Organic ionic plastic crystals : recent advances

AUTHOR(S)

Jenny Pringle, Patrick Howlett, D MacFarlane, Maria Forsyth

PUBLICATION DATE

01-01-2010

HANDLE

10536/DRO/DU:30031080

Organic ionic plastic crystals: recent advances

Jennifer M. Pringle,* Patrick C. Howlett, Douglas R. MacFarlane and Maria Forsyth

Investigations into the synthesis and utilisation of organic ionic plastic crystals have made significant progress in recent years, driven by a continued need for high conductivity solid state electrolytes for a range of electrochemical devices. There are a number of different aspects to research in this area; fundamental studies, utilising a wide range of analytical techniques, of both pure and doped plastic crystals, and the development of plastic crystal-based materials as electrolytes in, for example, lithium ion batteries. Progress in these areas is highlighted and the development of new organic ionic plastic crystals, including a new class of proton conductors, is discussed.

Introduction

Organic ionic plastic crystals (OIPCs) are unique materials that have been attracting increasing interest in recent years as their novel physical properties and potential applications are realised. The drive towards the development of high conductivity solid state electrolytes for devices such as fuel cells, batteries and solar cells is a compelling motivation for the continued study and advancement of these materials. Previously, attention in the room temperature solid electrolyte area has focused on polymer electrolytes;[1,2] unfortunately, the conductivity of these is often too low for most applications, the ion dynamics being limited by association to the backbone which is often not mobile enough to allow high

ARC Centre of Excellence for Electromaterials Science, Monash University, Wellington Rd, Clayton VIC, 3800, Australia. E-mail: jenny. pringle@sci.monash.edu.au

conductivities. On the other hand, unlike these highly coupled systems, ceramic conductors such as lithium titanium phosphate allow fast ion transport, for example of lithium ions, while the matrix itself remains static. This allows conductivities sufficiently high for some applications (ca. 10^{-3} S cm^{-1}) but with the considerable disadvantage of their brittle material properties. Plastic crystals exhibit states of coupling intermediate between these extremes, with a definite three-dimensional lattice, but with translational motion of some fraction of the species possible. It is these translational motions that allow the materials to flow under stress, hence the term plastic crystal.[3] This plasticity is highly desirable in electrochemical devices as it reduces the problems of poor contact between the electrolyte and the electrodes during volume changes that can occur, while eliminating the leakage problems associated with liquid electrolytes.

Plastic crystals were described in detail by Timmermans in the 1960s.[4] This early work on a range of molecular plastic crystalline materials identified a number of features of plastic crystal behaviour, such as a low entropy of melting, $\Delta S_f < 20$ J K^{-1} mol^{-1}. Plastic crystals have long range order but short-range disorder, which typically originates from rotational motions of the molecules. The plastic phase of one of these compounds is commonly reached via one or more solid–solid phase transitions, which represent the onset of these molecular rotations (hence such phases are often also termed "rotator phases"), as depicted in Fig. 1. Thus, as the rotational component of the entropy of fusion is already present in the solid phases, the entropy of fusion in the transition from phase I to the melt is small (by convention, the highest temperature solid phase is denoted phase I, with subsequent lower temperature phases denoted as phase II, III, etc.). However,

Dr Jenny Pringle received her degree and PhD, on ionic liquids, at The University of Edinburgh in Scotland before moving to Monash University in 2002. In 2008 she started an ARC QEII Fellowship, in association with the ARC Centre of Excellence for Electromaterials Science (ACES), which focuses her research on ionic liquids and plastic crystals into the area of dye-sensitised solar cells.

Jennifer M. Pringle

Dr Patrick Howlett received his chemistry degree from Curtin University in Perth in 1992. He then held various positions in industry before joining CSIRO in 1999, and received his PhD jointly with CSIRO Energy Technology and Monash University in 2004. He is now a Senior Research Fellow within ACES, investigating corrosion resistant coatings, batteries, etc., and also developing advanced surface characterisation methods, including synchrotron techniques, to look at the formation of ionic liquid interphases on reactive metal surfaces.
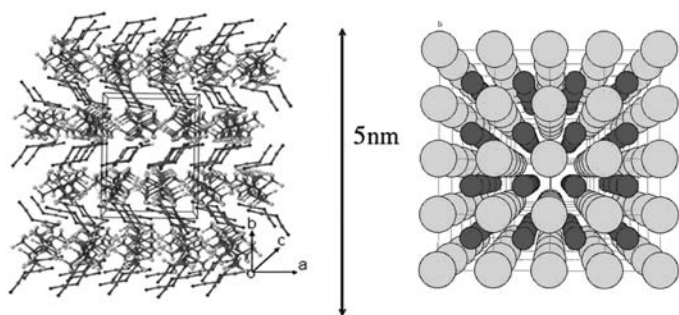
Patrick C. Howlett

Fig. 1 Illustration of the structure of different phases of tetramethylammonium dicyanamide ([Me$_4$N][DCA]). In phase IV (left) the material is an ordered crystalline lattice, but after increasing the temperature to phase I (right) the ions have considerable rotational motion.

this criterion may only be appropriate to plastic crystals containing one molecular species; if the plastic crystal contains two different molecular ions and only one of these exhibits rotor motions then the entropy of melting will be higher, as is observed for a number of organic ionic plastic crystals.[5]

There is significant interest in the use of molecular plastic crystals in applications such as lithium batteries.[6–10] The advantage of ionic plastic crystal materials over molecular plastic crystals is that they exhibit negligible vapour pressure, which is clearly desirable for electrochemical applications.

