OPEN ACCESS

Plastic Crystals Utilising Small Ammonium Cations and Sulfonylimide Anions as Electrolytes for Lithium Batteries

To cite this article: Ruhamah Yunis et al 2020 J. Electrochem. Soc. 167 070529

View the article online for updates and enhancements.
Plastic Crystals Utilising Small Ammonium Cations and Sulfonylimide Anions as Electrolytes for Lithium Batteries

Ruhamah Yunis,1, Danah Al-Masri,1 Anthony F. Hollenkamp,2 Cara M. Doherty,3 Haijin Zhu,4 and Jennifer M. Pringle1,*

1Institute for Frontier Materials, Deakin University, Burwood, Victoria 3125, Australia
2Commonwealth Scientific and Industrial Research Organisation (CSIRO), Energy, Clayton 3168, VIC, Australia
3Commonwealth Scientific and Industrial research Organization (CSIRO), Manufacturing, Clayton 3168, VIC, Australia
4Institute for Frontier Materials, Deakin University, Geelong VIC 3220, Australia

Organic ionic plastic crystals (OIPCs) are increasingly promising as a class of solid-state electrolyte for developing safer lithium batteries. However, their advancement relies on expanding the range of well-characterised cation/anion combinations. Here, we report the synthesis and characterization of OIPCs utilising small ammonium cations tetramethylammonium ([N1111]⁺), triethylmethylammonium ([N1222]⁺) and tetraethylammonium ([N2222]⁺), chosen to encourage significant rotational and translational motion, with the charge-diffuse and electrochemically stable bis(fluorosulfonyl)imide ([FSI]⁻) and bis(trifluoromethanesulfonyl)imide ([NTf2]⁻) anions. To investigate the physico-chemical properties of the OIPCs, the free volume was measured by positron annihilation spectroscopy (PALS) and correlated with the ionic conductivity and thermal analysis (DSC). Solid-state NMR analysis of the salts, is also reported. The salts with the less symmetric cation, [N1222][FSI] and [N1222][NTf2], were identified as the most promising electrolyte materials, and thus the electrochemical properties after mixing with 10 and 90 mol% lithium bis(fluorosulfonyl)imide ([LiFSI]) or lithium bis(trifluoromethanesulfonyl)imide (LiNTf2), respectively, were investigated. This study demonstrates the efficacy of these OIPC materials as new quasi-solid electrolytes with advantageous properties such as high conductivity, good thermal and electrochemical properties, the ability to incorporate high lithium salt concentrations and support efficient lithium electrochemistry.

The move towards more sustainable energy such as solar or wind, to mitigate the effects of climate change and decreasing fossil fuel resources, requires the support of safer, more efficient energy storage devices. Similarly, increased use of small consumer electronic devices and electric transportation demands significant improvements in device safety—most critically, elimination of flammable and toxic liquid electrolytes. Thus, the development of solid-state electrolytes is attracting global attention.

Plastic crystals represent a unique and increasingly promising class of material that can be utilised as solid-state electrolytes. These fall into two classes—molecular plastic crystals, such as succinonitrile, that have been known since the 1960s, and the more recently discovered organic ionic plastic crystals (OIPCs). Plastic crystals have a long-range crystalline lattice but short range rotational and/or translational motion of the molecules/ions, soft mechanical properties, and display one or more solid-solide phase transition before melting. The intrinsic disorder in OIPCs can result in significant ionic conductivity, support the transport of target ions such as lithium when a lithium salt is added and, thus, allows their use as solid-state electrolytes. However, while the development and application of OIPCs has advanced significantly in recent years, fundamental understanding is still lacking as to how different combinations of cation and anions impact plasticity, lattice structure, the extent of disorder and/or vacancies, and the resultant conductivity. Key to addressing this dearth of understanding is increasing the range of well-characterised OIPC families.

Classes of OIPCs developed to date include those utilising pyrrolidinium, phosphonium, sulphonium, and ammonium cations, or dications of imidazolium (1,2-bis(N’-alkylimidazolium)ethane), paired with anions such as bis(trifluoromethanesulfonyl)imide ([NTf2]⁻), bis(fluorosulfonyl)imide ([FSI]⁻), (trifluoromethane)sulfonylimide ([TFSI]⁻), tetrafluoroborate ([BF4]⁻) or hexafluorophosphate ([PF6]⁻). The latter, spherical anions ([BF4]⁻ and [PF6]⁻) can exhibit significant rotational disorder, while the [FSI]⁻ and [NTf2]⁻ species can also display conformational isomerism (cis and trans) that underpins plasticity.12,13

