Lithium Batteries

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Ionic-Liquid-Based Polymer Electrolytes for Battery Applications

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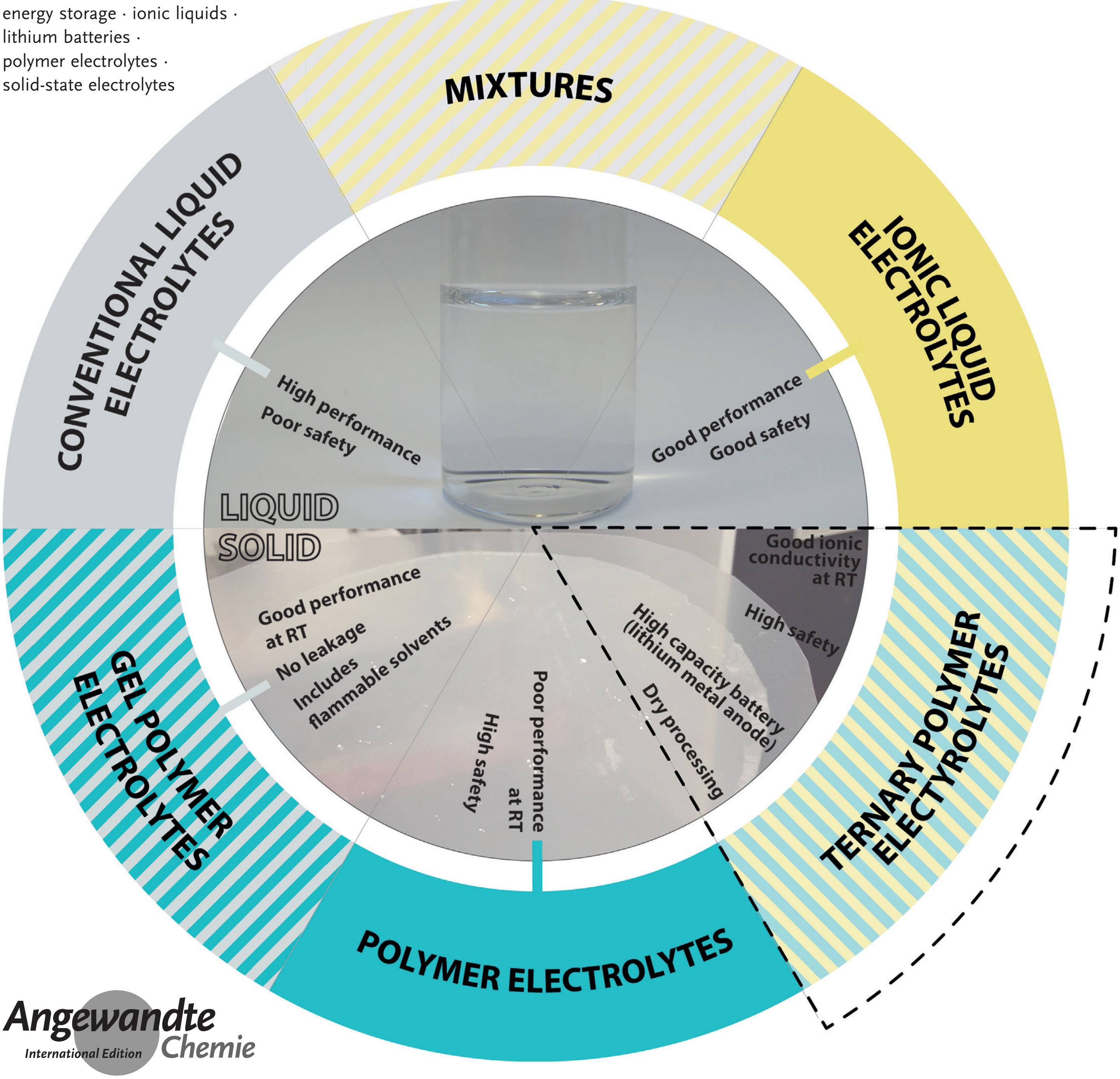

The advent of solid-state polymer electrolytes for application in lithium batteries took place more than four decades ago when the ability of polyethylene oxide (PEO) to dissolve suitable lithium salts was demonstrated. Since then, many modifications of this basic system have been proposed and tested, involving the addition of conventional, carbonate-based electrolytes, low molecular weight polymers, ceramic fillers, and others. This Review focuses on ternary polymer electrolytes, that is, ion-conducting systems consisting of a polymer incorporating two salts, one bearing the lithium cation and the other introducing additional anions capable of plasticizing the polymer chains. Assessing the state of the research field of solid-state, ternary polymer electrolytes, while giving background on the whole field of polymer electrolytes, this Review is expected to stimulate new thoughts and ideas on the challenges and opportunities of lithium-metal batteries.

From the Contents

1. Introduction

The awareness about limited fossil fuels has led today's politics to promote research into the areas of alternative energy production, storage, and distribution systems, particularly when given the irregular production of wind and solar energy. It is well accepted that lithium batteries are among the most promising technologies to meet the energy storage needs for regenerative energy use. Despite considerable efforts to tune lithium-ion batteries, already well-established in the consumer good market, no widespread and well-accepted solution has been presented to date for larger applications such as electric vehicles (EVs). The reason can be found in various issues associated with scaling up the current technology, leading to problems in thermal management and consequently safety, as well as the need for higher energy densities in general.[1]

One of the technologies able to answer these issues is the polymer battery, which was launched in commercial EV applications in 2011. As of today, more than 3500 pure-electric vehicles (Bluecar) have been introduced into the French market by Bolloré, which are powered by lithium-metal polymer batteries (LMPB).[2] These cars are also used in an EV car-sharing project in Indianapolis and will be used in London starting this year.

One of the most promising approaches to further optimize LMPBs is the introduction of ionic liquids into the polymer electrolyte. Ionic liquids (ILs) are salts that are molten below 100 °C or even at room temperature (RTILs). Depending on their chemistry they may show outstanding characteristics such as negligible vapor pressure, high temperature stability, and a large electrochemical stability window.[3] The addition of ionic liquids into polymer-and-salt systems has been investigated since 1995.[4] It is now recognized that this addition significantly improves the overall performance of lithium-metal electrodes. Apart from the electrochemical performance, a major advantage is the absence of low-temperature-flammable compounds. Most of the polymers and ionic liquids researched for battery applications feature high temperature stability and non-flammability upon heat stress. Furthermore, these electrolyte systems do not require the use of the conductive salt $LiPF_6$, which easily releases HF and other toxic compounds when the battery is damaged and the cell components are exposed to the atmosphere. Finally, the use of polymer-based electrolytes offers the possibility to produce thin-film batteries without an additional separator, which is an advantage in terms of energy density.

The main argument against the use of ionic liquids is cost. However, it can be expected that their cost will drop significantly once their production has surpassed a certain level. IL-producing companies estimate that scaling up the production by one order of magnitude will lead to a price reduction of 50–70 %. A production output of 3000 kg month^{-1} of IL is expected to result in prices around 100 € per kg. Another argument against the use of ILs is that many of the well-performing ILs are fluorinated compounds. However, the efforts to synthesize fluorine-free and yet electrochemically stable ionic liquids are recognizable.[5] In other contexts, such as a search for environmentally benign extraction or reaction media, many fluorine-free ILs have been synthesized and characterized, but not with regard to their electrochemical stability.[6]

We note that there is an unspecific use of terms regarding the various polymer electrolyte systems. Terms like "gel polymer electrolyte", "ion gel", "rubbery electrolyte", "plasticized electrolyte", or "solid (hybrid) polymer electrolyte" are often used without definition and different terms are used for identical systems. One reason might be that some of these names have historically been used without strict definition.

Over the years, different classification schemes have been established for different systems of polymer electrolytes.[7] Most of these classifications are made with respect to the compounds incorporated and/or processes used. This approach is reasonable, but it usually does not reflect the interactions at the molecular level. It is not useful to introduce one more classification herein, as there is no uniform use of

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terms even after different classifications were suggested. In this Review, we will distinguish between different interactions in the polymer electrolyte systems, since this understanding is important for optimizing future research.

Owing to the variety of ionic liquids available we will focus on those frequently used for electrolytes. These are ILs with highly delocalized fluorinated anions, which are usually hydrophobic even though they show comparatively highly polarity. In Table 1 we present those ionic liquids with their IUPAC names as well as the abbreviations, which will be used in this Review.

