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Potentialities of ionic liquids as new electrolyte media in advanced electrochemical devices

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Abstract This paper reviews the various classes of ionic liquids (ILs) in view of their established and expected applications in advanced electrochemical devices, such as lithium batteries, fuel cells, and supercapacitors. In this respect, particular attention is devoted to aprotic and protic ILs, with a related discussion in terms of their thermal and transport properties. In addition, the role in the electrochemical technology of a new class of ILs having cation and anion tethered in an intramolecular form is stressed. Due to their emerging importance, IL-based polymers are finally reported and discussed. A conclusion, where the expected evolution of the ILs research and development is evaluated, is also included.

Keywords Ionic liquids · Applications · Fuel cells · Lithium batteries

Introduction

Ionic liquids (ILs), i.e., molten salts at temperatures approaching room conditions, are of great actual interest for their unique characteristics, which include: (1) a liquid state over a wide temperature range, which opens a series of new applications; (2) nonvolatility, which assures thermal stability and nonflammability; (3) high ion content, which results in high ionic conductivity; and (4) great chemical and electrochemical stability [1–3]. The most common ILs are composed of organic ions, which undergo almost unlimited structural variations because of the easy preparation of a large variety of their components. A typical example of IL is that formed by a substituted

imidazolium cation and an anion such as tetrafluoroborate, BF_4 , or hexafluorophosphate, PF_6 (see scheme in Fig. 1).

Various kinds of salts can be used to design the IL which meets the desired properties for different applications exploiting ILs as novel “green” reaction media. Indeed, ILs are today considered as the new-generation electrolyte solutions for electrochemical devices such as lithium ion batteries [4], fuel cells [5], capacitors [6], and solar cells [7]. The main properties to take into account in the selection of ILs in view of their practical applications are thermal stability and, particularly, ionic conductivity.

A convenient way to clarify the mechanism of ionic conduction in ILs is to compare the values of conductivity obtained by pulsed gradient spin-echo (PGSE)-NMR with those obtained by impedance spectroscopy. PGSE-NMR measurements on ^{19}F and ^1H nuclei allow determining the self-diffusion coefficients of the cations and anions, D_+ and D_- , respectively. The molar conductivity, Λ_{NMR} , can be correlated with the diffusion coefficient by the Nernst–Einstein equation:

$$\Lambda_{\text{NMR}} = \frac{F^2(D_+ + D_-)}{RT} \quad (1)$$

where F is the Faraday’s constant, R the gas constant, and T the absolute temperature, and all the cations and anions are supposed to be mobile.

Impedance spectroscopy gives the ionic conductivity σ . The experimental molar conductivity, Λ_{exp} , can then be evaluated as the product between the ionic conductivity, σ , and the molar volume, V_e :

$$\Lambda_{\text{exp}} = V_e \sigma \quad (2)$$

This value may differ from that calculated from PGSE-NMR data, this difference providing indications about the possible transport mechanisms. If the value of the $\Lambda_{\text{exp}}/\Lambda_{\text{NMR}}$ ratio is 1, then the ionic conductivity can be considered due to the diffusion of the IL ionic species. However, this ratio is usually lower than unity because in

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Fig. 1 1-alkyl-3-methylimidazolium ILs

ILs not all diffusive species contribute to the ionic transport, due to the formation of ion pairs and ion aggregates [8]. It should be recalled that an NMR measurement detects a nucleus, and thus, this technique cannot distinguish between the ion and the associated species. For instance, the ILs formed by round-shaped anions (PF_6^- and BF_4^-), due to their easy dissociation and association with cations, have larger $\Lambda_{\text{exp}}/\Lambda_{\text{NMR}}$ values than those formed by rod-shaped anions. Probably, the round shape of the anions enables an easier association and dissociation process with the cations. Moreover, the $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ value increases if the orientation dependence of the interaction is small, this probably being associated to the fact that a large anisotropy of the interaction decreases the mobility of ions [9].

ILs come in different classes, which basically include aprotic, protic, and zwitterionic ILs. These classes will be briefly reviewed here in terms of their potentialities as new electrolyte media in electrochemical devices.

Aprotic ILs

The aprotic class of ILs based on organic cations is characterized by a low melting point associated with the difficulty of packing large irregular cations with small anions. Aprotic ILs have high mobility and ion concentration, these properties rendering them suitable for application as advanced electrolytes for lithium batteries [10, 11].

