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Alicyclic ammonium ionic liquids as lithium battery electrolytes

A review

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KEYWORDS

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ABSTRACT

Ionic liquids are reasonable alternatives to electrolytes used in energy storage devices, such as lithium batteries, both lithium-ion and lithium-metal, given the safety advantages they provide. This is due to the favourable properties they often possess, mainly non-flammability and non-volatility. Candidates with alicyclic ammonium cations exhibit high electrochemical stabilities, especially towards lithium, a unique feature which enables the fabrication of reversible lithium-metal batteries. Recent advances in this field are reviewed herein, with emphasis on two new families of ionic liquids, based on either azepanium or 3-methylpiperidinium cations, and having potential windows around or above 6 V.

THE RELEVANCE OF LITHIUM BATTERIES

During the past twenty years, advances in lithium battery technologies have boosted the sector of portable electronic devices (1-3). Currently, devices such as laptop computers, mobile phones, photographic cameras, audio players or electric tools are widely used on a daily basis. The lithium battery market is rapidly growing and an annual global production in excess of several thousand million units has been estimated (3). Therefore, lithium cell technologies are at a certainly advanced stage, at least for relatively small devices.

In brief, batteries are devices composed of one or more electrochemical cells which store electricity as chemical energy. Each of these electrochemical cells consists of a negative electrode (anode) and a positive electrode (cathode) internally connected by an electrolyte through which ions are transported, whereas the generated electric current flows externally through a conducting material. Battery voltage (*E*) is defined by convention (4) as the difference between the potentials of the positive and negative terminals, (E_+ and E_-, respectively); these are in turn close to cathode (E_c) and anode (E_a) redox potentials, respectively. The potentials of several anodic redox pairs typically found in commercial batteries are listed in Table 1. Clearly, those of Li^+/Li and Li^+/Li_xC_y pairs are the most negative, and in fact they are among the most negative known. Therefore, lithium cells may provide voltages of up to *ca.* 4 V, around twice as high as those of other kinds of common batteries. Nonetheless, lithium anodes are not compatible with aqueous electrolytes, such as those used in lead/acid batteries, since water decomposes in contact with reduced lithium releasing dihydrogen, thus implying serious hazards.

As compared to other metals frequently used for electrodes, lithium is light, and thus, energy densities of lithium batteries are high, as shown in Table 1. This is a crucial feature for electric vehicles. Energy densities of lithium batteries may be an order of magnitude higher than those of lead/acid counterparts (100–600 and 20–30 W h kg^{-1}, respectively).

Battery type	Redox pair (anode)	$E°_a$/V[a]	*E*/V[b]	Energy density/ W h kg^{-1}[b]
Li-metal[c]	Li^+/Li	−3.0	1.5–4.2	100–600
Li-ion[d]	Li^+/Li_xC_y	−2.8–−2.9	1.5–4.0	100–160
Alkaline[c]	ZnO/Zn	−1.3	1.5	110–170
Pb/acid[d]	$PbSO_4$/Pb	−0.4	2.1	20–30
Ni/Cd[d]	Cd^{2+}/Cd	−0.4	1.2	20–30

[a] From reference (5). [b] From references (6) and (7). [c] Primary (non-rechargeable) batteries. [d] Secondary (rechargeable) batteries.

Table 1. Approximate specifications for several types of batteries, including standard redox potentials related to their anodes ($E°_a$) and battery voltages (E).

Two kinds of lithium batteries are known: lithium-metal and lithium-ion (6). The former ones, based on lithium-metal anodes, are in general primary (non-rechargeable), whereas the latter, based on anodes where lithium ions intercalate within a matrix material (most often graphite or another carbon material), are secondary (rechargeable). The reaction involved in lithium-metal cells is:

$$Li^+ + e^- \rightleftharpoons Li(0)$$

whereas in lithium-ion cells it can be described as:

$$xLi^+ + yC + xe^- \rightleftharpoons Li_xC_y$$

where Li_xC_y is graphite with intercalated lithium ($x \approx 0.5$, $y = 6$). In the latter case, lithium intercalates in the host material or migrates into the electrolyte below or above the redox potential, respectively, being such potential close to that of metallic lithium (see Table 1).