To our knowledge, the research work on polymer electrolytes incorporating ionic liquids has not been reviewed on its own. These electrolytes have been briefly mentioned in Reviews dedicated to either polymer electrolytes in general or electrolytes including ionic liquids (not only for battery applications). However, the increase of research articles dealing with electrolytes combining polymers and ionic liquids calls for a closer look to be taken at this research field. We first present the interactions of the binary systems containing combinations of the components polymer, lithium salt, ionic liquid. On this basis, ternary systems based on PEO and poly(ionic liquids) (PILs) are elucidated. The latest results and progress in the field of polymer electrolytes containing ionic liquids are presented. Lastly, we give a comment on future research.

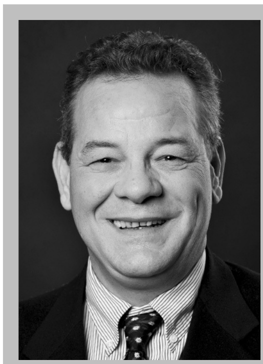
2. Interactions in Binary Systems

Polymers can interact with salts, or with ILs, or with both. ILs interact in turn with (lithium) salts. Explaining the binary interactions between polymers, lithium salts, and ionic liquids is the basis of a deeper understanding of ternary and more complex electrolyte systems.

2.1. Interactions between Polymers and Salts

The interactions between pure polymers and salts have been investigated and discussed since the development of polymer electrolytes, mainly with polyethylene oxide (PEO) as the polymer.[8] Two cases can be distinguished: 1) the conductive salt is dissolved in the polymer (e.g., PEO), and 2) the salt does not dissolve in the polymer.

Ion solvation occurs, like in liquid systems, when the lattice energy of the conductive salt (A) and the cohesive energy of the polymer (B) can be overcompensated by the solvation energy of the resulting polymer–ion complex (C).[8b] It is clear that a conductive salt of low lattice energy is favorable for ion complexation to occur. In the case of lithium, these are salts with large, “soft” anions that delocalize the electric charge. When a certain threshold for a given polymer is passed,[8b] the salt dissociates and the complex forms. However, to understand the interactions it is necessary



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Irene Osada studied business chemistry and philosophy in Aachen, Münster, and Milan. She received her diploma in business chemistry in 2012. Afterwards she joined the group of Prof. Stefano Passerini at the University of Münster, now at the Helmholtz-Institute Ulm. She is currently carrying out her Ph.D. research on ionic-liquid-based electrolytes for secondary lithium batteries.

Table 1: Names of ionic liquids and abbreviations used in this Review.

Acronym	Ionic Liquid
Pyr$_{13}$TFSI	*N*-propyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
Pyr$_{14}$TFSI	*N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
Pyr$_{1.2O1}$TFSI	*N*-methoxyethyl *N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
Pyr$_{1.2O2O2O1}$TFSI	*N*-{2-[2-(2-methoxyethoxy)ethoxy]ethyl}-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide
Im$_{12}$TFSI	1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide
Im$_{12}$BF$_4$	1-ethyl-3-methylimidazolium tetrafluoroborate
Im$_{12}$Tf	1-ethyl-3-methylimidazolium trifluoromethanesulfonate
Im$_{14}$PF$_6$	1-butyl-3-methylimidazolium hexafluorophosphate
Im$_{1.1.3}$BF$_4$	1-propyl-2,3-dimethylimidazolium tetrafluoroborate
Im$_{1.1.3}$PF$_6$	1-propyl-2,3-dimethylimidazolium hexafluorophosphate
Pip$_{13}$TFSI	*N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide
Py$_{41}$TFSI	1-butyl-4-methylpyridinium bis(trifluoromethanesulfonyl)imide
N$_{6.4.4.4}$CH$_3$SO$_3$	*N*-hexyl-N,*N*,*N*-tributyl ammonium methanesulfonate
N$_{1.1.3.4}$TCM	*N*,*N*-dimethyl-*N*-propyl-*N*-butyl ammonium tricyanomethanide
S$_{2.2.2}$TFSI	Triethylsulfonium bis(trifluoromethanesulfonyl)imide
Gua$_{13}$TFSI	*N*,*N*,*N*′,*N*′,*N*″-pentamethyl-*N*″-propylguanidinium bis(trifluoromethanesulfonyl)imide

to take into account further aspects, such as ion pair formation at higher salt concentrations and/or the effect of the free volume induced in the polymer on segmental motion.

Also the polymers' physico-chemical properties determine if a salt is dissolved or not. Corresponding data is shown in Table 2. However, it is rather difficult to obtain comparable data for different polymers, for example, the dielectric properties are not always given for the same frequency and solubility parameters are calculated with different computational models. The solubility parameter is a common measure for the cohesive energy of polymers. Even though a good complexation of the cations is necessary for the formation of the polymer electrolyte, too strong an interaction is detrimental since the cations might be hindered for moving, that is, conducting charge.

Table 2: Physical properties of polymers frequently used in polymer electrolytes. Data from Refs. [12–14].

Polymer	Dielectric constant ε[a]	Solubility parameter δ/[J cm^{-3}]$^{0.5}$	T_g/°C	T_m/°C
PEO	10–15	20.2	−50	65
PAN	5.5	25.27–31.51	97	319
PVdF[b]	8.2–10.5		−40	165
PVdF-HFP[c]	7.9–10.0		−36	142
PMMA	3.0	17.39–27.21	105	Amorphous

[a] At 1 kHz. [b] Kynar 740. [c] Kynar FLEX 2801.

One issue that needs to be addressed when the characteristics of polymer electrolytes are to be determined is that polymers are often in non-thermodynamically stable equilibrium states. The resulting long relaxation times are especially a problem when characteristics of different polymer systems shall be compared.

The ion transport in PEO polymer electrolytes is the best investigated of all polymer electrolyte systems. When PEO and low-lattice-energy Li salts are mixed, the glass transition temperature T_g of the mixtures increases. This increase is due to the coordination of Li$^+$ by ether oxygen atoms leading to impeded chain movement.[8]

Depending on the anion and relative amount of the conductive salt, different PEO$_x$:Li$^+$ phases form.[8,9] In the PEO-salt mixtures the polymer chains coil helically around the lithium cation, which is, then, coordinated by a specific number of ether oxygen atoms (4 to 5) acting as Lewis bases.[10] Depending on the composition the anions also coordinate to Li$^+$, especially at higher lithium salt contents.[11] Ion conduction occurs when the coordination to one of the oxygen atoms is broken and coordination to the next site takes place (Figure 1). Temperature influences this process and can be interpreted as a measure for the energy available for segmental motion of the polymer chains according to the free-volume model. This process is known as the dynamic percolation model.[12]

Polymerized or poly(ionic liquids) (PILs) are polymers derived from ionic liquids in which either the cation (to give a so-called PCIL) or the anion (PAIL) or both are incorporated into the polymer backbone. If not incorporated into the backbone, the counterion species are free. The ionic conductivity of PILs is usually measured without the addition of another salt. Not many studies have been performed on electrolytes made of solely PILs and lithium salt, as PILs are also used for many other applications, for example, binders or separation.[13]

A strong influence of the anion on T_g and ionic conductivity is found for PILs.[14] It is possible to add significant amounts of lithium salt with large anions, preferably the same anion which is already present in the system. Mixtures of the PCIL poly(diallyl dimethyl ammonium) bis(trifluoromethanesulfonyl)imide [PPyr$_{11}$TFSI] with up to 30% in weight of LiTFSI were investigated, partially with addition of ionic liquid.[15] It is clear that the lithium ion conduction mechanism is different compared to PEO–salt mixtures: the PPyr$_{11}$ backbone has cationic species incorporated and no Lewis electron donors. Therefore, coordination of Li$^+$ ions is unlikely.[15a] Ionic conductivities of the investigated samples ranged from 3.15×10^{-6} S cm^{-1} to 9.98×10^{-6} S cm^{-1}, increasing with LiTFSI content.