Most popular ILs consist of quaternary ammonium cations such as imidazolium, pyridinium, pyrrolidinium, ammonium, sulfonium, and phosphonium, and of anions with low Lewis basicities, e.g., BF_4^- , PF_6^- , CF_3SO_3^- , and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anions. The quaternary ammonium ions produce low melting point salts compared with many of the inorganic salts of the same anions. The melting points of these salts approach room temperature as the overall size of the ammonium ion becomes progressively larger by substitution of longer alkyl groups. It has been proposed that a depression of the melting point can be induced by the disruption of the symmetry of the cation, which interferes with crystal packing and destabilizes the crystalline state [12]. Such is for the family of pyrrolidinium salts, in which the smaller symmetrical cations have high melting points, while the larger, less symmetric members are glass-forming liquids at room temperature. In the imidazolium cations the geometric packing constraints of the planar imidazolium ring, its dangling alkyl groups, and the delocalization of the charge over the N–C–N moiety in the ring all serve to decrease ion–ion interactions and lower the melting points [9]. ILs comprising an imidazolium cation and an organic anion show mechanical strength, chemical stability, and

excellent ionic conductivity, even though the latter can be due to the molten salt itself.

There are certain problems related to the use of ILs as lithium ion battery electrolyte solvents. To assure lithium ion conduction, a lithium salt should be added to the IL. This addition results in a conductivity decrease, which corresponds to an elevation in the glass transition temperature. Lithium ions have a high Lewis acidity, which leads to ion-pairing with Lewis basic anions. For the design of lithium ILs, the reduction of Lewis basicity of the anionic center and the introduction of lithium-coordinating Lewis basic ligands into the anionic structure are therefore essential [8]. This strategy prevents the lithium ion pairing formation and allows obtaining lithium molten salts [13].

Also to be considered is that ILs designed for application in Li-ion batteries often show low specific conductivity, a narrow electrochemical window, a modest temperature range in the liquid state, and high viscosity [11]. A promising exception could be the family of salts based on 1-ethyl-3-methylimidazolium (EMI) cations (see scheme in Fig. 2) due to their conductivity, which reaches 10^{-2} S/cm, i.e., a value comparable with that offered by the common organic solvent electrolyte systems, low viscosity, and a rather wide electrochemical window.

Unfortunately, EMI-based ILs are not suitable as lithium battery electrolytes due to their poor stability toward reduction because of the acidic proton in C-2 on the imidazolium ring. Indeed, the reduction potential of EMI-based ILs is around 1 V vs Li/Li^+ [6], thus they decompose on lithium or lithiated carbon surface, and this does not result in the formation of a protective film on the electrodes as it occurs in conventional organic solvent systems. Consequently, the electrodes' charge–discharge processes cannot proceed.

Many efforts have been made to solve this problem and thus to exploit ILs as efficient lithium battery electrolytes. Hayashi et al. found that alkylation of an imidazolium salt is an effective approach for lowering the reduction potential. Accordingly, a 2-substituted imidazolium is, in principle, a more stable cation than EMI. However, 1,2,3-trialkylimidazolium salts have conductivities lower than those of the corresponding 1,3-dialkylimidazolium-based ILs, due to an increase of the crystallinity of these compounds [14].

Another approach has been that of applying film-forming additives in EMI-based ILs. Indeed, the addition of HCl , SOCl_2 , $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$ [15] or of organic solvents used in conventional lithium battery electrolytes [16], seems to improve the lithium deposition/dissolution behavior in EMI-based IL electrolytes. However, some of these additives poison the charge–discharge process of the high-voltage positive electrode of the lithium battery, while the addition of organic solvent additives, which may not

Fig. 2 Structure of the EMI cation

have such an inhibitory effect, eliminates the advantage of using IL electrolytes.

Egashira et al. reported [17] that an IL based on a cyano-substituted quaternary ammonium cation (see scheme in Fig. 3), having an ionic conductivity of 10^{-4} S/cm, allows reversible lithium deposition/dissolution. In fact, this study confirms that the cyano-containing quaternary ammonium cation may give rise to a surface protective film on lithium.