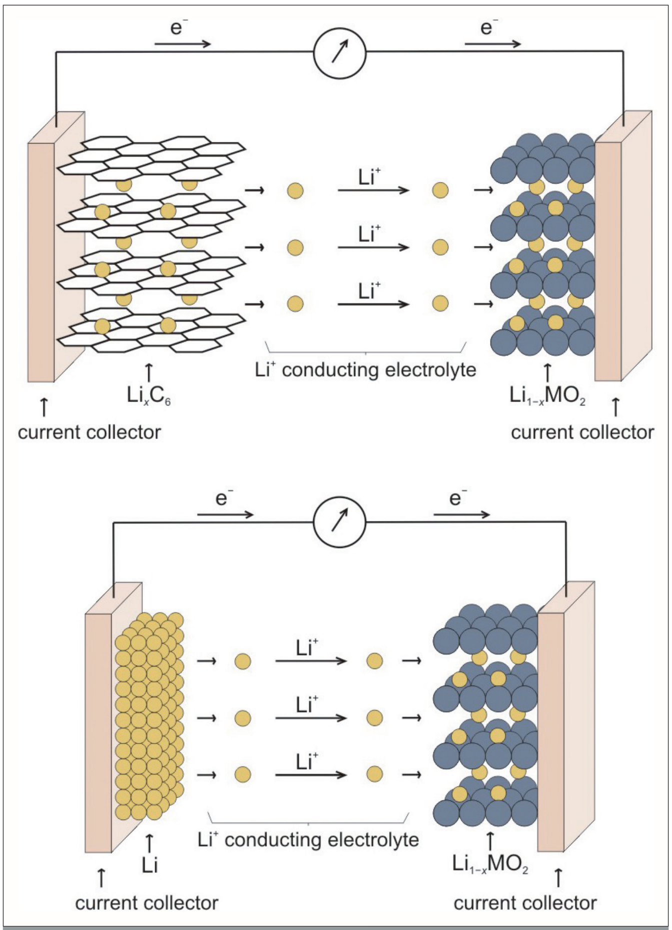


Figure 1. Schematic representations of a lithium-ion battery (top) based on a Li_xC_6 anode and a lithium-metal battery (bottom) with metallic lithium as anode. In both cases, the cathode consists of $Li_{1-x}MO_2$ (M = Co, Ni, Mn). Arrows indicate the transport of either electrons or lithium cations during discharge.

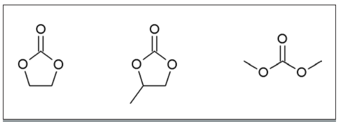


Figure 2. Structures of some of the most common solvents in lithium battery electrolytes. From left to right: ethylene carbonate, propylene carbonate and dimethyl carbonate.

Cathodes, on the other hand, may be composed of a large variety of materials based on diverse chemistries. Figure 1 shows schematic views of lithium-ion and lithium-metal batteries during discharge, whereby lithium ions are released from the anode (Li_xC_6 or Li(0), respectively), diffuse through the electrolyte and intercalate in the cathode ($Li_{1-x}MO_2$, M = Co, Ni, Mn).

For both lithium-metal and lithium-ion batteries, the electrolyte is a solution of a lithium salt (*e.g.* $Li[PF_6]$ or $Li[ClO_4]$) in an organic solvent. Among such solvents, the most popular ones, by virtue of their relative robustness at negative potentials, are cyclic or acyclic alkyl carbonates (Figure 2). However, there is still room for electrolyte improvement, since such carbonates may undergo decomposition throughout cell life (2, 3). Furthermore, they are flammable and volatile solvents, a fact that may lead to accidents in the event of shortcircuits. Lithium battery technologies are in a way limited by electrolyte stability.

SAFETY ISSUES OF LITHIUM BATTERIES

Though the Li^+/Li system is reversible, lithium-metal batteries are not rechargeable due to the high reactivity of pure lithium metal. During charge-discharge cycles, this fact might lead to decomposition of the electrolyte along with temperature increase and fire or explosion hazards. Thus, significant limitations involving safety prevent the commercialisation of rechargeable lithium-metal batteries, in spite of the fact that their voltages and energy densities are among the highest currently known (Table 1).

Rechargeable lithium-ion batteries were made possible thanks to the discovery of lithium intercalation anodes as those described above, in quest of safer systems. Despite the electrolyte does decompose in contact with the electrode, a protective layer is formed by products from such decomposition, similarly to oxide passivation on metallic (*e.g.* iron or aluminium) surfaces (2, 3, 8). This shield, known as solid-electrolyte interface (SEI), allows hundreds of charge/discharge cycles to be safely performed. Nevertheless, in the event of overheating or shortcircuit, fire hazards also exist (3, 9), a fact which has caused occasional accidents (10).