Ionic compounds such as Li$_2$SO$_4$ and Na$_3$PO$_4$ exhibit high temperature plastic phases, and significant ionic conductivity can be achieved at high temperatures. The use of organic ionic moieties, such as those shown in Fig. 2, allows the formation of plastic crystal phases, and high
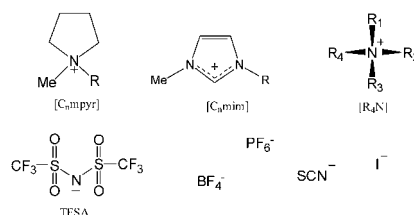

Fig. 2 Cation and anion structures commonly found in organic ionic plastic crystals (R = methyl, ethyl).

ionic conductivity, at ambient temperature.[11] Furthermore, and particularly important from a device perspective, the addition of dopant ions such as Li$^+$ can produce increases in conductivity of up to several orders of magnitude, forming materials that are an interesting new class of fast ion conductor.[12]

There are currently a number of challenges for researchers interested in organic ionic plastic crystals. Firstly, the

nature of the conduction processes in the pure and doped plastic crystals is not clear. Secondly, the relationship between the chemical structure of the cations or anions and the physical properties of the resultant salt is poorly understood. Identifying the structural variations that yield the desired plasticity, over the required temperature range, in addition to the highest possible conductivity, is clearly desirable for the development of new materials, but the physico-chemical relationships are non-trivial. The synthesis and analysis of new plastic crystal materials play an important role in helping to elucidate these relationships. Finally, the development of these materials as solid state electrolytes is still in the early stages. The field of plastic crystal electrolyte materials was reviewed in some detail in 2001;[11] the present article is intended to highlight more recent progress in the area, including their use in lithium batteries.

Pure plastic crystals

It is presently very difficult to predict which cation and anion combinations will yield plastic crystalline materials and which will form salts that melt before any rotator phase is achieved. Comparison of a range of imidazolium ([C$_n$mim]), pyrrolidinium ([C$_n$mpyr]) and tetraalkylammonium ([R$_4$N]) bis(trifluoromethanesulfonyl)amide (TFSA, also called NTf$_2$) salts indicates the importance of the cation structure in determining plasticity.[5] The [R$_4$N][TFSA] salts investigated do not show the high conductivities

Douglas R. MacFarlane

Professor Doug MacFarlane leads the Monash Ionic Liquids Group at Monash University. He was a PhD graduate of Purdue University in 1982 and took up a faculty position at Monash in 1983. Professor MacFarlane was recently awarded an Australian Research Council Federation Fellowship to extend his work on Ionic Liquids. His research interests include the chemistry and properties of ionic liquids and solids and their application in a wide range of technologies from electrochemical (batteries, fuel cells, solar cells and corrosion prevention), to biotechnology (drug ionic liquids and protein stabilisation) and biofuel processing.

Maria Forsyth

Professor Maria Forsyth is the Associate Director of ACES. She has been involved in the field of electromaterials science since graduating from her PhD at Monash University in 1990 and taking up a Fulbright fellowship at Northwestern University (USA) in the field of lithium battery electrolytes. Her current research focuses on developing an understanding of charge transport at metal/electrolyte interfaces and within electrolyte materials. Overall, she has co-authored over 230 refereed publications.

of the small [C$_n$mpyr] salts, and it is proposed that this high conductivity is due to rotation of the cation, which does not occur for the [R$_4$N] salts studied. [R$_4$N] salts that are plastic and show ion conduction can be achieved when combined with anions that are smaller and more symmetrical, *e.g.* Cl, Br or SCN,[13–15] but these have much higher melting points. However, the link between the rotator motions of the [C$_n$mpyr] cation and the conductivity mechanism is still not clear. It is hypothesised that ion transport results from lattice defects, and the thermodynamic cost of formation of these lattice defects is lower if there is ion rotation. However, the conductivity mechanism may change with even small changes in cation structure; the activation energies and the temperature dependence of the conductivity of the [C$_1$mpyr][TFSA] and [C$_2$mpyr][TFSA] salts across the phase changes is quite different.[5]