Another approach to solve the problems of applicability of ILs in lithium batteries is to choose an anion which could improve the electrochemical performance of the final salt. To study the effect of the anion, ILs comprising the same cation and different anions have been compared in terms of their physical properties [18].

Table 1 reports the thermal stability of an IL series formed by 1-butyl-3-methylimidazolium (BMI) (see scheme in Fig. 4) as the fixed cation and BF_4 , PF_6 , bis(trifluoromethanesulfonyl)imide (TFSI), CF_3SO_3 , $(\text{C}_2\text{F}_5\text{SO}_2)_2\text{N}$, and CF_3CO_2 as the different anions, in terms of their decomposition temperature, T_d , and the extent of their liquid-state existence in terms of their melting point, T_m .

The decomposition temperatures follow the order $\text{PF}_6 > \text{BF}_4 \approx \text{TFSI} > \text{CF}_3\text{SO}_3 > (\text{C}_2\text{F}_5\text{SO}_2)_2\text{N} > \text{CF}_3\text{CO}_2$. This observation may be explained in terms of a pyrolysis of imidazolium salts proceeding via a $\text{S}_\text{N}2$ mechanism. The changes in the basicity or nucleophilicity of the anions thus influence the thermal stability. Indeed, the mechanism of the pyrolysis depends on the type of isomeric structures of the alkyl groups, e.g., for 1,2-dimethyl-3-isopropylimidazolium salts, the pyrolysis has been presumed to proceed via an $\text{S}_\text{N}1$ reaction [19].

PGSE-NMR measurements show that there is no time-dependency of the self-diffusion coefficients, D , expressed as the sum of D_+ and D_- , of the salts 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, 1-*n*-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, and 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMIPF_6). This means that for these salts the diffusion is a Fickian process. The values of D for BMI salts are comprised in the range $1.6\text{--}6.0 \times 10^{-7} \text{ cm}^2/\text{s}$ at 30°C , and they follow the order $\text{TFSI} > \text{CF}_3\text{CO}_2 > \text{CF}_3\text{SO}_3 > \text{BF}_4 > (\text{C}_2\text{F}_5\text{SO}_2)_2\text{N} > \text{PF}_6$.

The value of the $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ ratio evidences ionic association in ILs: This value depends on the anionic moiety, following the order $\text{PF}_6 > \text{BF}_4 > \text{TFSI} > \text{CF}_3\text{SO}_3 > \text{CF}_3\text{CO}_2$. This sequence can be explained by the effect of the electronegative F atom and of the electron-withdrawing CF_3SO_3 group, which favors the delocalization of the charge and, therefore, a weaker interaction with the cation. On the basis of these considerations, one of the most effective anions in producing low melting points appears to be the bis

Fig. 3 Structural formula of cyano-containing quaternary ammonium cations

Fig. 4 Structure of a BMI salt

(trifluoromethane sulfonyl)imide ($(\text{CF}_3\text{SO}_2)_2\text{N}$ (TFSI) ion (see scheme in Fig. 5).

It has been shown that the ammonium salt family based on this anion has a melting point at least 100°C lower than that of the corresponding iodides [16]. In fact, TFSI is a weakly interacting and flexible anion, and there is strong evidence of delocalization of the charge from the nitrogen atom onto the neighboring sulfur atoms. This results in a little delocalization onto oxygens, so that the delocalized charge is shielded, thereby diminishing the strength of ion-ion interactions with nearby cations [12]. The imide ion is therefore the progenitor of high fluidity and conductivity. The low basicity of the TFSI anion inhibits the formation of a hydrogen bond with H(2) of the imidazolium cation, this resulting in a random aggregation [20] of the ions in the IL. The effectiveness of the TFSI anion in enhancing the kinetic stability toward the Li electrode of an imidazolium-based IL was demonstrated in a pioneering work by Koch et al. [4].

In an alternative to EMI-based salts, *N*-methyl-*N*-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (MPP TFSI)-based ILs (see scheme in Fig. 6) have been proposed as electrolytes. Indeed, these salts are sufficiently stable toward lithium and provide rather reversible lithium deposition/dissolution [21]. Generally, ILs applying non-EMI cations suffer from low conductivity, due to the restricted mobility of the nonplanar structure of the rings. However, structural models of the methyl pyrrolidinium series attribute to this subgroup an almost planar arrangement, which is expected to provide fast ionic transport. Indeed, MPPTFSI has a conductivity of $1.4 \times 10^{-3} \text{ S/cm}$, this being a rather interesting value.