Due to the abovementioned safety issues, the application of lithium cells to electric vehicles or large-scale energy storage is still under intense investigation. In spite of the fact that lithium battery prototypes for electric vehicles have already been manufactured, their wide implementation and commercialisation is still prevented by safety concerns, mainly related to the high reactivity of lithium. Given the large sizes and demanding operating conditions of devices for electric vehicles or renewable energy storage, lithium batteries for such applications must meet strict requirements and therefore, manufacturers are committed to ensure full health and safety credentials prior to commercialisation and implementation.

In order to improve safety, real advances concerning the materials used for such cells are needed. In particular, electrolyte and electrode materials are of crucial importance.

Electrolytes more resistant to lithium are still intensely sought. Among the alternatives, systems based on ionic liquids are some of the most promising, since they are non-flammable and non-volatile materials.

IONIC LIQUIDS

Ionic liquids (more correctly named room temperature ionic liquids) are materials totally composed of ions, which are in the liquid state around or below 100 °C (11). Whereas many inorganic salts melt at very high temperatures, some salts having large and/or asymmetric organic ions remain in their liquid state even below 0 °C. Table 2 shows the melting temperatures of several salts. For example, sodium chloride is a crystalline salt which melts above 800 °C, whereas trihexyl(tetradecyl) phosphonium chloride, based on the same anion although on a much larger cation, is a liquid at room temperature, and cannot crystallise upon cooling, forming a glassy solid below −61 °C instead. The structures of some cations found in the composition of ionic liquids are shown in Figure 3.

Salt	T_m/°C	Salt	T_m/°C
NaCl	801	$[N_{4\,4\,4\,4}]Cl$	74
LiCl	610	$[C_4mim]Cl$	67
$Na[NO_3]$	306	$[P_{6\,6\,6\,14}]Cl$	−61[c,d]
$Li[ClO_4]$	236	$[C_4mim][BF_4]$	−85[c]

[a] Data taken from reference (5) unless otherwise specified. [b] See structures and names of organic cations for each abbreviation in Figure 3. [c] Glass transition temperature, *i.e.* from glassy solid to liquid. [d] From reference (12).

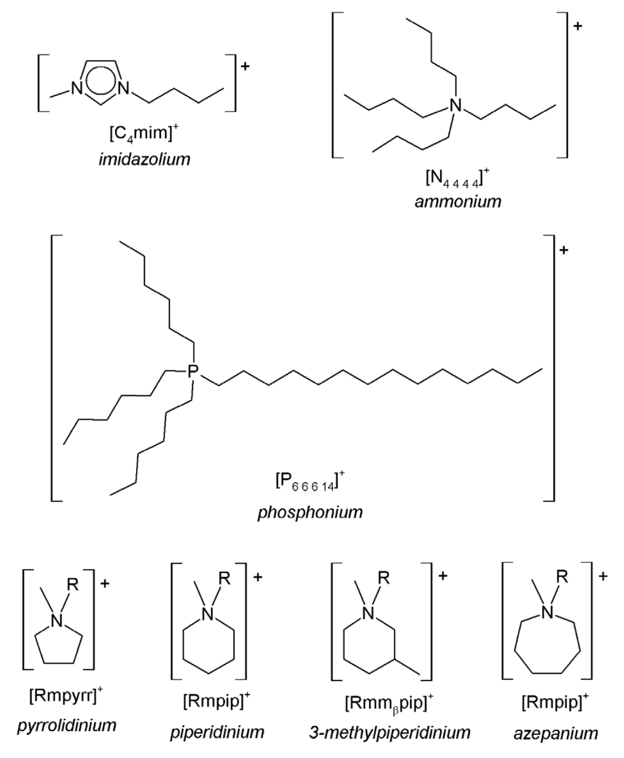
Table 2. Melting points (T_m) of some classic inorganic salts (left) and of some ionic liquids based on organic cations (right) [a,b].

Despite the interest in using ionic liquids as electrolytes, this technology has only gained relevance in the field of electrochemistry after the nineties, thanks to the discovery of air- and water-stable materials (13).

Ionic liquids as electrolytes

Owing to their ionic nature, ionic liquids display features of remarkable practical relevance, including [*a*] extremely low volatility (they do not evaporate in most cases), [*b*] nonflammability, [*c*] inherent ionic conductivity, and [*d*] high electrochemical stability (depending on the nature of their constituent ions). The combination of such properties is well suited for electrochemical applications, *e.g.* metal electrodeposition (14-16), fuel cells (16, 17), batteries (1, 3, 8, 15, 16) or super-capacitors (15, 18).