Matsumi et al. prepared 1,3-diallylimidazolium-based (PIm) PCILs,[16] including a methoxyboron or a mesitylboron unit into the polymer backbone to trap the TFSI anion. The PILs were mixed with equimolar amounts of LiTFSI, leading to ionic conductivities of 3.7×10^{-5} S cm^{-1} and 1.9×10^{-5} S cm^{-1} at 50 °C. When LiTFSI was substituted with

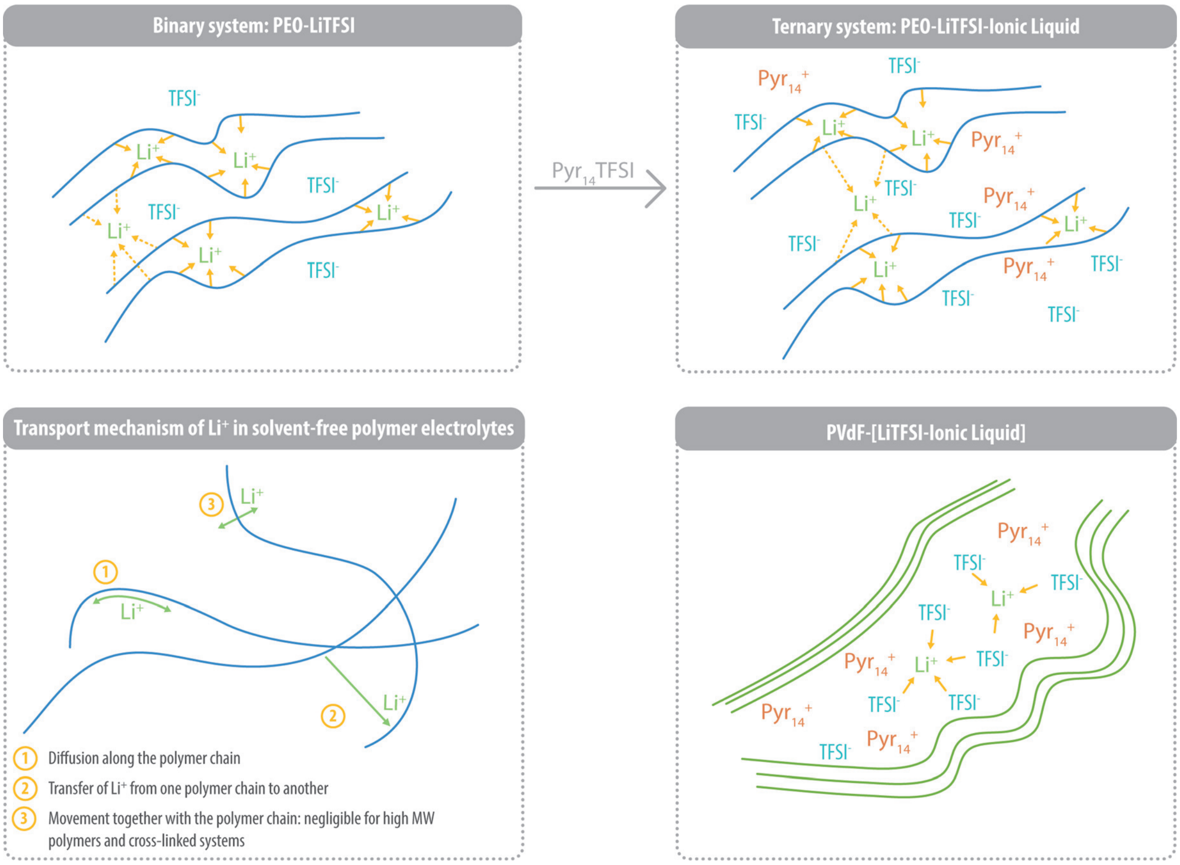

Figure 1. a) Li^+ ion coordination and c) transport mechanisms (from Ref. [36]) in PEO-based, binary polymer electrolytes. Li^+-ion coordination in ternary polymer electrolytes containing b) active polymers (e.g., PEO) and d) inactive polymers (e.g., PVdF).

lithium triflate (LiTf), the ionic conductivity decreased by around two orders of magnitude and the T_g increased significantly. Ogihara et al. observed that the ionic conductivity of several PCILs with the TFSI counter anion decreased upon addition of LiTFSI and on polymerization in presence of a cross-linker.[17]

PEO and PILs are the only polymer hosts for which a strong interaction and ionic conduction via segmental motion were reported. Our focus, also concerning the comparison of performance, is based on these systems and their derivatives. We mention other polymers to contrast the different working principles.

The addition of LiTf to PAN results in a weakening of the dipole–dipole interactions between the polymer chains' CN groups and results in CN–Li coordination instead.[18] On addition of the salt, unlike with PEO, the T_g decreases. This change can be understood as being a result of the weakening of the interactions between the polymer chains' CN groups and an increase in free volume induced upon salt addition. Even though the Li^+ ions do somehow interact with the polymer's functional groups, recently it was found that in PAN–$LiBF_4$ systems the polymer chains are not involved in the ion transport.[19] This result is in agreement with the very low ionic conductivity of the polymer–salt mixtures. At low to moderate salt concentrations, the ionic conductivity is very poor with $10^{-9}\,S\,cm^{-1}$ at over 100 °C.

Poly(vinylidene fluoride) (PVdF) and its copolymer Poly(vinylidene fluoride-co-hexafluoropropane) (PVdF-HFP) are not expected to form complexes with salts. Even though these polymers are elastomers and have a comparably high dielectric constant, they are known for their inertness, hydrophobicity, and generally high chemical persistence. No complex is formed owing to the inability of the fluorinated alkyl chains to act as Lewis donors.

Polymethacrylates were mostly used and investigated in conjunction with organic liquid electrolytes. They include an ester function in the polymer backbone and offer the possibility to attach different functional alkyl chains. By means of FTIR spectroscopy the ester function was shown to interact with the lithium cation.[20] In most cases, the attached functional groups are a methyl group or alkyl chains with ether functions.

2.2. Interactions between Polymers and Ionic Liquids

Terms like "plasticization" or "plasticized" are frequently found in the literature of polymer electrolytes. In polymer chemistry, the term "plasticizer" is used to describe a compound that alters properties, such as rigidity, flexibility or shock resistance, of a polymer.[21] In the field of polymer electrolytes, the term "plasticizer" is often used for additives lowering the glass transition temperature of the host polymer and therefore improving ionic conductivity. Beside this effect, the term “plasticizer” is used if the additive reduces the brittleness, or increases the flexibility and processability of the polymer electrolyte. In the case of organic solvents this is often accompanied by the gelation of the electrolyte. However, the physical background of the alterations induced when a liquid is added to a polymer is not always the same. Furthermore, the interactions do not only depend on the chemical and physical structure, but also on the history of the polymer. For example, a polymer that was heated and quenched can have a different amount of crystalline phase, which, in turn, can influence the effect of a given plasticizer.

In this Section, we will only deal with external plasticizers, for example, compounds that are added to a polymer and interact with it, compared to internal plasticizers that are part of the polymer chain and increase the amorphous fraction by hindering crystallization.

The compounds that are used as plasticizers for polymer electrolytes can be categorized as: ionic liquids, conventional organic electrolytes, monomer/oligomer units of the polymer, and other organic solvents and compounds.

From Table 3 it becomes clear that the plasticizers’ modes of operation must be different as a result of their different properties. Apart from the melting and boiling points or viscosity, the ionicity of the ionic liquids causes different interactions with other materials. The advantage of the ionic liquids’ negligible vapor pressure and higher thermal stability also becomes clear. However, it is also clear that the high viscosity of the ionic liquids is an issue that needs to be addressed when the IL is incorporated in a non-interacting polymer matrix, that is, the IL is used as a “liquid solvent”. It is necessary to consider all of these interactions to understand the different interactions in polymer electrolytes.

Table 3: Physical properties of chemicals frequently used as plasticizers in polymer electrolytes.

Substance	T_b/°C	T_m/°C	$\eta^{[a]}$/mPa s	$\rho^{[b]}$/g cm^{-1}	Vapor pressure/kPa
Dimethyl carbonate (DMC)	90	2.4	0.585	1.0697	2.40 (21 °C)
Diethyl carbonate (DEC)	126	−43.0	0.748	0.9752	1.63 (25 °C)
Propylene carbonate (PC)	242	−48.8	2.53	1.2047	0.004–0.017 (20 °C)
Ethylene carbonate (EC)	248	−36.4	1.93 (40 °C)	1.321 (25 °C)	0.003 (25 °C)
Pyr_{14} TFSI	–	−6.3	60 ± 3	1.41	–
$Pyr_{1.201}$ TFSI	–	n/a	57.6	1.40	–
Im_{12} TFSI	–	−15 to −3	34 (20 °C)	1.52	–
Pip_{13} TFSI	–	8.7	117		–

[a] At 25 °C unless differently indicated. [b] At 20 °C unless differently indicated. n/a = not available.

There are not many studies available on the interactions of ILs with polymers because electrolytes for battery application require investigations with conductive salts. Most publications in this field are dedicated to dye-sensitized solar cells, supercapacitors, or fuel cells, which, however, make use of ionic liquids that are not suitable for battery applications.