The relationship between the ion conduction and defects in the [C$_1$mpyr][TFSA] species has been studied in more detail using positron annihilation lifetime spectroscopy (PALS).[16,17] It is believed that rotation in a plastic crystal is less hindered in the vicinity of defects, thus enhancing the rotational motion through the material.[16] The mechanical flexibility of plastic crystals may also be explained by the diffusion of vacancies and dislocations facilitating crystalline plane slip. Defects have also been suggested to be associated with ionic diffusion through the material, occurring through either vacancies or through extended defects such as dislocations or grain boundaries. PALS analysis allows the number and size of defects in a plastic crystal to be probed. Analysis of [C$_1$mpyr][TFSA] shows a close correlation between the ionic conduction and the defects in the material. In the sub-ambient phase III, the vacancies measured are smaller than the ions and therefore motion of the ions is concluded to be mostly rotational. In phase II the vacancies are larger but the critical volume (the minimum volume required to accommodate the mobile ions) is bigger than one vacancy or a cation–anion divacancy and thus it is concluded that ions diffuse through extended defects such as dislocations *via* a pipe diffusion mechanism. This highlights the fact that it is not only

the size of the vacancies in a plastic crystal that can influence the conduction mechanism but also the connectivity between the vacancies.

The crystal structures of [C$_2$mpyr]-[TFSA] in both phases III and IV indicate that the packing of the ions is almost identical,[18] but in phase III all of the ions are disordered. Both the cations and anions in phase III seem to possess rotational disorder, plus the conformations of the ions also change. Interestingly, the type of disorder that is observed involves minimal additional volume, requiring only a 3% change in volume on moving from phase IV to phase III. The disorder in the TFSA anions is a C$_2$ ↔ C$_2$ disordering mode (rather than a mixture of C$_1$ and C$_2$ conformations as one might expect). This new mode of disorder has also been observed in other TFSA salts,[18,19] implying that it is a common mode of disorder for solid state materials of this anion. It is an interesting observation that the volume change associated with phase transitions in different OIPCs can be markedly different; measurement of this property can provide useful information but it is seldom performed.[20,21]

Tetraethylammonium dicyanamide ([Et$_4$N][DCA]) has a highly conductive plastic crystal phase that spans room temperature (Fig. 3) and is therefore the kind of material that is of interest for solid state electrolyte applications. It has a ΔS_f of 4 ± 0.5 J K^{-1} mol^{-1}, which is one of the lowest known. The material exhibits a substantial increase in volume across the solid–solid phase transition (Fig. 3), whereas there is only a very slight increase

in volume upon melting.[20] This suggests that phase I is structurally very similar to the melt, and/or that there is an onset of ion association in the liquid[22,23] that has a negative effect on the volume change. There is also an increase in the heat capacity of the material on moving from phase II to phase I,[20] which may be the result of the number of motional degrees of freedom available. Unlike some other OIPCs (*e.g.* the structurally similar [Me$_4$N][DCA]) the material shows dramatic increases in the ionic conductivity with temperature, both before and after the solid–solid transition temperature, with different activation energies (Fig. 3). This suggests that the processes responsible for the observed phase changes are also responsible for the ionic conductivity, and that not all of the degrees of translational freedom are present immediately after the solid–solid transition. This is also indicated by the ^{1}H NMR analysis, which indicates isotropic rotation as the predominant motion in phase I, with translation only finally becoming predominant in the melt. It is interesting to note that this [Et$_4$N][DCA] displays dramatically different behaviour to the Me$_4$N analogue[24] and it is postulated that the isotropic tumbling of the larger cation in phase I leads to a larger volume expansion and therefore easier translation of the anion than occurs with the smaller cation.

Raman spectroscopy can also help to elucidate changes in ionic interactions with temperature, as illustrated by a recent study of [C$_1$mpyr][SCN].[25] This material has a solid–solid phase transition
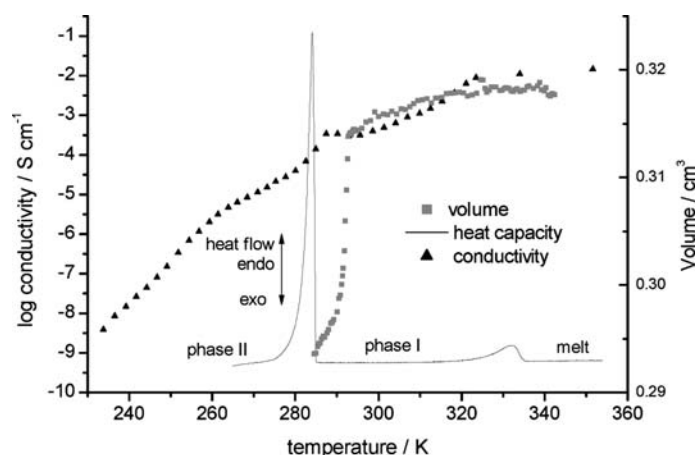