Non-flammability and non-volatility of most ionic liquids are key properties, since they may help minimise safety hazards in power storage devices. Therefore, the construction of lithium batteries using ionic liquids as the main electrolyte component is currently an active area of research (8, 19). As an example, commercial battery prototypes exhibiting excellent flame resistance have been fabricated (20).



R	structure
C_3	$CH_3CH_2CH_2$-
C_4	$CH_3CH_2CH_2CH_2$-
$MeOC_2$	$CH_3OCH_2CH_2$-

Figure 3. Structures of ionic liquid-forming cations (families designated in italics); [C_4mim]$^+$ = 1-butyl-3-methylimidazolium; [$N_{4\,4\,4\,4}$]$^+$ = tetrabutylammonium; [$P_{6\,6\,6\,14}$]$^+$ = trihexyl(tetradecyl)-phosphonium; [Rmpyrr]+ = 1-R-1-methylpyrrolidinium; [Rmpip]+ = 1-R-1-methylpiperidinium; [Rmm$_\beta$pip]$^+$ = 1-R-1,3-dimethylpiperidinium; [Rmazp]$^+$ = 1-R-1-methylazepanium.

Lithium salt solutions in the appropriate ionic liquids may display conductivities within 1–10 mS cm^{-1}, close to those of electrolytes based on organic carbonates frequently used in lithium batteries (15). The most popular ionic liquids for electrolytes are those based on fluorinated anions, due to their low viscosities, and in turn, elevated conductivities. That is the case of the [NTf_2]$^-$ anion ([$N(SO_2CF_3)_2$]$^-$, bis{(trifluoromethyl)sulfonyl}amide). Table 3 shows viscosity and conductivity data for several ionic liquids based on [NTf_2]$^-$; the inverse relationship between both magnitudes may be clearly observed therein. Cation structures also exert an influence: imidazolium systems tend to be better ionic conductors than pyrrolidinium or piperidinium counterparts. For example, compared to [C_4mim][NTf_2] is almost half as viscous and twice as conducting as [C_4mpyrr][NTf_2] (50 cP/3.8 mS cm^{-1} and 85 cP/2.2 mS cm^{-1}, respectively, at 25 °C).

In order to be used for lithium batteries, electrolyte materials must exhibit high electrochemical stabilities, especially at the highly negative lithium anode potentials and towards lithium metal itself. In general, the resistance to reduction of an ionic liquid at negative potentials is dictated by the cation. Aromatic systems (imidazolium in Figure 3) are less stable at negative potentials than aliphatic ones (all except imidazolium in Figure 3), since the relatively acidic hydrogen atoms and vacant π orbitals in the former are prone to be reduced (16, 21). Thus, reduction reactions start at −2.7 and −3.4 V vs. the ferrocenium/ferrocene redox pair for [C_4mim][NTf_2] and [C_3mpip][NTf_2], respectively (Table 3). It should be noted that potential limits may vary significantly when measured against different electrolyte materials. Therefore, electrochemical windows (as those listed in Table 3) are not directly comparable figures and they should be merely seen as approximate indications of stability.

Cation[b]	η/cP	σ/ mS cm^{-1}	E_c/V	E_a/V	ΔE/V
[C_4mim]$^+$	50	3.8	−2.7[c]	2.3[c]	5.0[c]
[C_4mpyrr]$^+$	85	2.2	−3.0[d]	2.5[d]	5.5[d]
[C_3mpip]$^+$	151	1.4	−3.4[c]	2.5[c]	5.9[c]
[C_4mpip]$^+$	182	1.1	−0.1[e]	5.2[e]	5.3[e]
[C_4mm$_\beta$pip]$^+$	315	0.55	−3.0[f]	3.2[f]	6.2[f]
[$MeOC_2$mm$_\beta$pip]$^+$	136	1.2	−3.0[f]	3.0[f]	6.0[f]
[C_4mazp]$^+$	315	0.56	−3.3[f]	3.2[f]	6.5[f]
[$MeOC_2$mazp]$^+$	160	1.1	−2.7[f]	2.8[f]	5.5[f]

[a] Data recorded at 25 °C, adapted from references (22) and (23). [b] See structures and names of cations for each abbreviation in Figure 3. [c] Measured against a ferrocenium/ferrocene redox pair. [d] Measured on a silver wire quasi-reference electrode. [e] Measured using lithium as a reference electrode. [f] Measured against Ag$^+$/Ag reference electrodes.