Interactions of PEO with different ionic liquids have been characterized based on the hard and soft acid and base (HSAB) theory. The PEO ether oxygen atom is a hard base. The most pronounced effect on the interaction has been found to depend on the hardness of the ionic liquid cation. ILs with hard cations, such as those of the imidazolium family, show good miscibility with PEO while soft cations, such as those from the pyrrolidinium family, show poor miscibility. In the first case, a dependence of ionic conductivity on the IL content is found, while this does not occur in the second case. In fact, PEO and an excess of $Pyr_{14}TFSI$ form a cloudy mixture at 25 °C after heating. Ionic conductivity in PEO–IL mixtures is believed to take place mainly in IL regions that are said to be micro-phase separated.[22] Simulations predict the presence of remaining ion pairs in the mixtures.[23]

Susan et al. investigated the radical polymerization of seven different vinyl monomers in the presence of $Im_{12}TFSI$.[24] It was found that PMMA and poly(methyl acrylate) are compatible with the ionic liquid, giving self-standing transparent films, whereas PAN, polystyrene, poly(2-hydroxy ethyl methacrylate), and poly(acrylamide) are not compatible.

Mixtures of ILs and PILs were prepared with IL contents up to 50 wt %.[15a] The samples did not show phase separation, which is reasonable because of the chemical similarity between the two substances. The PIL and corresponding ionic liquid seem to be miscible in any composition, but the more ionic liquid was added, the stickier was the sample. PVdF-HFP forms a gel with ILs in which the polymer is not dissolved, but can act as an inert support that immobilizes the ionic liquid.

2.3. Interactions between ionic liquids and Li salts

Mixtures of ionic liquids and lithium salts have been widely investigated as electrolytes for secondary battery applications. Their detailed properties can be found elsewhere.[25] As in other electrolytes, the conductivity is dominated by the viscosity of the resulting electrolyte,[25b,26] although in pure ionic liquids the interaction between the cation and the anion seems to be more important.[27] Their viscosity and conductivity show the same temperature behavior in the Arrhenius plot. This can be seen from the almost linear interdependence when the viscosity is plotted logarithmically versus the conductivity, as is shown in Figure 2. Such interdependence was not found for the T_g and conductivity of ternary polymer electrolytes.

The interactions between lithium cations and the anions were intensively studied by NMR and Raman spectroscopy, in combination with computational methods.[25c,28] It has been found that the Li^+ ion transport primarily takes place via the structure diffusion mechanism, that is, by anion exchange in the first coordination shell, as opposed to diffusion of Li^+

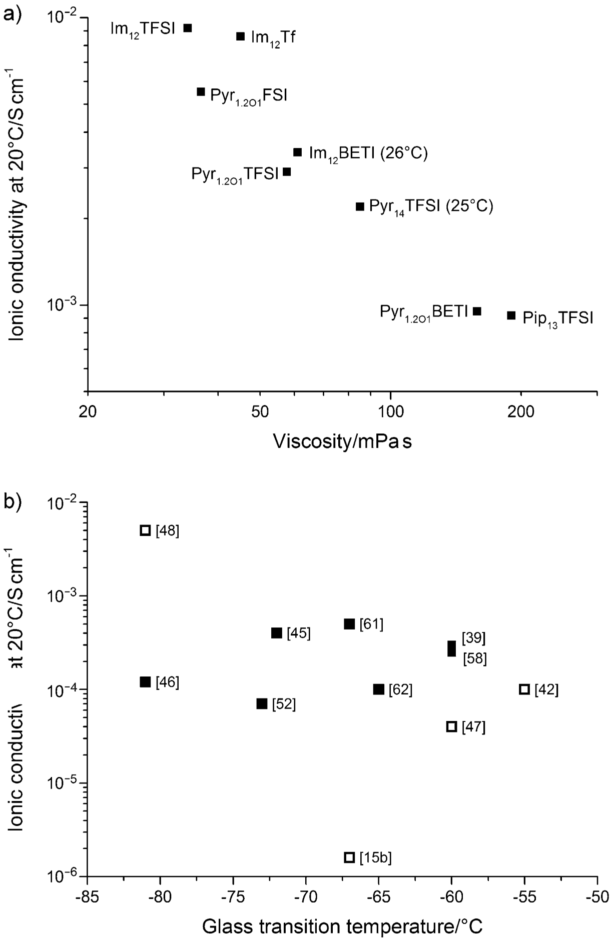

Figure 2. Relationship between a) viscosity and conductivity of ILs and b) T_g and conductivity of ternary polymer electrolytes. Solid symbols refer to PEO-based systems and empty symbols to PIL-based systems; all values are taken from literature (see reference numbers).

cations together with their coordination shell (vehicular mechanism).[29] Furthermore, in a mixture (1:9 molar ratio) of LiTFSI:PYR$_{14}$TFSI the Li$^+$ and TFSI$^-$ ions experience the same molecular environment in a 2D-NMR experiment, which is interpreted as evidence for strong $[\mathrm{Li(TFSI^-)}_x]^{(x-1)-}$ adducts.[28c] The average number of TFSI$^-$ ions that are coordinated by Li$^+$ varies with the concentration of LiTFSI and was determined to range from 4 TFSI$^-$ at low salt concentration to 2 TFSI$^-$ at mol fractions greater than 0.15.[28a]

3. Ternary Polymer Electrolyte Systems

From Section 2 it becomes clear that the major drawback of polymer and salt systems is their low ionic conductivity at room temperature. It was shown that the polymers show different interactions with lithium salts and plasticizers, whereby ionic liquids are the only plasticizers not to compromise important safety issues. Herein, we discuss the interactions of ionic liquids and conductive salts with different polymer host materials. This overview, extending over the 20 years of the development of ternary polymer electrolytes, shows the progress already achieved for polymer electrolytes in battery applications. The two most promising approaches to improve the existing systems, cross-linking of the polymer host and addition of inorganic fillers, will be discussed in further detail. Finally, we describe the progress in the application of ternary polymer electrolytes in LMPB.

3.1. Comparison of the interactions in ternary systems

As discussed before, some polymers can strongly interact with lithium ions, while others mostly or solely build a framework. The effect of plasticizers, in this case ionic liquids, can be best understood in relation to the polymer and salt interaction. Only some electrolyte systems based on polymers interacting with lithium cations (e.g., PEO or PILs) show large improvements on the incorporation of ionic liquids. PILs, as well as PAN, have been introduced into ternary polymer electrolytes since 1993.[30] Systems based on PEO followed ten years later.[31] Copolymers, which often combine ethylene oxide or ionic liquid units with acrylates, are another group of well-researched polymer hosts for ternary electrolytes. The most important “inactive” framework (no interaction with both the IL and lithium salt) is PVdF.

The function of PVdF in a polymer electrolyte is to guarantee mechanical stability, also preventing short circuit between anode and cathode, as well as leakage of the electrolyte in case of cell damage. The polymer acts as a separator and host of the liquid electrolyte (solvent and lithium salt). Thus, a high porosity and high liquid electrolyte to polymer ratio are beneficial.

Shortly after ternary polymer electrolytes arose, Sutto et al. performed a comparative study of PEO and PVdF “gels” with Im$_{1.1.3}$BF$_4$ and Im$_{1.1.3}$PF$_6$ and 0.5 M of the corresponding lithium salt. They found PVdF to be superior owing to the ability of the polymer to form ionic conducting channels filled with ionic liquid/lithium salt mixture (see Figure 1 d), in a similar manner to the water-filled channels in Nafion.[32] Singh and Sekhon came to the same result in the case of ternary electrolytes composed of PVdF incorporating a mixture 0.5 M LiTf in 2,3-dimethyl-1-octylimidazolium triflate (IM$_{1.1.8}$Tf).[33] However, such PVdF gels usually show a lower conductivity compared to systems with a separator (e.g., ionic-liquid electrolytes with glass fiber or ceramic separators).[34] Therefore, we do not include publications on ternary PVdF–ionic-liquid electrolytes in this Review.