Fig. 3 The correlation between volume, conductivity and thermal behaviour with temperature for [Et$_4$N][DCA].

at 82 °C, melts at 122 °C and has conductivity in phase I of around 10^{-3} S cm^{-1}. There is a step in the conductivity at each of the phase transitions of one order of magnitude while the activation energy decreases by a factor of two at each transition, indicating a significant decrease in the energy barrier to mobility. The vibrational modes of the thiocyanate anion are very sensitive to its coordination environment and Raman measurements of the material confirm that the cation, and probably also the anion, are tumbling isotropically in phase I. NMR linewidth analysis can provide valuable information about the mobility of the cations and/or anions in a plastic crystal, the more mobile the species the sharper the line will be, and it is often possible to see the superimposition of broad and narrow lines in the same spectra, indicating the presence of species with two different mobilities. In addition to this, pulse field gradient NMR analysis can quantify the diffusion coefficient of mobile species in the plastic crystal. ^{1}H NMR analysis of the $[C_1mpyr][SCN]$ shows a significant decrease in the linewidths across the phase II to phase I transition, indicating a sudden onset of mobility of the cation, which is consistent with the observed step increase in the conductivity. The second moment analysis of the ^{1}H NMR data indicates that the cation goes from being static in phase II to full isotropic tumbling in phase I. This is an unusually large increase in rotational mobility; the iodide and TFSA

salts of this cation,[26] as well as the plastic crystal $[Me_4N][DCA]$,[24] all go through several phases with anisotropic tumbling of the cations before the state of isotropic tumbling is reached.

Volel *et al.*[27] have also demonstrated the use of temperature-controlled scanning probe microscopy (in this case AFM) to measure the Young modulus, hardness and roughness of a range of *N,N'*-cyclised pyrazolium TFSA salts across their phase transitions. The plastic crystals showed three states—brittle, elastoplastic and viscoplastic—and the conductivity values suggest that the conduction mechanism is different in each state.

In addition to the utilisation of a wider range of analytical techniques in recent years, there have also been a number of new organic ionic plastic crystals reported.[28–34] Zhou and co-workers prepared fifty-two different salts utilising quaternary ammonium cations and a range of perfluoroalkyltrifluoroborate anions, a number of which exhibit one or more solid–solid phase transitions.[31] For example, $[C_4mpyr][C_3F_7BF_3]$ goes through four different solid–solid phase transitions before melting at 53 °C. Our group has also recently reported a number of different plastic crystalline materials utilising fluorinated anions (Fig. 4a), illustrating the influence that the anion can have on the plasticity of the salt.[35,36] The nonafluoro-1-butane sulfonate salts are particularly interesting materials as all six of the series are in plastic phase I at ambient temperature,

and up to at least 90 °C, and they exhibit excellent electrochemical and thermal stability.[35]

Finally, a new class of proton-conducting OIPC has been reported (Fig. 4b).[32] These utilise the dihydrogenphosphate (DHP) anion, which can generate protons as a carrier and thereby obviates the need for the addition of a dopant acid that may be incompatible with the host matrix. Choline DHP is in phase II between 23 °C and 119 °C, and the conductivity increases from 10^{-6} to 10^{-3} S cm^{-1} in phase I. Investigations into the use of these new materials as proton-conducting electrolytes in fuel cells are ongoing.

Doped plastic crystals

Interest in organic ionic plastic crystal materials stems from their use as fast ion Li^+ or H^+ conductors where these are present as low level dopants.[11] The addition of dopants can result in conductivity increases of several orders of magnitude and produce materials suitable for use in devices such as lithium batteries, as discussed later. An investigation into the effect of LiI addition to $[C_1mpyr][I]$ shows an almost 3 orders of magnitude increase in ionic conductivity arising from relatively mobile lithium ions and an increase in the mobility of the matrix cations.[38] Although the material exhibits only limited plasticity, this is a noteworthy study as it demonstrates the first direct evidence of solid solution behaviour in the pyrrolidinium family. In previous work on different $[C_nmpyr][TFSA]$ salts there has been some debate about the solubility of the lithium salts and whether, in fact, a mixture of pure compounds had been formed. It is important to note, however, that there is a maximum solid solubility of LiI above which a second, low-conductivity phase is produced, and this is likely to be the case for other lithium-doped plastic crystal electrolyte systems. The existence of a solid solution in this system is evidenced by the fact that the phase transitions of the material are shifted to lower temperatures with doping. A change in transition temperatures has also been observed when the plastic crystal $[C_2mpyr][BF_4]$ is modified with supercritical CO_2;[39] such modification increases the ionic conductivity and also effects stabilisation of the most ordered phase to
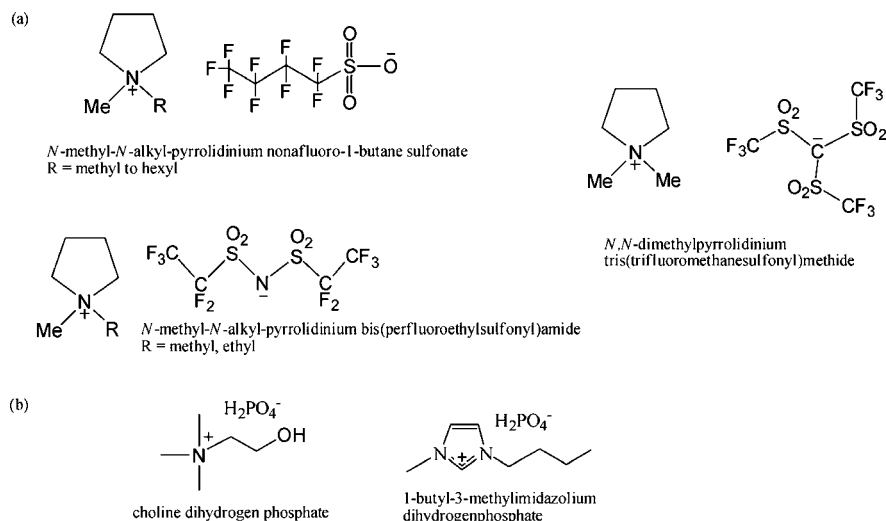