Table 3. Viscosities (η), conductivities (σ) and electrochemical windows (ΔE), specifying cathodic (E_c) and anodic (E_a) limits, for ionic liquids based on the [NTf_2]$^-$ anion.[a]

Alicyclic ammonium ionic liquids: improving the stability of electrolytes against lithium

Due to their high resistance to reduction, *i.e.* cathodic stability, ionic liquids based on aliphatic ammonium cations exhibit good stability against Li(0). This is the case for both cyclic and non-cyclic cations. Nevertheless, cyclic aliphatic (alicyclic) ammonium liquid salts are generally better ionic conductors than non-cyclic counterparts (15). In addition, members of the cyclic family tend to be more resistant to reduction (24). As a consequence of all this evidence, these alicyclic ammonium systems have been intensely investigated for safe lithium batteries during the last decade.

Such materials have enabled electrodeposition and subsequent reoxidation of Li(0) over a number of cycles, therefore opening up new possibilities for the demanding goal of manufacturing rechargeable lithium metal batteries. A few recent examples follow.

Howlett *et al.* reported the safe cycling of lithium with good reversibility in [$C_n$mpyrr][NTf_2] (n = 3, 4) (25). Later, it was confirmed that pyrrolidinium systems are more stable towards lithium than their imidazolium analogues (26). A comparative study proved that pyrrolidinium and piperidinium ionic liquids can be compatible with lithium-metal anodes and offer enhanced cycle life and improved reversibility as compared to organic carbonate electrolytes in high voltage lithium-metal cells (27). Very recently, electrolytes based on [C_4mpyrr][NTf_2] have been shown to improve the reversibility of lithium-metal battery prototypes over up to one thousand cycles (28). A similar ionic liquid, [C_3mpyrr][NTf_2], has been used as electrolyte solvent for batteries with lithium-metal anodes and sulfur-based cathodes, offering high stability and capacity and fast charge-transfer kinetics (29). Finally, it is worth noting that etherfunctionalised analogues of these ionic liquids are frequently chosen for battery applications, due to their increased conductivities (*vide infra*), as is the case of [MeOC_2mpyrr][NTf_2], used in conjunction with acrylic polymers for flexible electrolyte films (30); lithium-metal cells fabricated with such electrolytes showed high stability and good cycling performance.

Azepanium and 3-methylpiperidinium ionic liquids

Two new families of ionic liquids containing either azepanium (seven-membered alicyclic ammonium) or 3-methylpiperidinium cations (Figure 3) are presented herein. Relevant physical and electrochemical data for these [Rmazp][NTf_2] and [Rmm$_\beta$pip][NTf_2] ionic liquids are listed in Table 3; a systematic comparison with those for analogous [Rmpip][NTf_2] and [Rmpyrr][NTf_2] (widely studied for electrochemical devices) is reviewed in the following paragraphs.

The viscosities and conductivities (at 25 °C) of several salts based on the [NTf_2]$^-$ anion are compared in Figure 4, confirming that they follow opposing trends, *i.e.* the lower the viscosity, the higher the conductivity (see above). In addition, two main patterns relating such magnitudes with the cationic structures are observed:

– Fluidity (as the inverse of viscosity) and conductivity increase with decreasing cationic ring size ([Rmm$_\beta$pip]$^+$ ≈ [Rmazp]$^+$ > [Rmpip]$^+$ > [Rmpyrr]$^+$, left to right in Figure 4), probably due to higher mobility of smaller cations.