If the polymer host is PEO, the ether oxygen atom interacts with the lithium ions. An explanation was given by the group of Ohno, defining both as hard functional groups.[22] Compared to binary systems, ionic liquids in ternary polymer electrolytes may either interact with the polymer host, which is the case for imidazolium cations and PEO where the ionic conductivity is decreased,[22] or they may not interact and consequently enhance the mobility of the polymer chains (see Figure 1 b). For Pyr$_{14}$TFSI-incorporating polymer electrolytes, Raman spectroscopy showed no interaction between lithium and the TFSI anion if the EO/LiTFSI ratio is greater than or equal to 10.[35] In 2013, Chaurasia et al. performed

Raman investigations of ternary systems incorporating $IM_{14}PF_6$ with the corresponding lithium salt in PEO.[36] Polymer–cation interactions between ether oxygen atoms and lithium or imidazolium were identified as well as contact ion pairs of both cations with PF_6^-.

In a theoretical study, Diddens and Heuer modelled the effects of the ionic liquid in ternary polymer electrolytes.[37] It was found that Li^+ is virtually completely coordinated by PEO and therefore the cation transport is coupled to the polymer chains. Two effects of ILs were identified as shown in Figure 1c). First, the IL addition leads to a dilution of the electrolyte which slightly decreases the interchain transfers of the lithium cation. However, the predominant effect is the enhancement of the segmental motion of the PEO chains, overall leading to a higher lithium diffusivity in the ternary system.

Other mechanisms take place in polyelectrolytes and their subclass poly(ionic liquids). Most of the work, so far, focused on polycations, which may be due to the difficulty in polymerizing the perfluorinated anions of ionic liquids.[13] The reduced lithium mobility resulting from the strong coordination of the polyanionic backbone to lithium is an issue. Sun et al. investigated a lithium polyelectrolyte, poly(2-acrylamido-2-methyl-1-propane-sulfonate) [LiPAMPS], in combination with the ionic liquid $N_{6.4.4.4}CH_3SO_3$.[38] The lithium mobility was found to be low in the homopolymer owing to polydentate coordination of the lithium cation. This effect was reduced by introducing 90 mol% of N-vinyl formamid copolymer (PVF). Ionic conductivity was several times higher in the copolymer even though the lithium content was reduced by the factor of four. Other polyanions mimic the highly conductive anions TFSI, tricyanomethanide (TCM), and dicyanamide (DCA).[39] However, ionic conductivity with Pyr_{14} counterion was found to be very low (2.0×10^{-8}–$1.6\times10^{-7}\,S\,cm^{-1}$) at 25 °C. Another concept is anion trapping in PILs. For example, boric ester anion receptors are incorporated in the polymer backbone to enhance the lithium transference number in polycations.[16] Nevertheless, the effect of the high transference number on the Li^+ limiting current was not verified in battery tests. Often spacers between polymerized backbone and ionic end group are used to enhance the flexibility of the polymer, for example some ethylenoxy[40] or hydrocarbon[17] units.

3.2. Development of Ternary Polymer Electrolytes

The group of Watanabe introduced ternary systems in 1993[30] and 1995[4b] using a PIL, 1-butyl pyridinium halide (Cl or Br) and $AlCl_3$. In 1996 they introduced an ionic-liquid electrolyte with LiTFSI, lithium acetate (LiOAc), and triethylmethylammonium benzoate (TEMAB). Properties of the ionic-liquid electrolyte were discussed as well as polymer complexes with poly(acrylonitrile) (PAN) and poly(vinyl butyral).[4a]

In 2003, Shin et al. presented a fundamental study on a ternary electrolyte based on PEO, Pyr_{13}TFSI, and LiTFSI.[31] The addition of different amounts of ionic liquid was investigated. Additionally, a cell composed of such an electrolyte, the lithium metal anode, and the composite cathode electrode made of V_2O_5 and carbon additive embedded in the ternary polymer electrolyte matrix was realized and tested, showing extremely promising performance at relatively low temperatures (60 °C). Some years later the same group presented a study of Pyr_{1x}TFSI ternary electrolytes with $x = n$-propyl ($n3$), *sec*-propyl (*sec*3), *n*-butyl ($n4$), *sec*-butyl (*sec*4), isobutyl (*iso*4), *n*-pentyl ($n5$) in which Pyr_{1n4}TFSI was identified as the best performing system.[41] A typical, fully amorphous ternary polymer electrolyte is shown in Figure 3. The plasticizing effect of the ionic liquid is shown by stretching and relaxing the electrolyte.

Pappenfus et al. tested an equimolar mixture of tetraethylene glycol dimethyl ether (tetraglyme, G4) and LiTFSI forming the complex [Li(G4)]TFSI in combination with two poly(ionic liquids) in 2004.[42] The mixture was called RTIL though it is a complex between a salt and an uncharged species. Later, Angell et al. introduced the "solvate" or "chelate" definition for this group of ionic liquids.[43] The group of Watanabe lately presented criteria for this new family of ILs[44] and the application of [Li(G4)]TFSI in polymer electrolytes.[45] A comparison of [Li(G4)]TFSI in different polymer hosts (PEO, PMMA, and poly[butyl acrylate]) revealed a ligand exchange from tetraglyme to host material only for PEO.

A ternary electrolyte with 1 M $LiBF_4$ in $Im_{12}BF_4$ with a highly branched polymerized poly(ethylene glycol) diacrylate (PPEGDA) was tested in combination with $Li[Li_{1/3}Ti_{5/3}]O_4$ and $LiCoO_2$ in 2003.[46] The two acryl groups of the macromonomer ($M_w = 600$) lead to a high degree of

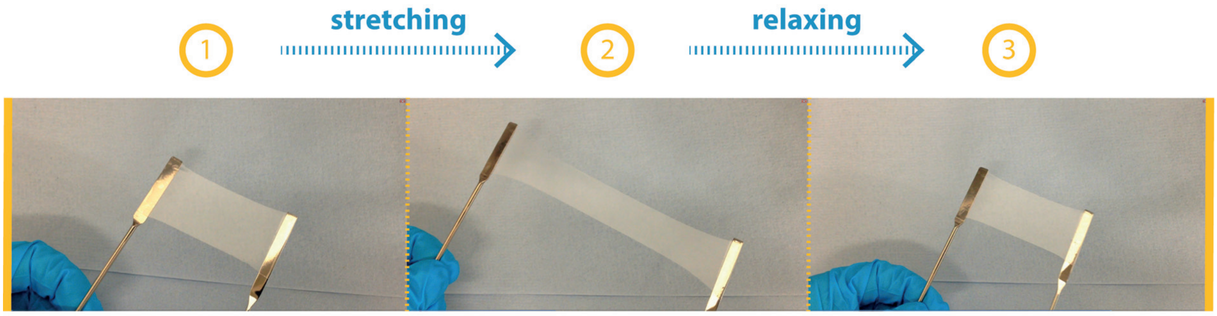

Figure 3. Mechanical properties of a PEO–LiTFSI–Pyr_{14}TFSI ternary polymer electrolyte.

cross-linking; therefore, only 15 wt % of polymer were required to build a matrix of the electrolyte.

In 2005 the group of Watanabe presented a binary electrolyte which incorporates a room-temperature ionic liquid (RTIL) with lithium as cation in P(EO/PO) triacrylate.[47] Though the pure salt showed lithium conductivity the performance of the corresponding polymer electrolyte was not higher compared to binary PEO–LiTFSI electrolytes. A combination of LiPAMPS and its copolymer LiPAMPS–PVF with Im$_{12}$TCM and N$_{1.1.3.4}$TCM was investigated by Cha et al. in 2008.[48] Again the ionic conductivity of the copolymer with lower lithium content was several times higher. The comparison of the conductivity performance obtained with two different ILs incorporated in the copolymer demonstrated the beneficial influence of lower viscosity. However, the ionic liquid (90 wt % of the electrolyte) might be the reason for the very high ionic conductivity (5.4×10^{-3} S cm^{-1} at 25 °C) rather than the lithium ions.