Fig. 4 New plastic crystal materials reported recently: (a) with new fluorinated anions[35,36] and (b) proton-conducting OIPCs.[32,37]

a lower temperature. In contrast, addition of a miscible polymer to the plastic crystal [C$_3$mpyr][PF$_6$] significantly increases the mechanical strength of the material, and decreases the conductivity, but does not affect its phase behaviour.[21]

An alternative additive for plastic crystals, and one that is receiving increasing attention, is the use of nanoparticles such as TiO$_2$ and SiO$_2$. Studies on [C$_2$mpyr][TFSA] show that addition of nanosized TiO$_2$ or SiO$_2$ increases the ionic conductivity by one or two orders of magnitude respectively.[40,41] Both fillers show an optimum concentration of about 10 wt%. It is probable that the conductivity enhancement is associated with an increase in the number of mobile defects, as well as an increase in the plastic flow of the material (which increases the mobility in the matrix). However, it is interesting to note that while both lithium doping and addition of SiO$_2$ nanoparticles result in significant increases in conductivity, the use of these two additives together results in a decrease in conductivity.[42] Analysis of this system suggests two possible reasons for the unexpected drop in conductivity; either addition of the silica nanoparticles to the lithium-doped system disrupts the grain boundary regions, or the lithium and/or anion transport is decreased. Addition of a lithium-functionalised nanoparticles yields a conductivity enhancement, but not as substantial as the addition of unsubstituted nanoparticles.[43] Analysis of the nanocomposites indicate that addition of the functionalised nanoparticles results in an increase in the size and number of defects in the matrix, with a concomitant increase in both the number of mobile cations and anions and their mobility through the matrix. As higher mobility resulting from an increase in defect size and number are observed, we postulate that the conductivity enhancement is due to "strain-induced defects". However, more studies are needed to fully investigate the influence of nanoparticle fillers on OIPCs and to allow the promising properties of these nanocomposite electrolyte materials to be fully exploited.

Lithium battery applications

The non-flammability, non-volatility, plasticity and high electrochemical and thermal stability make organic ionic plastic crystals potentially ideal electrolytes for lithium batteries. Armand and co-workers studied a range of doped N,N′ cyclised pyrazolium TFSA plastic crystal electrolytes for application in lithium based devices (Fig. 5).[7,44–46] The relatively poor cathodic stability of these materials (∼1.4 V vs. Li$^+$/Li) limits the electrolytes to application with Li$_4$Ti$_5$O$_{12}$ negative electrodes (for lithium ion batteries rather than lithium metal batteries). Li$_4$Ti$_5$O$_{12}$/LiFePO$_4$ cells cycled at 40 °C and slow scan voltammetry indicated an accessible capacity of 137 mAh g^{-1}. More recently, N,N′-diethyl-3-methylpyrazolium TFSA (DEMpyr123TFSA, Fig. 5), which exhibits a single plastic crystalline phase from 4.2 °C to 11.3 °C, has been studied in LiFePO$_4$–Li$_4$Ti$_5$O$_{12}$ cells.[7] The batteries showed a charge/discharge efficiency of 93% and 87% (67% of theoretical) in the liquid and the plastic phase, respectively, at 20 °C. This important series of contributions has clearly demonstrated that plastic crystal electrolytes are both compatible and applicable in batteries incorporating common lithium intercalation electrodes.
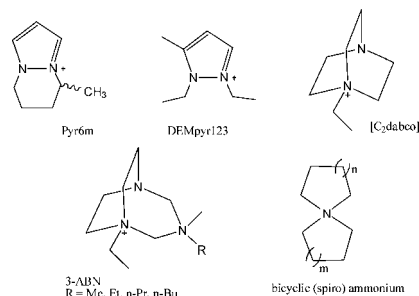
The [C$_n$mpyr]TFSA plastic crystals have also been investigated in the context of lithium battery applications.[5,47,48] The related ionic liquids have been extensively investigated and shown to support stable lithium electrochemistry.[49,50] Recently, we have reported LiTFSA-doped [C$_2$mpyr]-[TFSA] plastic crystal electrolytes in which substantial currents can be supported after initial cycling (approaching 0.5 mA cm^{-2} at 50 °C).[51] The reduction in cell impedance with cycling (Fig. 6a) appears to be related to a change in the plastic crystal microstructure as a result of the applied current. The behaviour also appears to be related to the formation of improved interfacial 'contact' between the solid electrolyte and the electrode, as shown in Fig. 6b.

