Ahn, K.W. Kim, H.J. Ahn, D.S. Choi, C.E. Song, *Macromol. Symp.* 249–250 (2007) 183.
- [51] D.M. Tigelaar, M.A.B. Meador, W.R. Bennett, *Macromolecules* 40 (2007) 4159.
- [52] G. Cheruvally, J.-K. Kim, J.W. Choi, J.-H. Ahn, Y.-J. Shin, J. Manuel, P. Raghavan, K.-W. Kim, H.-J. Ahn, D.S. Choi, C.E. Song, *J. Power Sources* 172 (2007) 863.
- [53] G.T. Kim, G.B. Appetecchi, F. Alessandrini, S. Passerini, *J. Power Sources* 171 (2007) 861.

- [54] V. Baranchugov, E. Markevich, E. Pollak, G. Salitra, D. Aurbach, *Electrochem. Commun.* 9 (2007) 796.
- [55] S. Seki, Y. Mita, H. Tokuda, Y. Ohno, Y. Kobayashi, A. Usami, M. Watanabe, N. Terada, H. Miyashiro, *Electrochem. Solid-State Lett.* 10 (2007) A237.
- [56] S. Seki, Y. Ohno, Y. Kobayashi, H. Miyashiro, A. Usami, Y. Mita, H. Tokuda, M. Watanabe, K. Hayamizu, S. Tsuzuki, M. Hattori, N. Terada, *J. Electrochem. Soc.* 154 (2007) A173.
- [57] Y. Kobayashi, Y. Mita, S. Seki, Y. Ohno, H. Miyashiro, N. Terada, *J. Electrochem. Soc.* 154 (2007) A677.
- [58] H. Nakagawa, Y. Fujino, S. Kozono, Y. Katayama, T. Nukuda, H. Sakaebe, H. Matsumoto, K. Tatsumi, *J. Power Sources* 174 (2007) 1021.
- [59] A. Farnicola, F. Croce, B. Scrosati, T. Watanabe, H. Ohno, *J. Power Sources* 174 (2007) 342.
- [60] L. Zhao, J.-I. Yamaki, M. Egashira, *J. Power Sources* 174 (2007) 352.
- [61] M. Egashira, H. Todo, N. Yoshimoto, M. Morita, J.-I. Yamaki, *J. Power Sources* 174 (2007) 560.
- [62] H. Ye, J. Huang, J.J. Xu, A. Khalfan, S.G. Greenbaum, *J. Electrochem. Soc.* 154 (2007) A1048.
- [63] H. Sakaebe, H. Matsumoto, K. Tatsumi, *Electrochim. Acta* 53 (2007) 1048.
- [64] A. Guerfi, S. Duchesne, Y. Kobayashi, A. Vijn, K. Zaghbi, *J. Power Sources* 175 (2008) 866.
- [65] D.-W. Kim, S.R. Sivakumar, D.R. MacFarlane, M. Forsyth, Y.-K. Sun, *J. Power Sources* 180 (2008) 591.
- [66] J. Saint, A.S. Best, A.F. Hollenkamp, J. Kerr, J.-H. Shin, M.M. Doeff, *J. Electrochem. Soc.* 155 (2008) A172.
- [67] K. Ui, K. Yamamoto, K. Ishikawa, T. Minami, K. Takeuchi, M. Itagaki, K. Watanabe, N. Koura, *J. Power Sources* 183 (2008) 347.
- [68] J. Rymarczyk, M. Carewska, G.B. Appetecchi, D. Zane, F. Alessandrini, S. Passerini, *Eur. Polym. J.* 44 (2008) 2153.
- [69] J. Wang, S.Y. Chew, Z.W. Zhao, S. Ashraf, D. Wexler, J. Chen, S.H. Ng, S.L. Chou, H.K. Liu, *Carbon* 46 (2008) 229.
- [70] Z.X. Zhang, H.Y. Zhou, L. Yang, K. Tachibana, K. Kamijima, J. Xu, *Electrochim. Acta* 53 (2008) 4833.
- [71] M. Taggougui, M. Diaw, B. Carre, P. Willmann, D. Lemordant, *Electrochim. Acta* 53 (2008) 5496.
- [72] J.H. Shin, E.J. Cairns, *J. Power Sources* 177 (2008) 537.
- [73] J.-K. Kim, G. Cheruvally, X. Li, J.-H. Ahn, K.-W. Kim, H.-J. Ahn, *J. Power Sources* 178 (2008) 815.
- [74] T. Sugimoto, Y. Atsumi, M. Kikuta, E. Ishiko, M. Kono, M. Ishikawa, *J. Power Sources* 189 (2009) 802.
- [75] L. Larush, V. Borgel, E. Markevich, O. Haik, E. Zinigrad, D. Aurbach, G. Semrau, M. Schmidt, *J. Power Sources* 189 (2009) 217.
- [76] C. Sirisopanaporn, A. Farnicola, B. Scrosati, *J. Power Sources* 186 (2009) 490.
- [77] V. Borgel, E. Markevich, D. Aurbach, G. Semrau, M. Schmidt, *J. Power Sources* 189 (2009) 331.
- [78] N. Munichandraiah, L.G. Scanlon, R.A. Marsh, *J. Power Sources* 72 (1998) 203.
- [79] D. Aurbach, B. Markovsky, G. Salitra, E. Markevich, Y. Talyossef, M. Koltypin, L. Nazar, B. Ellis, D. Kovacheva, *J. Power Sources* 165 (2007) 491.
- [80] S.S. Zhang, *J. Power Sources* 162 (2006) 1379.
- [81] V. Eshkenazi, E. Peled, L. Burstein, D. Golodnitsky, *Solid State Ionics* 170 (2004) 83.
- [82] K. Edstrom, M. Herstedt, D.P. Abraham, *J. Power Sources* 153 (2006) 380.
- [83] N. Byrne, P.C. Howlett, D.R. MacFarlane, M.E. Smith, A. Howes, A.F. Hollenkamp, T. Bastow, P. Hale, M. Forsyth, *J. Power Sources* 184 (2008) 288.
- [84] H. Tokuda, K. Hayamizu, K. Ishii, A.B.H. Susan, M. Watanabe, *J. Phys. Chem. B* 108 (2004) 16593.
- [85] K. Hayamizu, Y. Aihara, H. Nakagawa, T. Nukuda, W.S. Price, *J. Phys. Chem. B* 108 (2004) 19527.