The cation 1-butyl-4-methylpyridinium (Py$_{14}$) was introduced into polymer electrolytes by Cheng et al. in 2007.[49] However, the ionic conductivity was substantially lower compared to pyrrolidinium. Ternary polymer electrolytes with IM$_{12}$TFSI or Pip$_{13}$TFSI were presented in 2008.[50] The systems are investigated in terms of conductivity, electrochemical stability, and cells performance (with LiFePO$_4$ as cathode). Though improvements in conductivity were achieved, these electrolytes were still partly crystalline. Improved performance with Pip$_{13}$TFSI were shown by An et al. in 2012.[51]

Abitelli et al. tested ternary polymer electrolytes with pyrrolidinium cations with ether side chains in 2010.[52] Pyr$_{1.2O1}$TFSI as well as Pyr$_{1.2O2O2O1}$TFSI were expected to improve the conductivity as a result of the interaction of Li$^+$ with the more mobile Pyr$^+$ cation.[53] However, all the polymer electrolytes were partly crystalline and the electrochemical stability window (ESW) was smaller compared to that of Pyr$^+$ cations with alkyl side chains.[53] Another example for a polymer electrolyte incorporating an IL cation with ether side chain is Pip$_{1.1O1}$TFSI which was presented one year later.[54] Döbbelin et al. used pyrrolidinium monomers with ethylene glycol side chains to form PILs.[55] They reported the highest conductivity for Pyr$_{1.201}$TFSI in a comparison between Pyr$_{14}$TFSI and Pyr$_{1.(20)x1}$TFSI with $x = 1$–3. For PILs with corresponding monomers PPyr$_{1.2O2O2O1}$ gave the highest ionic conductivity in combination with 80 wt % of Pyr$_{1.2O1}$TFSI. A ternary electrolyte with LiTFSI (10 wt %) showed a conductivity of 1.2×10^{-3} S cm^{-1} at 60 °C.

Poly(diallyldimethylammonium)TFSI (PPyr$_{11}$TFSI) in combination with Pyr$_{14}$TFSI and LiTFSI was tested with different PIL–IL ratios, showing that higher ionic-liquid content leads to higher conductivity.[15] The ionic conductivity of 5×10^{-4} S cm^{-1} was found at 40 °C for an ionic-liquid content of 60 wt %; lithium stripping–plating was performed for 4000 h with 0.05 mA cm^{-2} at 40 °C.[15b] However, the evolution of overpotential showed a constant increase, indicating a less-stable SEI for this system when compared to a similar PEO-based ternary electrolyte. A PIL copolymer composed of a guanidinium-based IL and PMMA was introduced in 2011.[56] The comparison of different anions (PF$_6^-$, BF$_4^-$, ClO$_4^-$, and TFSI), in both the lithium salt and the guanidinium-based IL, showed the TFSI anion enhanced the ionic conductivity. Furthermore, TFSI was found to increase the amorphous phase, giving a T_g of −60 °C (compared to 6.4 °C for BF$_4^-$).

Triethylsulfonium (S$_{2.2.2}$) was tested by Fisher et al. in 2011 with very promising results.[57] Although the polymer with S$_{2.2.2}$TFSI was not fully amorphous, high ionic conductivities were achieved with compositions of 20:1:1 and 20:1:1.5 (EO:LiTFSI:S$_{2.2.2}$TFSI) even at room temperature.

While there is a substantial number of publications for ternary polymer electrolytes, only few of them compare different ionic liquids. Our group recently published a study of ternary polymer electrolytes incorporating PEO, LiTFSI, and one of eight different ionic liquids in the molar ratio 20:2:4.[58] It was found that the replacement of Pyr$_{14}$ with Pyr$_{12O1}$ slightly increases the ionic conductivity while all other properties were almost constant for samples with TFSI, FSI, BETI, and IM$_{14}$ anions. Mixtures incorporating BETI and IM$_{14}$ showed, however, higher overpotential upon lithium plating/stripping, most likely a result of the larger size of the anion. Samples with FSI show superior ionic conductivities but no stable lithium stripping and plating. Fisher et al. investigated ternary polymer electrolytes based on triethyl sulfonium with five anions: TFSI, BETI, PF$_6^-$, BOB, and ClO$_4^-$.[59] They found that the lithium transference number depends on the anion size with higher values for bigger anions (BETI > TFSI, BOB > PF$_6$, ClO$_4$) using the method of Evans et al., although this method applies only to measurements cells offering negligible charge-transfer resistance with respect to the electrolyte (ionic) resistance, which is rarely the case with IL-containing polymer electrolytes.[60] In both studies the TFSI anions showed the best performance in terms of stability and conductivity in lithium batteries.

In summary, many RTILs have been incorporated in polymer electrolytes since the concept was developed in 2003. It was shown that the addition of several ionic liquids can lead to completely amorphous polymer electrolytes if the ratio between the three components is chosen carefully.[58,61] The performance of the ternary polymer electrolytes is correlated to the ionic liquid used in terms of ionic conductivity, and electrochemical and thermal stabilities. For example, Pyr$_{14}$TFSI shows a wide ESW and high ionic conductivity, significantly improving the performance of a polymer electrolyte when incorporated in it.[7a]

The development of the ternary system in terms of amorphicity, T_g, ionic conductivity at 20 °C and 60 °C, and interfacial resistance is summarized in Table 4. Though the lithium transference or transport number was often calculated for ternary polymer electrolytes we did not include these values herein owing to the restrictions of the method mentioned above.[60] The overall ionic conductivities at room and elevated temperature illustrate the capability of the polymer to allow ion transport (including lithium). The interfacial resistance is by far highest resistance in lithium polymer cells. Unfortunately, it is seldom reported, just like lithium stripping/plating tests. Thus, it is difficult to estimate the performance of a polymer electrolyte without testing it in batteries with lithium electrodes.

Table 4: Composition and performance of ternary electrolytes.[a]

Year	Electrolyte composition	Am.	T_g/°C	σ at 20 °C/mS cm^{-1}	σ at 60 °C/mS cm^{-1}	R_{SEI} at 20 °C Ω^{-1}	Ref.
1996	$PAN_4[TEMAB_7LiOAc_2LiTFSI_1]_6$	–	–	1.0×10^{-6}	3.0×10^{-5}	–	[4a]
2003	$PEO_{20}LiTFSI\ [Pyr_{13}TFSI]_{2.15}$	no	−60	3.0×10^{-4}	1.5×10^{-3}	–	[31]
2003	$PPEGDA_{15\%}[LiBF_4Im_{12}BF_4]_{85\%}$	–	−81	1.2×10^{-4}	1.8×10^{-4}	–	[46]
2004	$[PPyr_{11}TFSI]_{50\%}[Li(G4)]TFSI_{50\%}$	yes	−55	1.0×10^{-4}	8.0×10^{-4}	1800	[42]
2005	$[PEO_{50\%}[Im_{1.1.8}Tf]_{50\%}]LiTf_{0.5M}$	no	–	2.0×10^{-6}	2.0×10^{-4}	–	[33]
2005	$P(P[PEO\text{-}PPO]Acr_3)_{0.84}\ LiTFSA\text{-}30_{0.16}$	yes	−60	4.0×10^{-5}	2.0×10^{-4}	–	[47]
2007	$PEO_{20}LiTFSI_2\ [Pyr_{14}TFSI]_{1.92}$	yes	–	1.1×10^{-4}	1.0×10^{-3}	3000	[41]
2007	$PEO_{20}LiTFSI_1[Py_{4.1}TFSI]_1$	no	−51	–	6.0×10^{-4}	480	[49]
2008	$P([AMPS\text{-}Li]_1\text{-}VF_9)_{10\%}\ [Im_{12}TCM]_{90\%}$	yes	−81	5.0×10^{-3}	2.0×10^{-2}	-	[48]
2008	$PEO_{20}LiTFSI_1[Pip_{13}TFSI]_1$	no	−49	–	1.2×10^{-3}	2000 (50 °C)	[50]
2008	$PEO_{20}LiTFSI_2\ [Pyr_{14}TFSI]_2$	yes	−65	1.0×10^{-4}	2.0×10^{-4}	–	[62]
2009	$[PPyr_{11}TFSI]_{36\%}LiTFSI_{14\%}\ [Pyr_{14}TFSI]_{50\%}$	–	–	1.0×10^{-4}	1.5×10^{-3}	–	[15a]
2010	$[PPyr_{11}TFSI]_{28\%}LiTFSI_{12\%}\ [Pyr_{14}TFSI]_{60\%}$	no	−67	1.6×10^{-6}	1.0×10^{-3}	2200	[15b]
2010	$PEO_{20}LiTFSI_1\ [Pyr_{1.2O1}TFSI]_{1.5}$	no	−73	7.0×10^{-5}	1.4×10^{-3}	–	[52]
2011	$[P(Gua_{33\%}\text{-}MMA_{67\%})TFSI]_{70\%}\ LiTFSI_{30\%}$	–	−60	–	1.8×10^{-4}	–	[56]
2011	$[P(Gua\text{-}MMA)]_{59\%}LiTFSI_{12\%}\ [Gua_{13}TFSI]_{23\%}\ [SiO_2]_{6\%}$	yes	−60	–	2.3×10^{-5}	4000 (80 °C)	[63]
2011	$PEO_{20}LiTFSI_1\ [S_{2.2.2}TFSI]_1$	no	–	5.0×10^{-4}	2.0×10^{-2}	11 000	[57]
2011	$PEO_{20}LiTFSI_1\ [Pip_{1.1O1}TFSI]_1$	no	–	–	6.3×10^{-4}	22 000	[54]
2012	$[PPyr_{1.2O2O2O1}TFSI]_{40\%}[Pyr_{1.2O1}TFSI]_{50\%}\ LiTFSI_{10\%}$	–	–	3.5×10^{-4}	2.0×10^{-3}	–	[55]
2012	$PEO_{20}LiTFSI_1\ [Pip_{13}TFSI]_{1.27}$	no	–	2.1×10^{-4}	8.7×10^{-4}	30 000	[51]
2013	$PEO_{20}LiTFSI_2\ [Pyr_{14}TFSI]_6$	yes	−67	5.0×10^{-4}	2.5×10^{-3}	–	[61]
2015	$PEO_{20}LiTFSI_2\ [Pyr_{1.2O1}TFSI]_4$	yes	−60	2.5×10^{-4}	1.8×10^{-3}	2400	[58]
2015	$PEO_{20\%}[Li(G4)]TFSI_{80\%}$	–	−72	4.0×10^{-4}	2.5×10^{-4}	–	[45]