Zhou et al.[31] have studied organic salts based on the perfluoroalkyltrifluoroborate anion, which are typically very electrochemically stable. Recently, they have reported the behaviour of the lithium-doped systems which exhibit phase I from −20 °C to 95 °C, conductivity from 10^{-4} to 10^{-3} S cm^{-1} and an electrochemical window of approximately 5.5 V. A 5 mol% LiCF$_3$BF$_3$ doped electrolyte displayed efficient lithium deposition and dissolution at 25 °C. These properties indicate a very promising electrolyte for application in lithium battery systems. Thus far there are no reports describing its application in cells with lithium intercalation electrodes. There are also a number of [C$_n$mpyr][BF$_4$] salts (n = 1–4) that exhibit plastic crystal phases, and an

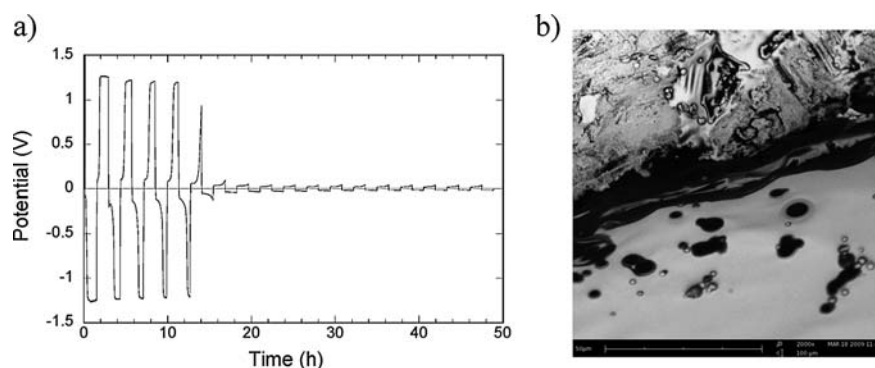**Fig. 5** The range of cations utilised in TFSA-based plastic crystals for lithium battery applications.

Fig. 6 (a) Galvanostatic cycling (0.01 mA cm^{-2}) of a symmetrical lithium cell using 1 mol% LiTFSA in [C$_2$mpyr][TFSA] at 50 °C, (b) back-scattered SEM image of the lithium/electrolyte interface taken from a 'conditioned' cell. The dark region at the interface implies the formation of a conductive lithium-rich interphase that is approximately 10 μm thick.[51]

2060 | J. Mater. Chem., 2010, 20, 2056–2062

This journal is © The Royal Society of Chemistry 2010

electrochemical window exceeding 4 V was demonstrated for the propyl derivative at 100 °C, sufficient for use with a range of lithium intercalation electrodes.[52] Also of potential interest are the series of [C$_n$mpyr] nonafluoro-1-butane sulfonate (NfO) salts which all exhibit multiple solid–solid transitions below the melt,[35] suggestive of the presence of plastic crystal phases. An electrochemical window approaching 6 V and a wide temperature range for phase I (e.g. [C$_2$mpyr][NfO] extending from −50 °C to 175 °C) is reported. This is important from a device perspective, where uniform and consistent behaviour over a wide temperature range is advantageous. Other plastic crystal systems that fit within this category of lithium-compatible electrolytes are all based on variations of quaternary ammonium TFSA salts (Fig. 5).[53–55] These systems uniformly exhibit wide electrochemical windows and have been shown to support lithium deposition and dissolution.