In general, room-temperature ILs (RTILs) containing aliphatic quaternary ammonium and TFSI are reported to possess a high cathodic stability compared with EMI-based ILs; in addition, lithium plating and stripping could be observed to occur in these media without any additives [22]. However, the viscosity of these systems is about twice that of the EMI system. With the aim of lowering the viscosity of the aliphatic quaternary ammonium systems, it has been attempted to substitute TFSI with (2,2,2-trifluoro-*N*-trifluoromethylsulfonyl) acetamide (TSAC) anion (see scheme in Fig. 7), which has an asymmetrical structure and a molecular weight lower than that of the TFSI anion, such as to form low melting and low viscous RTILs [23]. Unfortunately, the electrochemical stability of

Fig. 5 Structure of the TFSI anion

Table 1 Thermal and electrochemical properties of different BMI salts

Name	Abbreviation	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$	$T_d/^\circ\text{C}$	Ionic conductivity, σ/Scm^{-1}
1- <i>n</i> -Butyl-3-methylimidazolium bis(perfluoroethanesulfonyl) imide	BMI(C ₂ F ₅ SO ₂) ₂ N	-84	—	402	1.8×10^{-3} at 25 °C
1- <i>n</i> -Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide	BMITFSI	-87	-3	423	9.9×10^{-3} at 25 °C
1- <i>n</i> -Butyl-3-methylimidazolium trifluoromethanesulfonate	BMIS	—	17	409	3.7×10^{-3} at 20 °C
1- <i>n</i> -Butyl-3-methylimidazolium hexafluorophosphate	BMIPF ₆	-77	10	433	1.8×10^{-3} at 22 °C
1- <i>n</i> -Butyl-3-methylimidazolium trifluoroacetate	BMICF ₃ CO ₂	-78	—	176	3.2×10^{-3} at 20 °C
1- <i>n</i> -Butyl-3-methylimidazolium tetrafluoroborate	BMIBF ₄	-83	—	425	7×10^{-3} at 25 °C

Fig. 6 Structure of the MPPTFSI salt

the TSAC systems is very limited, possibly due to the carbonyl group in the TSAC anion.

Another method to reduce the viscosity and the melting point of the aliphatic ammonium systems could be the introduction of an alkoxy group into the tetraalkylammonium cation [22]. However, even this approach is not satisfactory because the presence of the alkoxy group lowers the electrochemical stability of the systems.

In conclusion, so far, no IL whose electrochemical stability and ionic conductivity are both satisfactory for effective applications in lithium batteries has been identified, although recent improvements in the design of ILs seem to be promising in this respect. However, ILs such as BMIPF₆ have been successfully tested in activated carbon//poly(3-methylthiophene) hybrid supercapacitors. Recent results demonstrate that the use of these ILs allows enhancing the performance of these devices in terms of voltage and cycle life [24].

Protic ILs

Though the first IL ever reported, i.e., EtH₃NNO₃ in 1914, belonged to this family, the research on protic ILs is still emerging. Protic ILs are originated by the transfer of a proton from a Brönsted acid to a Brönsted base (usually an amine). This process is reversible if the energy that is required for the proton jump is small; in this case, the formed liquid has low conductivity and high vapor pressure. Good properties of an IL are achieved when the proton largely remains on the cation due to the wide energy gap associated to the recovery of the pristine acid and base [25]. The strong long-range Coulomb interaction between the so-stabilized cation and anion lowers the vapor pressure over the liquid.

The synthesis of the protic ILs can follow two different routes, the first of which consists in the neutralization of an

aqueous solution of the starting amine with a suitable acid [26]; the second method is carried out under solvent-free conditions, by directly mixing the reagents and heating the mixture above the components' melting points in argon atmosphere [20].