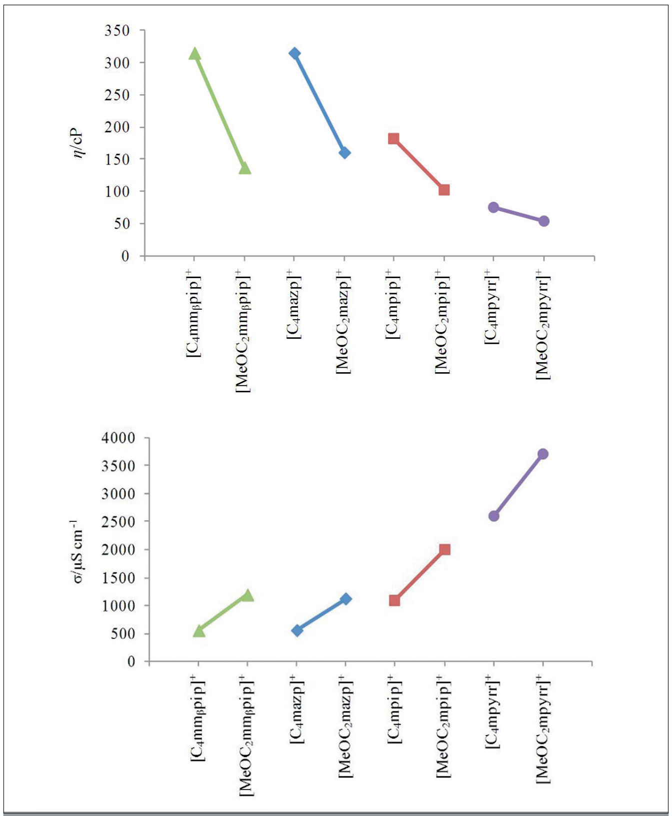
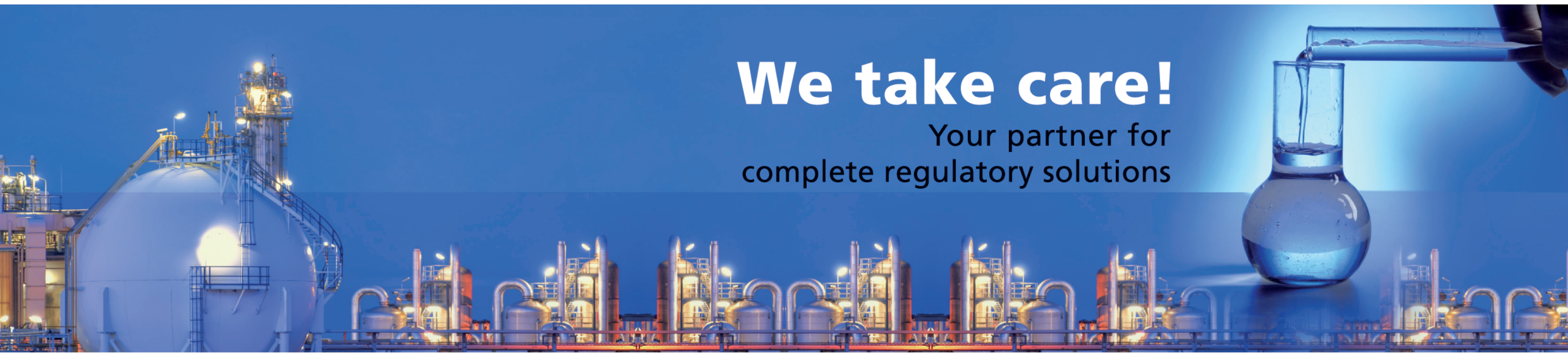


Figure 4. Viscosities (up) and conductivities (down) for ionic liquids based on [NTf_2]− anions and 3methylpiperidinium (triangles), azepanium (diamonds), piperidinium (squares) or pyrrolidinium (circles) cations. See cationic structures for each abbreviation in Figure 3.



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– The introduction of ether functionalities in the R chains cause noticeable viscosity reductions and, therefore, conductivity increases (solid lines in Figure 4); such effect is found for all cationic cores, although it is more pronounced for the new ionic liquids. For example, by replacing the butyl group in $[\mathrm{C_4mm_\beta pip}][\mathrm{NTf_2}]$ with 2-methoxyethyl in $[\mathrm{MeOC_2mm_\beta pip}][\mathrm{NTf_2}]$, ionic conductivity is increased by more than 100% (0.55 and 1.2 mS $\mathrm{cm^{-1}}$, respectively, see Table 3).