Conclusion

The field of organic ionic plastic crystals is in its infancy in terms of our understanding and in the full realisation of the potential of these materials as solid state electrolytes. The range of techniques applicable to the study of these unique materials is growing, with the application of PALS, X-ray crystallography, Raman spectroscopy, solid state NMR, etc. all providing valuable information about the conduction mechanisms and physical changes occurring. The development of new organic ionic plastic crystals is also paramount in enhancing our understanding of these materials and taking us closer to being able to design physical properties. The use of additives in organic ionic plastic crystals is clearly important in the development of these materials as solid state electrolytes, and there have been some interesting developments in this area in recent years. Indeed, the use of doped OIPC materials in lithium ion batteries is starting to show real promise, which suggests that the wider use of organic ionic plastic crystals as electrolytes in a range of electrochemical devices could soon be a reality.[56,57]

References

1 M. Forsyth, P. Meakin, D. R. MacFarlane and A. J. Hill, J. Phys.: Condens. Matter, 1995, 7, 7601.
2 D. R. MacFarlane, J. Sun, P. Meakin, P. Fasoulopoulos, J. Hey and M. Forsyth, Electrochim. Acta, 1995, 40, 2131.
3 J. N. Sherwood, Plastically Crystalline State; Orientationally Disordered Crystals, John Wiley & Sons Ltd, London, 1979.
4 J. Timmermans, Phys. Chem. Solids, 1961, 18, 1.
5 D. R. MacFarlane, P. Meakin, N. Amini and M. Forsyth, J. Phys.: Condens. Matter, 2001, 13, 8257.
6 M. Patel, K. G. Chandrappa and A. J. Bhattacharyya, Electrochim. Acta, 2008, 54, 209.
7 Y. Abu-Lebdeh, A. Abouimrane, P. J. Alarco and M. Armand, J. Power Sources, 2006, 154, 255.
8 S. Long, P. C. Howlett, D. R. MacFarlane and M. Forsyth, Solid State Ionics, 2006, 177, 647.
9 A. Abouimrane, P. S. Whitfield, S. Niketic and I. J. Davidson, J. Power Sources, 2007, 174, 883.
10 P.-J. Alarco, Y. Abu-Lebdeh, A. Abouimrane and M. Armand, Nat. Mater., 2004, 3, 476.
11 D. R. MacFarlane and M. Forsyth, Adv. Mater. (Weinheim, Ger.), 2001, 13, 957.
12 D. R. MacFarlane, J. H. Huang and M. Forsyth, Nature, 1999, 402, 792.
13 T. Shimizu, S. Tanaka, N. Onoda-Yamamuro, S. i. Ishimaru and R. Ikeda, J. Chem. Soc., Faraday Trans., 1997, 93, 321.
14 M. Tansho, D. Nakamura and R. Ikeda, Ber. Bunsen-Ges. Phys. Chem., 1991, 95, 1643.
15 M. Hattori, S. Fukada, D. Nakamura and R. Ikeda, J. Chem. Soc., Faraday Trans., 1990, 86, 3777.
16 S. J. Pas, J. Huang, M. Forsyth, D. R. MacFarlane and A. J. Hill, J. Chem. Phys., 2005, 122, 064704/1–064704/5.
17 J. Huang, A. Hill, M. Forsyth, D. MacFarlane and A. Hollenkamp, Solid State Ionics, 2006, 177, 2569.
18 W. A. Henderson, V. G. Young, Jr, S. Passerini, P. C. Trulove and H. C. De Long, Chem. Mater., 2006, 18, 934.
19 W. A. Henderson, M. Herstedt, V. G. Young, Jr, S. Passerini, H. C. De Long and P. C. Trulove, Inorg. Chem., 2006, 45, 1412.
20 G. Annat, J. Adebahr, I. R. McKinnon, D. R. MacFarlane and M. Forsyth, Solid State Ionics, 2007, 178, 1065.
21 S. J. Pas, J. M. Pringle, M. Forsyth and D. R. MacFarlane, Phys. Chem. Chem. Phys., 2004, 6, 3721.
22 K. J. Fraser, E. I. Izgorodina, M. Forsyth, J. L. Scott and D. R. MacFarlane, Chem. Commun., 2007, 3817.
23 D. R. MacFarlane, M. Forsyth, E. I. Izgorodina, A. P. Abbott, G. Annat and K. Fraser, Phys. Chem. Chem. Phys., 2009, 11, 4962.
24 A. J. Seeber, M. Forsyth, C. M. Forsyth, S. A. Forsyth, G. Annat and D. R. MacFarlane, Phys. Chem. Chem. Phys., 2003, 5, 2692.
25 J. Adebahr, M. Grimsley, N. M. Rocher, D. R. MacFarlane and M. Forsyth, Solid State Ionics, 2008, 178, 1798.
26 J. Adebahr, M. Forsyth and D. R. MacFarlane, Electrochim. Acta, 2005, 50, 3853.
27 M. Volel, P.-J. Alarco, Y. Abu-Lebdeh and M. Armand, Chemphyschem, 2004, 5, 1027.
28 P. M. Dean, B. R. Clare, V. Armel, J. M. Pringle, C. M. Forsyth, M. Forsyth and D. R. MacFarlane, Aust. J. Chem., 2009, 62, 334.
29 J. Sun, D. R. MacFarlane and M. Forsyth, Solid State Ionics, 2002, 148, 145.
30 S. A. Forsyth and D. R. MacFarlane, J. Mater. Chem., 2003, 13, 2451.
31 Z. B. Zhou, H. Matsumoto and K. Tatsumi, Chem.–Eur. J., 2006, 12, 2196.
32 M. Yoshizawa-Fujita, K. Fujita, M. Forsyth and D. R. MacFarlane, Electrochem. Commun., 2007, 9, 1202.
33 J. Efthimiadis, G. J. Annat, J. Efthimiadis, M. Forsyth and D. R. MacFarlane, Phys. Chem. Chem. Phys., 2003, 5, 5558.
34 S. A. Forsyth, S. R. Batten, Q. Dai and D. R. MacFarlane, Aust. J. Chem., 2004, 57, 121.
35 S. A. Forsyth, K. J. Fraser, P. C. Howlett, D. R. MacFarlane and M. Forsyth, Green Chem., 2006, 8, 256.
36 K. M. Johansson, J. Adebahr, P. C. Howlett, M. Forsyth and D. R. MacFarlane, Aust. J. Chem., 2007, 60, 57.
37 K. Fujita, D. R. MacFarlane, K. Noguchi and H. Ohno, Acta Crystallogr., Sect. E, 2009, 65, O797.
38 J. Adebahr, A. J. Seeber, D. R. MacFarlane and M. Forsyth, J. Phys. Chem. B, 2005, 109, 20087.
39 S. J. Pas, J. Efthimiadis, J. M. Pringle, M. Forsyth and D. R. MacFarlane, J. Mater. Chem., 2004, 14, 2603.
40 J. Adebahr, N. Ciccosillo, Y. Shekibi, D. R. MacFarlane, A. J. Hill and M. Forsyth, Solid State Ionics, 2006, 177, 827.
41 Y. Shekibi, A. Gray-Weale, D. R. MacFarlane, A. J. Hill and M. Forsyth, J. Phys. Chem. C, 2007, 111, 11463.
42 Y. Shekibi, S. J. Pas, N. M. Rocher, B. R. Clare, A. J. Hill, D. R. MacFarlane and M. Forsyth, J. Mater. Chem., 2009, 19, 1635.
43 Y. Shekibi, J. M. Pringle, J. Sun, S. J. Pas, N. M. Rocher, B. R. Clare, A. J. Hill, D. R. MacFarlane and M. Forsyth, J. Mater. Chem., 2010, 20, 338.
44 Y. Abu-Lebdeh, P. J. Alarco and M. Armand, Angew. Chem., Int. Ed., 2003, 42, 4499.
45 P. J. Alarco, Y. Abu-Lebdeh and M. Armand, Solid State Ionics, 2004, 175, 717.
46 Y. Abu-Lebdeh, P. J. Alarco, A. Abouimrane, L. Ionescu-Vasii, A. Hammami and M. Armand, J. New Mater. Electrochem. Syst., 2005, 8, 197.
47 J. Huang, M. Forsyth and D. R. MacFarlane, Solid State Ionics, 2000, 136–137, 447.
48 A. Martinelli, A. Matic, P. Jacobsson, L. Börjesson, A. Fernicola and