The neutralization reaction is a rather simple method to obtain equimolar mixtures of a Brönsted acid and a Brönsted base because the possible unreacted compounds are eliminated during the purification step of the synthesis. Typical IL properties are revealed for neutralized imidazole (Im) derivatives, in dependence of the nature of the acidic counterpart [27]. For example, low or nondetectable melting points are obtained for the salts containing large anions because the anionic radius affects the electrostatic interaction with the imidazolium cations. However, some exceptions for this trend, coupled with a nondirect relationship between the ion size and the viscosity, suggest that other characteristics must be considered, such as the structure of the anion, the acidity of the pristine component, and so on [27]. The imide anions resulted to improve the thermal stability of the neutralized amines, as well as in the case of aprotic ILs; for example, 1-ethylimidazolium bis(trifluoromethanesulfonyl) imide (EImTFSI) and 1-ethylimidazolium bis(perfluoroethanesulfonyl) imide (EImBETI) (see scheme in Fig. 8) show decomposition temperatures above 400 °C [27]. Nonetheless, while the Ims neutralized with HTFSI show a high ionic conductivity, i.e., of the order of 10^{-3} S/cm at room temperature, the salts neutralized with HBETI unexpectedly result in poorer ion conduction, in spite of their low glass transition temperature, e.g., -86 °C for EImBETI. In this case, the larger anion size provides a high viscosity, which affects the conductivity of the imidazolium-based salts [28].

The effect of the cation structure has been studied by Hirao et al. [26]. By neutralizing a series of tertiary amines, e.g., pyrroline, indole, pyrazole, and pyrrolidine derivatives, with tetrafluoroboric acid, several RTILs have been obtained. Fundamental properties, such as low glass-transition temperature, low melting point, and high ionic conductivity, were found to be a result of the neutralization of low-symmetry heterocyclic amines with alkyl substituents on 1- and 2- positions of the ring [26].

Fig. 7 Structure of the TSAC anion **Fig. 8** Structures of EImTFSI and EImBETI

The protic ILs based on mixtures of Brønsted acids and Brønsted bases under free-solvent conditions, obtained from the second synthesis route, show melting points which depend on the composition, but not on the number of proton acceptor sites and on the melting points of the starting amines [20]. HTFSI is usually used to neutralize organic amines by mixing and heating above the components' melting points in argon atmosphere. The TFSI anion acts as a proton acceptor site. Im/HTFSI (see scheme in Fig. 9) salt may be taken as a representative of this family of Brønsted acid–base ILs.

Conductivity measurements run above the melting point of the equimolar Im–HTFSI mixture show values of about 10^{-2} S/cm and increasing values by increasing the Im fraction, which are higher than those for pure Im. This trend demonstrates that the conductivity is due both to ionic species (HIm^+ and TFSI^-) and to intermolecular proton transfer between HIm^+ and Im. By increasing the HTFSI fraction, the conductivity decreases, this indicating that despite its strong acidity, HTFSI has no intermolecular proton transference ability: In HTFSI-rich compositions, the number of proton defects decreases. Thus, the particular mechanism of proton conduction is a variable of the composition.

PGSE-NMR measurements [29] conducted on Im-excess compositions reveal that the proton transport occurs via a Grotthuss mechanism (intermolecular exchange process), because the experimental diffusion coefficient of HIm , which includes the diffusion of the protonated form and of pristine Im, is larger than that of Im. In HTFSI-excess compositions, all Im molecules are protonated. In this condition, Im and HIm show identical diffusion values, and the proton is therefore transported within the matrix Im following a vehicle mechanism. Still, under HTFSI excess the diffusion coefficient of H-TFSI is larger than that of TFSI anion. The conductivity for these acid-rich mixtures is lower than that of the equimolar mixtures. The combination of these two effects suggests that the proton is blocked on the TFSI anion, and thus that the excess acid exists dominantly as associated molecular HTFSI.

Direct current polarization experiments, carried out at 130 °C in a U-shaped cell with Pt-wire electrodes and the Im/HTFSI mixture as the electrolyte, have confirmed that the conductivity in protic ILs is based on proton transport [20]. The current detected in the cell that is used under nitrogen atmosphere is very low; however, operating in a hydrogen gas atmosphere, which assures the ongoing of the anodic reaction, the current increases. The evolution of gas

(H_2) at the cathode is revealed by bubbles formation, according to the following electrochemical process:

Due to these properties, Im/HTFSI ILs are of interest for applications in fuel cells. Indeed, tests run in a H_2/O_2 cell of the type described above and using an Im/HTFSI IL as electrolyte under nonhumidifying conditions at 130 °C have provided evidence of electric power generation [20].