[a] $Polymer_xLi\text{-}salt_yIL_z$ [x, y, z = molar ratio] respectively $Polymer_{x\%}Li\text{-}salt_{y\%}IL_{z\%}$ [x%, y%, z% = weight ratio]. For empty fields the property was not reported in the article. Am. = fully amorphous.

It is worth mentioning that even the statically determined R_{SEI} is insufficient information because of the continuous lithium–electrolyte SEI evolution. While the primary SEI reacts in contact with the electrolyte, the resulting secondary SEI is not permanent. In our opinion, stripping/plating tests with lithium give the highest quality of information: The overpotential indirectly measures the (overall) resistance of the cell, the evolution of the overpotential reveals the stability of the SEI.

Figure 4 shows the development of ionic conductivities of polymer electrolytes induced by the addition of ionic liquids in recent years. Many systems reach an ionic conductivity of 10^{-4} S cm^{-1} at room temperature and 10^{-3} S cm^{-1} at 60 °C which is desirable for practical applications. Compared to ionic-liquid electrolytes, no correlation was found between the chain mobility (T_g) of the polymer and the ionic conductivity (see Figure 2b). However, some articles did not report the conductivity at room temperature although reduced crystallinity at low temperatures is a main target of IL addition to polymer electrolytes.

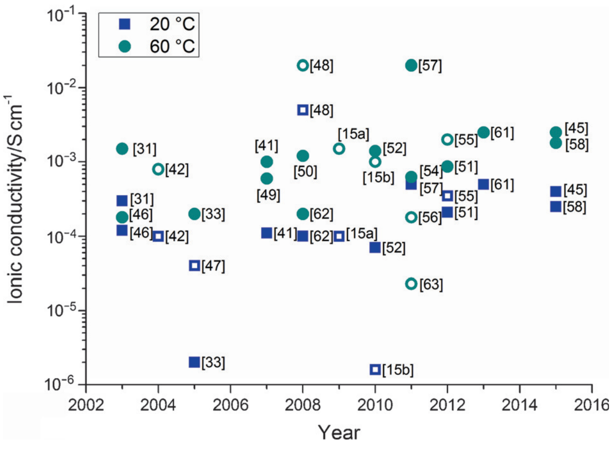

Figure 4. Progress in the field of ternary polymer electrolytes at 20 °C (squares) and 60 °C (circles). Solid symbols refer to PEO-based systems and empty symbols to PIL-based systems. All values are taken from literature (see reference numbers).

Unfortunately, not all the properties were reported in each article thereby preventing definite conclusions being drawing for some of the systems reported in this Review. Therefore, we propose that particular attention should be paid to the following tests in future investigations on ternary polymer electrolytes: Thermal stability to confirm the high safety of the system; DSC to define the degree of crystallinity and homogeneity (phase separation); ionic conductivity between 20 °C and 60 °C or, even better, in a broader temperature range; lithium stripping/plating or limiting current tests in combination with EIS measurements. This characterization may, if necessary to understand some features, be accompanied by, for example, Raman and FTIR spectroscopy, PFG-NMR spectroscopy, tensile-strength measurements, and, most important, cycling tests of lithium-metal polymer batteries (LMPB).

3.3. Optimization of Ternary Polymer Electrolytes

It was shown that ternary systems (polymer, lithium salt, and ionic liquid) are the state of the art solvent-free, polymer electrolytes for battery applications. In fact, ILs enhance the battery performance at room temperature without drawbacks in safety, even compared to a binary PEO–lithium salt electrolyte.[51] Since the introduction of ternary polymer electrolytes, two major approaches were investigated to improve their properties: Cross-linking of the polymer and addition of inorganic fillers.

Sylla et al. used dibenzoyl peroxide and azobisisobutyronitrile (AIBN) as free-radical initiators for the cross-linking of PEO.[64] The cross-linking agents were activated at 70 °C to form—via H-abstraction—radicals on the polymer chain, leading to cross-links when the radicals recombine. However, in the binary PEO–LiTFSI system, this does not lead to substantial improvements but rather to a decrease of the ionic conductivity with respect to the non-cross-linked electrolyte. Rupp et al. presented a study on benzophenone as a cross-linker for PEO, activated by UV radiation.[62] They showed that a partly crystalline ternary polymer electrolyte $PEO_{20}LiTFSI_1[Pyr_{14}TFSI]_1$ was fully amorphous after cross-linking. Kim et al. came to the same result and showed that the amorphous phase can be stabilized by cross-linking, leading to higher ionic conductivity over the whole temperature range from −40 to 100 °C.[65] In Figure 5, a three-phase diagram from our group illustrates the ratios of PEO, LiTFSI, and $Pyr_{14}TFSI$ forming an amorphous, ternary polymer electrolytes.[61]

Inorganic fillers, for example, SiO_2, TiO_2, ZrO_2, and Al_2O_3, were reported to plasticize PEO-based electrolytes thus improving their low-temperature conductivity. In 1998 Croce et al. presented a nanocomposite polymer electrolyte based on PEO, $LiClO_4$, and 10 wt % TiO_2 (particle size: 13 nm) with an ionic conductivity of $10^{-5}\,S\,cm^{-1}$ at 30 °C.[66] A similar electrolyte with Al_2O_3 (5.8 nm) showed in comparison a lower conductivity. Another approach was to modify mesoporous silica by filling it with ionic liquid.[67] Though the ionic conductivity was increased compared to the pure polymer–Li salt and also neat silica, the ionic conductivity dropped significantly below 60 °C. Another type of filler, ZrO_2, was presented in 2006 with improvements compared to the binary system.[68] However, the sharp drop in ionic conductivity below 60 °C still occurred for all these systems, showing that the crystallization of the PEO was not completely suppressed by the inorganic fillers.

A quaternary polymer electrolyte using the PIL (guanidinium-based)-PMMA copolymer was presented by Li et al. in 2011.[63] However, the ionic conductivity was decreased by the factor ten after the addition of SiO_2 filler. In 2013 Wetjen et al. investigated a quaternary system in which SiO_2 filler was added to PEO, LiTFSI, and $Pyr_{14}TFSI$.[69] The melting point was decreased to less than 50 °C, but owing to a low IL content cycling was not possible below this temperature. Thus, it seems to be not possible to reduce the IL content significantly by the addition of fillers because the full amorphicity is not maintained at room temperature.

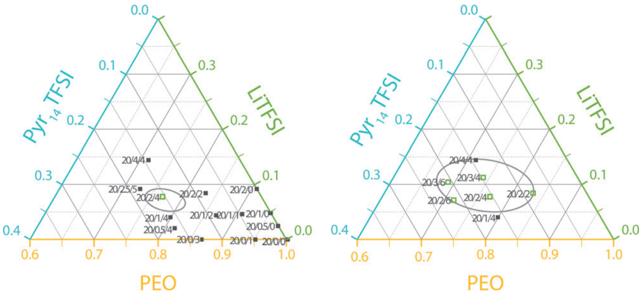

Figure 5. Ternary phase diagram of linked PEO-LiTFSI-$Pyr_{14}TFSI$ polymer electrolytes a) not-cross-linked and b) cross-linked. The green data points indicate the thermodynamically stable compositions showing no phase separation.