This journal is © The Royal Society of Chemistry 2010

J. Mater. Chem., 2010, 20, 2056–2062 | 2061

B. Scrosati, *J. Phys. Chem. B*, 2009, **113**, 11247.

49 P. C. Howlett, D. R. MacFarlane and A. F. Hollenkamp, *Electrochem. Solid-State Lett.*, 2004, **7**, A97.

50 P. C. Howlett, N. Brack, A. F. Hollenkamp, M. Forsyth and D. R. MacFarlane, *J. Electrochem. Soc.*, 2006, **153**, A595.

51 P. C. Howlett, Y. Shekibi, D. R. MacFarlane and M. Forsyth, *Adv. Eng. Mater.*, 2010, **11**, 1044–1048.

52 S. Forsyth, J. Golding, D. R. MacFarlane and M. Forsyth, *Electrochim. Acta*, 2001, **46**, 1753.

53 M. Yoshizawa-Fujita, D. R. MacFarlane, P. C. Howlett and M. Forsyth, *Electrochem. Commun.*, 2006, **8**, 445.

54 T. Rüther, J. Huang and A. F. Hollenkamp, *Chem. Commun.*, 2007, 5226.

55 Y. Abu-Lebdeh, E. Austin and I. J. Davidson, *Chem. Lett.*, 2009, **38**, 782.

56 J. Z. Sun, L. R. Jordan, M. Forsyth and D. R. MacFarlane, *Electrochim. Acta*, 2001, **46**, 1703.

57 J. Z. Sun, D. R. MacFarlane and M. Forsyth, *Electrochim. Acta*, 2001, **46**, 1673.