Zwitterionic liquids (ZILs)

ILs based on a zwitterionic liquid (ZIL) are characterized by having cation and anion tethered in an intramolecular form, so that the migration of IL component ions is inhibited [30, 31]. ZILs can undergo easy structural modification and may therefore be suitable for different applications, such as fuel cells and lithium batteries.

The thermal properties of a sulfonate-containing ZIL, such as 1-(1-ethyl-3-imidazolium)propane-3-sulfonate (EIm3S) (see scheme in Fig. 10) show evidence of a strong electrostatic interaction, especially when compared with a conventional IL such as ethylimidazolium methanesulfonate. In the ZIL, the bond between the cationic and the anionic moieties is indeed responsible for a decrease of freedom degrees of the ions, this resulting in a melting point higher than that of the corresponding IL (see Table 2).

In view of possible applications in electrochemical devices, such as lithium batteries or fuel cells, a Li^+ or H^+ component has to be added to the ZIL. When investigated as a mixture with LiTFSI, EIm3S shows only glass transition temperature, T_g , due to the shielding effects of the TFSI anion. It is interesting to note that the addition of LiTFSI to a conventional IL, such as 3-ethyl-1-methylimidazolium tetrafluoroborate, causes, on the contrary, an elevation in T_g . This difference indicates the effective formation of a molten salt domain due to the plasticity of the TFSI anion. The conductivity values for pristine EIm3S are below 10^{-9} S/cm at 50 °C, so the ions do not significantly contribute to the ionic conductivity. Equimolar mixtures with LiTFSI guarantee increases in conductivity up to 10^{-5} S/cm at 50 °C [32]. In view of possible applications in the fuel cell area, a proton-conducting binary ZIL based on 1-(1-butyl-3-imidazolium)propane-3-sulfonate (see scheme in Fig. 11) and HTFSI has been considered. This salt has an ionic conductivity of 10^{-4} S/cm at room temperature and up to 10^{-2} S/cm at 150 °C [33]. However, despite these encouraging properties, there is no literature evidence of effective applications in fuel cells.

Fig. 9 Structures of Im and HTFSI

Fig. 10 Structure of EIm3S

Table 2 Comparison of ZILs and corresponding aprotic ILs

Class	Name	Abbreviation	T_m (°C)
Aprotic IL	Ethylimidazolium methanesulfonate	EImS	55
ZIL	1-(1-Ethyl-3-imidazolio)-propane-3-sulfonate	EIm3S	150
Aprotic IL	1- <i>n</i> -Butyl-3-methylimidazolium trifluoromethanesulfonate	BMIS	17
ZIL	1-(1-Butyl-3-imidazolio)propane-3-sulfonate	BIm3S	56

Fig. 11 Structure of 1-(1-butyl-3-imidazolio)propane-3-sulfonate

Other types of ZILs include sulfonamide salts, carboxylate salts, and dicyanoethenolate salts. Sulfonamide-containing ZILs only show glass transition temperature (lower than the corresponding sulfonate-containing ZILs), thus resulting in molten salts at room temperature. On the other hand, carboxylate salts have melting points similar to those of the sulfonate-containing ZILs, but it is possible to observe a lowering in T_m when the spacer is longer, due to an increase in flexibility and a decrease in ion density. Dicyanoethenolate-containing ZILs show low melting points because the electron-withdrawing effect of cyano groups weakens the ions' interaction. Unfortunately, the starting material, dicyanoketene cyclic acetal, is produced from toxic reagents such as potassium cyanide, and this obviously limits the interest in these ZILs.

Polymers

Batteries addressed to small and light-weight electronics require film-like electrolyte materials such as polymer electrolytes. The choice of solid electrolyte materials implies several advantages, e.g., (1) the absence of liquids or gases which may leach out, damaging the cell; (2) the possible realization of low-specific-capacity electrochemical devices; (3) a long lifetime due to the high mechanical resistance of the materials; and (4) an utilization temperature range larger than that for liquid electrolyte-based systems. ILs are important in this respect because their unique physicochemical properties meet the requirements of plasticizing salts for polymers. Furthermore, ILs may expand the temperature range where flexible polymers can be used.

There are three methods to obtain an ILs-based polymer electrolyte: the first is the incorporation of IL in a polymer matrix [2]; the second is the polymerization of a vinyl monomer in ILs as a solvent [34]; in the third case, the cation or the anion structure is fixed in the polymer segments [35, 36].