The electrochemical stabilities of the ionic liquids herein presented were studied by cyclic voltammetry. Reduction and oxidation potentials and the derived potential windows are summarised in Table 3. The new salts exhibit high electrochemical stabilities, as suggested by their large potential windows (up to 6.5 V for $[\mathrm{C_4mazp}][\mathrm{NTf_2}]$). It is worth noting that cathodic limits are found around −3.0 V against $\mathrm{Ag^+/Ag}$ for all azepanium or 3-methylpiperidinium ionic liquids, that is, at highly negative potentials. According to these results, $[\mathrm{Rmazp}][\mathrm{NTf_2}]$ and $[\mathrm{Rmm_\beta pip}][\mathrm{NTf_2}]$ are among the most electrochemically stable ionic liquids currently known. Therefore, such materials are promising candidates to enlarge the range of robust electrolytes for highly demanding applications, such as lithium batteries or super-capacitors. Not surprisingly, shortly after being disclosed (22, 23, 31), interesting practical applications have been reported for azepanium and 3-methylpiperidinium ionic liquid electrolytes. For example, it has been proved that $[\mathrm{C_4mazp}][\mathrm{NTf_2}]$ can perform as the main electrolyte component for reversible lithium-metal cells, enabling the fabrication of high charge capacity batteries (32). Furthermore, a recent patent claims that, as compared to non-substituted piperidinium ($[\mathrm{Rmpip}]^+$) ionic liquids, 3-methylpiperidinium ($[\mathrm{Rmm_\beta pip}]^+$) analogues are more stable in lithium-ion cells, giving rise to improved capacities after repeated charge/discharge cycles (33).

CONCLUSIONS

The technology of lithium batteries and other energy storage devices (super-capacitors, *etc.*) is well advanced. However, safety issues related to such devices still exist, as is the case of fire or explosion related to failure, overheating or short-circuit. Such risks are often due to the flammability and volatility of the solvents used for the electrolytes. In order to improve safety in daily use energy storage devices, intense investigation on stable electrolytes continues. Among the alternatives, ionic liquids deserve special attention since the large majority of them are non-flammable and non-volatile. Furthermore, cation and anion structures can be designed for enhanced electrochemical stability. Given their high stability at negative potentials, ionic liquids based on alicyclic ammonium cations provide satisfactory results in lithium-metal cells. Among them, it is here shown that not only pyrrolidinium or piperidinium, but also azepanium or 3-methylpiperidinium ionic liquids, exhibit desirable properties for the purpose of producing lithium battery electrolytes. Moreover, the introduction of ether linkages in the side chains of the cations improves both liquid ranges and ionic conductivities.

Given the favourable features of ionic liquids such as those presented in this article, the fabrication of safely rechargeable lithium-metal batteries (which may offer higher energy densities than commercial lithium-ion cells) may still be a demanding goal... but a realistic one.