3.4. Application of Ternary Polymer Electrolytes

Many reports include, besides thermal and electrochemical tests, also the application of the electrolyte in LMPBs. Since one of the main advantages of polymers (in particular PEO) is the stable SEI with lithium-metal electrodes, full cells with other anode materials (graphite, LTO) are rare.[32,46,54]

Tables 5 and Table 6 show that stable operation for several hundred cycles is possible for LMPBs with lithium iron phosphate (LFP) and vanadium pentoxide (V_2O_5). Operation temperatures below the melting point of PEO are possible with ternary polymer electrolytes. Apart from a few studies on $PPyr_{11}$ and poly(guanidinium) (PGua), all

Table 5: Development in V_2O_5 polymer batteries.

Year	Electrolyte	T/ °C	C-Rate	Cycle	Specific Capacity/ mAh g^{-1}	Ref.
2003	$PEO_{20}LiTFSI$ $[Pyr_{13}TFSI]_{2.15}$	60	C/20	5	250	[31]
2005	$PEO_{20}LiTFSI$ $[Pyr_{13}TFSI]_{1,94}$	60	C/2	250	150	[70]
2014	$PEO_{20}LiTFSI_2$ $[Pyr_{14}TFSI]_4$	40	C/10	200	250	[71]

Table 6: Development in $LiFePO_4$ polymer batteries.

Year	Electrolyte	T/ °C	C-Rate	Cycle	Specific Capacity/ mAh g^{-1}	Ref.
2005	$PEO_{20}LiTFSI$ $[Pyr_{13}TFSI]_{1,73}$	40	C/20	50	145	[72]
2005	$PEO_{20}LiTFSI$ $[Pyr_{13}TFSI]_{1.73}$	40	C/20	250	125	[73]
2008	$PEO_{20}LiTFSI$ $[Im_{12}TFSI]$	50	C/20 (CC); C/5 (DC)	20	110	[50]
2010	$[PPyr_{11}TFSI]_{28\%}LiTFSI_{12\%}$ $[Pyr_{14}TFSI]_{60\%}$	40	C/20 (CC); C/10 (DC)	70	140	[15b]
2010	$PEO_{20}LiTFSI_2$ $[Pyr_{14}TFSI]_4$	40	C/10	450	140	[65]
2011	$PEO_{20}LiTFSI$ $[Pip_{1.101}TFSI]$	RT	C/20	35	120	[54]
2011	$PEO_{20}LiTFSI_2$ $[Pyr_{14}TFSI]_2$	40	C/5	180	160	[74]
2011	$[P(Gua\text{-}MMA)]_{59\%}LiTFSI_{12\%}$ $[Gua_{13}TFSI]_{23\%}$ $[SiO_2]_{6\%}$	80	C/10	100	130	[63]
2012	$PEO_{20}LiTFSI$ $[Pyr_{13}TFSI]_{1.27}$	RT	C/10	20	115	[51]
2014	$PEO_{20}LiTFSI_2$ $[Pyr_{14}TFSI]_4$	40	C/10	100	160	[69]

electrolytes are based on PEO. Cycling at room temperature gave only low discharge capacities (120 mAh g^{-1})[51,54] while almost the full theoretical capacity of LFP was reached at 40 °C after testing the batteries for a hundred or more cycles.[69]

Figure 6 shows a cycling plot of a lithium-metal battery with a LFP composite cathode in which conductive carbon and active material are embedded in the ternary polymer electrolyte. A stable cycling performance was achieved with a specific discharge capacity of 130 mAh g^{-1} after 250 cycles. The voltage profile shows a relatively high gap between the average charge and discharge potential compared to conventional liquid electrolytes. This effect increases upon cycling owing to the evolution of the SEI on lithium metal and particularly on the cathode active material. It is worth mentioning that a high ESW was reported for many ternary polymer electrolytes. However, stable performances were only demonstrated for low-voltage materials, such as V_2O_5 and LFP. Cycling tests with NCM and NCA showed strong fading and high irreversible capacity in the first charge if the cut-off voltage was higher than 4 V (upper limit of PEO's electrochemical stability window).[69] Thus, in practical applications the electrochemical stability of PEO is still the limiting factor, even if a higher anodic stability was found after addition of ionic liquids.

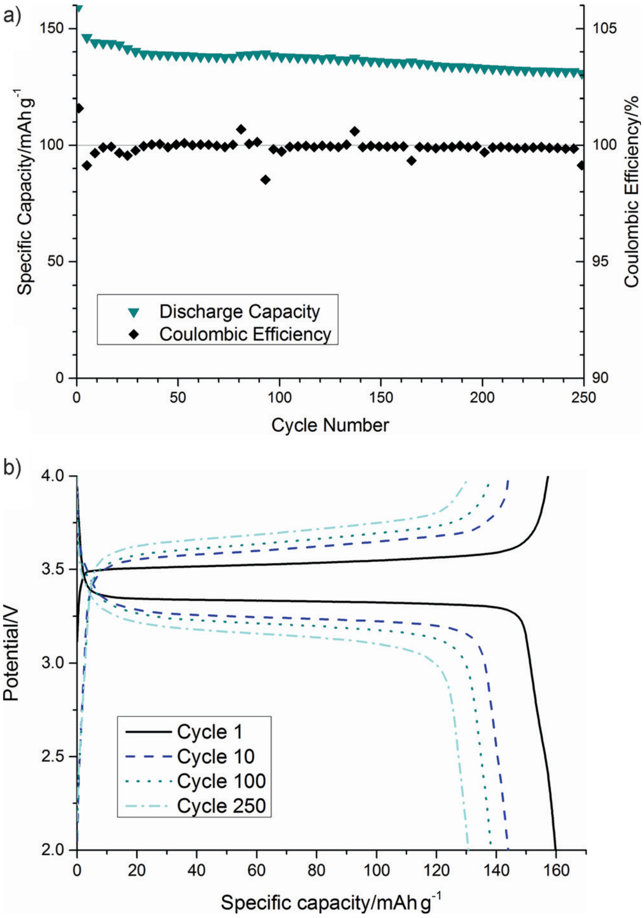

Figure 6. LMPB with LFP composite cathode (43 wt% LFP, areal loading: 4 $mg_{LFP}\,cm^{-2}$, prepared according to Kim et al.,[73] ternary polymer electrolyte: cross-linked $PEO_{20}LiTFSI_2[Pyr_{14}TFSI]_4$), a) Cycling at C/10 at 40 °C b) Voltage profiles for selected cycles.

4. Summary and Outlook

In summary, it is possible to significantly increase the ionic conductivity of PEO-based electrolytes at temperatures below the melting point of the polymer by the addition of ionic liquids. In the last decade substantial improvements were achieved by developing new formulations, including various polymers, lithium salts, and ionic liquids. It was found that the TFSI anion shows the best performance in view of battery applications, that is, a wide electrochemical stability window, low lithium SEI resistance, and low crystallinity. The pyrrolidinium cation with different side chains (Pyr_{13}, Pyr_{14}, and $Pyr_{1.2O1}$) has been investigated in detail because of its good stability with lithium metal and the ability to favor amorphous polymer electrolytes. Also promising appears to be the triethylsulfonium ($S_{2.2.2}^{+}$) cation, though the limited number of reports on it does not allow reliable statements about the long-term stability in lithium metal batteries.

Several approaches have been attempted to improve the performance of the ternary system. The most common ones are cross-linking of the polymer matrix, sometimes in block-copolymers with ethylene oxide units, and the addition of inorganic fillers. While the fillers do increase the conductivity significantly for binary systems, the improvements for ternary systems seems to be quite small. On the other hand, it was shown that cross-linking has a positive effect on the formation of a fully amorphous system.

Poly(ionic liquids) (PILs) showed similar performances to PEO-based ternary electrolytes. Owing to their stronger interactions with PILs, much higher ionic liquid/polymer ratios are possible compared to PEO. However, this does not lead to higher ionic conductivities in general.

One remaining issue today is to reduce the high interfacial resistance shown by any kind of polymer electrolytes, including ternary polymer electrolyte, with the lithium anode without losing the good properties, such as mechanical and thermal stabilities and ionic conductivity. On the cathode side, research has to be done to improve the performance of the ternary polymer electrolytes in batteries with high-voltage active materials, which is limited by the electrochemical stability of PEO. Though it was often reported that the ESW of the polymer electrolytes is increased by the addition of ionic liquid, no stable cycling of high-voltage materials has been reported so far.

Contributions

I.O. and H.d.V. drafted the outline of the Review Article, the manuscript and the Figures and Tables. S.P. and B.S. supervised the work and revised the writing.

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