Incorporation of ILs in a polymer matrix

Highly ion-conducting rubbery gel electrolytes from non-chloroaluminate ILs and poly-(vinylidene fluoride-*co*-hexa-fluoropropylene) (PVdF-HFP) have been reported by Carlin and coworkers [2]. Stable solid gel electrolytes and membranes can be formed by the addition of PVdF-HFP to 1,3-dialkylimidazolium ILs. These solid gel electrolytes provide the structural and stability advantages of a polymer, even maintaining the ionic conductivity of a molten salt.

Casting procedures allow synthesizing membranes, such as those formed by the gelification of PVdF-HFP in 1,2-dimethyl-3-*n*-propylimidazolium TFSI, with conductivities around 2×10^{-3} S/cm at room temperature and up to 0.01 S/cm at 100 °C. The protonic transport is here assured by the addition of trifluoromethanesulfonic acid (TFA) into the polymer matrix [37]. These membranes have been successfully used as new electrolytes for advanced fuel cells (Fericola et al., unpublished).

ZIL-based polymers may also be obtained by incorporating ZILs in a polymer matrix. Even if the pristine ZIL is not liquid at room temperature, the addition of LiTFSI provides a liquid mixture with IL properties. The preparation of the polymer follows the casting procedure described above for conventional IL-based polymers. The polymer resulting from the mixture of PVdF-HFP and EIm3S/LiTFSI shows the thermal stability which characterizes the pristine ZIL, this being higher than that of polymer gel electrolytes using typical organic solvents [30]. An ionic conductivity of 10^{-4} S/cm at 200 °C, although this value is possibly influenced by the release of the ZIL mixture, occurring near the matrix melting point, i.e., at 150 °C, has been reported.

Polymerization of a vinyl monomer in ILs

Watanabe and coworkers have reported a new methodology to prepare highly conductive polymer electrolytes by in situ radical polymerization of vinyl monomers in ILs [38]. This method yields transparent, mechanically strong, and highly conductive polymer electrolyte films. When the incorporation of IL into polymer networks affords a completely compatible combination, such as the case of poly(methyl-methacrylate) in 1-ethyl-3-methylimidazolium TFSI, the resulting polymer gels are named "ion gels," which are distinctly discriminated from conventional polymer gels in terms of nonvolatility and high thermal stability and show ionic conductivities of the order of 10^{-2} S/cm.

Polymerizable ILs

Preparations of polymerizable ILs as precursors of stable polymer electrolytes where only target ions can migrate are reported [34]. This class of ILs is obtained by the introduction of a polymerizable group, such as the vinyl group, in the cationic or anionic structure. The radical polymerization produces a polymer chain on which one of the IL ions is fixed, thus constituting a single ion-conducting IL polymer. However, the high ionic conductivity of the pristine IL is depressed after polymerization, for both polycations and polyanions. This is the case of 1-vinyl-3-ethylimidazolium TFSI, whose conductivity drops from 10^{-2} S/cm at 60 °C for the monomer to 10^{-5} S/cm at 50 °C after polymerization [39]. Another example is the ILs composed of sulfopropyl acrylic acid or vinylsulfonic acid as polymerizable moieties [40].

The decay in conductivity is associated with the decrease in segmental motion of the ions. To minimize this effect, polymerizable ILs composed of vinyl monomers tethering a more flexible imidazolium cation have been studied [39]. Effectively, the introduction of a spacer between the imidazolium ring and the polymer main chain provides conductivities up to 10^{-4} S/cm. The smaller the conductivity of the monomer, the larger is the effect of polymerization, which is, however, relevant for high degrees of polymerization.

Another class of polymerizable ILs is that formed by hetero-type poly(ethylene oxide) (PEO) having both vinyl group and imidazolium salt structure as terminals (see scheme in Fig. 12). These may be polymerized to prepare molten-salt type polymers, which show quite high conductivity (about 10^{-4} S/cm at 30 °C) even after the polymerization [36]. Moreover, the ionic conductivity increases with increasing the number of EO units, this being due to the higher mobility of imidazolium cation in polymers with longer, flexible spacers.