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REFERENCES AND NOTES

1. W.A. van Schalkwijk and B. Scrosati (eds.), 'Advances in Lithium-Ion Batteries', Kluwer Academic/Plenum Publishers, New York, 2002.
2. K. Ozawa (ed.), 'Lithium Ion Rechargeable Batteries', Wiley-VCH, Weinheim, 2009.
3. B. Scrosati and J. Garche, *J. Power Sources*, 2010, **195**, 2419–2430.
4. I.N. Levine, 'Physical Chemistry', 6th Edit., McGraw-Hill, New York, 2008.
5. D.R. Lide (ed.), 'CRC Handbook of Chemistry and Physics', 89th Edit., CRC Press Boca Raton, London, 2008.
6. D. Linden and T.B. Reddy, 'Handbook of Batteries', McGraw-Hill, New York, 2002.
7. C. Wadia, P. Albertus and V. Srinivasan, *J. Power Sources*, 2011, **196**, 1593–1598.
8. A. Lewandowski and A. Świderska-Mocek, *J. Power Sources*, 2009, **194**, 601–609.
9. A. Hammami, N. Raymond and M. Armand, *Nature*, 2003, **424**, 635–636.
10. 'Dell recalls 4m laptop batteries', http://news.bbc.co.uk/2/hi/4793143.stm, 2006.
11. M. Freemantle, 'An Introduction to Ionic Liquids', Royal Society of Chemistry, Cambridge, 2009.
12. G. Adamová, 'Phosphonium Ionic Liquids', Doctoral Thesis, The Queen's University of Belfast, Belfast, 2011.
13. J.S. Wilkes and M.J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, 1992, 965–967; P. Bonhôte, A.P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168–1178; J.S. Wilkes, *Green Chem.*, 2002, **4**, 73–80.
14. F. Endres, A.P. Abbott and D.R. MacFarlane (eds.), 'Electrodeposition from Ionic Liquids', Wiley-VCH, Weinheim, 2008.
15. M. Galiński, A. Lewandowski and I. Stępniak, *Electrochim. Acta*, 2006, **51**, 5567–5580.
16. M. Armand, F. Endres, D.R. MacFarlane, H. Ohno and B. Scrosati, *Nat. Mater.*, 2009, **8**, 621–629.
17. H. Nakamoto and M. Watanabe, *Chem. Commun.*, 2007, 2539–2541.
18. A. Lewandowski, A. Olejniczak, M. Galinski and I. Stepniak, *J. Power Sources*, 2010, **195**, 5814–5819.
19. B. Scrosati, J. Hassoun and Y.K. Sun, *Energy Environ. Sci.*, 2011, **4**, 3287–3295.
20. D. Teramoto, R. Yokoyama, H. Kagawa, T. Sada and N. Ogata, in 'Molten Salts and Ionic Liquids: Never the Twain?' eds. M. Gaune-Escard and K.R. Seddon, John Wiley & Sons, Inc., Hoboken, 2010, pp. 367–388.
21. M.C. Buzzeo, R.G. Evans and R.G. Compton, *ChemPhysChem*, 2004, **5**, 1106–1120; G.H. Lane, *Electrochim. Acta*, 2012, **83**, 513-528.
22. T. Belhocine, S.A. Forsyth, H.Q.N. Gunaratne, M. Nieuwenhuyzen, P. Nockemann, A.V. Puga, K.R. Seddon, G. Srinivasan and K. Whiston, *Green Chem.*, 2011, **13**, 3137–3155.
23. T. Belhocine, S.A. Forsyth, H.Q.N. Gunaratne, M. Nieuwenhuyzen, A.V. Puga, K.R. Seddon, G. Srinivasan and K. Whiston, *Green Chem.*, 2011, **13**, 59–63.
24. D.R. MacFarlane, P. Meakin, J. Sun, N. Amini and M. Forsyth, *J. Phys. Chem. B*, 1999, **103**, 4164–4170.
25. P.C. Howlett, D.R. MacFarlane and A.F. Hollenkamp, *Electrochem. Solid State Lett.*, 2004, **7**, A97–A101.
26. H. Sakaebe, H. Matsumoto and K. Tatsumi, *Electrochim. Acta*, 2007, **53**, 1048–1054; A. Fernicola, F. Croce, B. Scrosati, T. Watanabe and H. Ohno, *J. Power Sources*, 2007, **174**, 342–348.
27. V. Borgel, E. Markevich, D. Aurbach, G. Semrau and M. Schmidt, *J. Power Sources*, 2009, **189**, 331–336.
28. G.T. Kim, S.S. Jeong, M.Z. Xue, A. Balducci, M. Winter, S. Passerini, F. Alessandrini and G.B. Appetecchi, *J. Power Sources*, 2012, **199**, 239–246.
29. X.-G. Sun, X. Wang, R.T. Mayes and S. Dai, *ChemSusChem*, 2012, **5**, 2079–2085.
30. C. Gerbaldi, J.R. Nair, S. Ferrari, A. Chiappone, G. Meligrana, S. Zanarini, P. Mustarelli, N. Penazzi and R. Bongiovanni, *J. Membr. Sci.*, 2012, **423–424**, 459–467.
31. K.R. Seddon, T. Belhocine, A.V. Puga and K. Whiston, *Low Viscosity Ionic Liquids*, PCT World Pat., 100232 A1 (2011); S. Forsyth, K.R. Seddon and K. Whiston, *Ionic Liquids as Electrolytes*, World Pat., 150842 A1 (2008).
32. N. Salem, L. Nicodemou, Y. Abu-Lebdeh and I.J. Davidson, *J. Electrochem. Soc.*, 2012, **159**, A172–A176.
33. K. Ito and T. Itakura, *Power Storage Device, Lithium-Ion Secondary Battery, Electric Double Layer Capacitor and Lithium-Ion Capacitor*, US Pat., 0002349 A1 (2012).

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Clariant improves automotive, decorative and industrial coatings with high-performance additives, luminous pigments and outstanding innovations. This is how we make modern paints and coatings not only safer, but also significantly more colorful and long-lasting.

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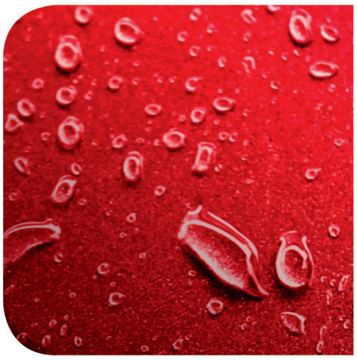

Clariant products make surfaces colorful and resistant, for example against corrosion or UV light.

what is precious to you?