ZIL-based polymers may also be obtained by the radical-initiated polymerization of suitable macromonomers. When the imidazolium ring of the ZIL is fixed on the polymer main chain, ionic conductivities of 10^{-8} – 10^{-9} S/cm are achieved by adding LiTFSI to the polymer, while, when the immobilized species on the main chain is the anion, conductivities of the order of 10^{-5} S/cm have been reported at 50 °C [30]. Higher values of conductivity may be obtained by widening the alkyl spacer and/or by increasing the LiTFSI concentration. This trend is quite different from that observed with vinylimidazolium TFSI and PEO spacer-based polymers, where the conductivity after poly-

merization is, at best, similar to that of the monomer (about 10^{-4} S/cm). So far, there is no explanation of this difference in the conductivity behavior, although it evidences the key role of the distance between the chains of the vinyl polymer and the imidazolium moiety.

Conclusions

All the classes of ILs here reviewed are very appealing as advanced materials in electrochemical devices. Indeed, ILs appear as ideal electrolytes due to their nonflammability, high temperature stability, and environmental compatibility. However, despite these appealing features, very few successes have so far been achieved in terms of practical applications. In fact, the use of IL-based electrolytes in emerging devices, such as lithium ion batteries, is still prevented by the yet-unsolved difficulty of designing ILs having the desired properties, especially in terms of wide electrochemical stability combined with high conductivity.

Some success has been obtained by adding ILs such as *N*-methyl-*N*-propylpyrrolidinium TFSI in a PEO–lithium TFSI matrix. The obtained system appears to be a good ionically conductive polymer electrolyte, with rather good electrochemical stability, depending on the amount of IL incorporated [41]. However, so far, ILs have not found their way in lithium battery technology. On the other hand, considering their basic properties, IL-based electrolytes would be highly welcome in this field. Thus, this area is still open to research to overcome the remaining problems and to finally widen the road for the successful, practical use of IL-based liquid or polymer electrolytes. This type of research is already in progress in many academic and industrial laboratories, and thus, positive results are expected in the near future.

Fuel cells, as well as lithium batteries, would greatly benefit from the introduction of IL-based electrolytes. However, also in this field, the use of ILs is still limited. Some encouraging results have been reported for protic ILs. However, these results are very preliminary and obtained in laboratory-type cells. No IL-based fuel cell stacks, or even fuel cells with practical structures, have, to our knowledge, so far been reported. This is quite surprising because the replacement of conventional perfluorosulfonic polymer electrolytes with IL-based polymer electrolytes may solve one of the major problems which still prevent the large-scale production of polymer electrolyte membrane fuel cells (PEMFCs), namely, the low thermal stability. Thus, in this area too, extended research is needed to develop IL-based polymers, which may be effectively used as improved separators in PEMFCs. Promising results in this direction have been obtained by the fabrication of membranes based on adding TFA to a polymer matrix formed by gelification of PVdF in 1,2-dimethyl-3-*n*-propylimidazolium *bis*(trifluoromethylsulfonyl)imide [37] (Fericola et al., unpublished). However, the road to reaching conclusive results in this area is still long and requires extended studies

Fig. 12 Structure of a hetero-type PEO macromonomer

both in terms of membrane and of fuel cell (i.e., membrane-electrode assembly structure) optimization.

The device area where the use of ILs appears to be in an advanced state is that related to supercapacitors. Recent results reported by Mastragostino and coworkers show that the replacement of conventional electrolytes based on aprotic organic solvents, typically acetonitrile, with a BMIPF₆ or a *N*-butyl-*N*-methylpyrrolidinium TFSI IL greatly improves the performance of hybrid supercapacitors in terms of voltage, specific energy and power, and cycle life [24]. These results demonstrate that when properly designed, ILs can effectively make a dramatic change in the progress of a given electrochemical device. In the case of supercapacitors, the selected ILs assure an electrochemical window which matches the potential range of the charge-discharge process of the electrodes and, being hydrophobic, prevents water-soluble by-products, and thus, allows long cycle life.

Obviously, meeting the same favorable conditions in the cases of lithium batteries and fuel cells is a more difficult task. However, the almost unlimited structural variations of ILs, associated with the various modifications which may be induced in the organic component, gives hope that the right IL architecture may eventually be identified, and thus, that ILs may soon find the role that they deserve in the full range of advanced electrochemical technology.

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