Recent research has also investigated OIPCs with new anions tricyanomethanide (TCM or [CN3]⁻), 1,1,2,2,3,3-hexafluoro-N-[1,1,2,2,3,3-hexafluoro-1,3-disulfonylimide ([CFSA]⁻), 1,1,2,2,2-pentafluoro-N-[1,1,2,2,2-pentafluoroethyl)sulfonyl]imide ([BETA]⁻) and nonafluorobutanesulfonate ([NFS]) in combination with the N-ethyl-N-methylpyrrolidinium cation.14 Phase behaviour in OIPCs has also been studied by pairing carborane anion ([CBx12Hx12]⁻) with quaternary ammonium and bispyrrolidinium cations. These salts display plastic phases, as identified by DSC and crystallographic data.8 New ionic plastic crystals were also detected in a unique family of ammonium salts ([C,NEt],[BF4],[Me] = triethyl(methyl)borane), where this family adopted the entire range of mesophases: plastic, rotator and liquid crystal phases.15 Recently, we reported new families of OIPCs with the N,N-diethylpyrrolidinium ([C2epyr]⁺) cation, and the hexamethygluclidinium cation ([HMG]⁺), and in both cases the FSI-based salt was identified as particularly interesting for use as a solid-state electrolyte.

For the fundamental OIPC investigations and subsequent electrolyte development reported here, tetraalkylammonium cations with short alkyl chains were identified as particularly advantageous for OIPC formation as their high symmetry and small size is likely to promote significant rotational disorder. Thus, the tetramethylammonium ([N1111]⁺), methyl(triethyl)ammonium([N1222] and tetraethylammonium ([N2222] cations were chosen for investigation. Combining these ammonium cations with anions that exhibit conformational changes—i.e. cis/trans—was pursued in order to engineer a combination of disordering mechanisms anticipated to result in highly

*Electrochemical Society Member.
**E-mail: jenny.pringle@deakin.edu.au
disordered and conductive materials. Further, the asymmetry and larger size of the [FSI] and [NTf2] anions was predicted to hinder the packing and thus reduce the lattice energy (and thus melting point) compared to analogous ammonium [BF4] or [PF6] salts. This is advantageous for achieving the optimum disorder in phase I within the temperature range most relevant for practical applications.

A range of ammonium salts with small alkyl chains have been previously synthesized. However, aside from the detailed study by Henderson et al. on the [N2222][NTf2] system, until now a detailed investigation and comparison of the different thermal, structural and transport properties and potential application of this range of OIPCs as solid-state electrolytes has not been performed: [N1111][FSI], [N1111][NTf2], [N1222][FSI], [N1222][NTf2], [N2222][FSI], and [N2222][NTf2]. Single crystal data has been reported for [N1111][FSI] at 0 °C, [N1111][NTf2] at 0 °C, and [N2222][NTf2] (100 K). Further, to enable the use of OIPCs as electrolytes for lithium or sodium batteries, they must be combined with salts of the target ion (i.e. Li+ or Na+). The addition of alkali metal salts can significantly increase the ion mobility in the electrolyte, as demonstrated by Henderson et al.18 where the addition of 1 to 70 mol% lithium bis(trifluoromethanesulfonylimide) (LiNTf2) into [N2222][NTf2] resulted in a several fold increase in the ionic conductivity compared to the neat OIPC. Moreover, the utilization of high lithium salt concentration has been associated with reduced dendrite formation, higher lithium transference numbers and reduced degradation of sulfur cathodes in lithium-sulfur cells.26,28

The electrochemical performance of N,N-diethyl-N-methyl-N-(n-propyl)ammonium trifluoromethyltrifluoroborate ([N2222][CF3BF4]) has been reported for lithium metal battery applications. A wide electrochemical window (−5.5V) and lithium plating/stripping using a solid-state electrolyte employing the OIPC ([N2222][CF3BF4]) in combination with lithium trifluoromethanesulfonilfluoroborate (LiCF3BF4) salt was reported. Quaternary ammonium based solid-state electrolytes have also been utilised within flexible films, by combination with polymers. Solid-state electrolytes were prepared by mixing [N2222][FSI] with poly(vinylidenefluoride-co-hexafluoropropylene) (P(VDF-HFP)) and lithium bis(trifluorosulfonylimide) (LiFSI) in different ratios. The optimum ratio ([N2222][FSI])/P(VDF-HFP)/LiFSI): [0.20/0.20] displayed a two magnitude higher conductivity value of 8.62 × 10−4 S cm−1 at 30 °C than neat [N2222][FSI] and a lithium transference number of 0.56 at 30 °C. The ability of the electrolyte to stabilise and cycle lithium metal was demonstrated by symmetrical Li | Li cell cycling for ∼800 h at 0.2 mA cm−2 current density. An alternative polymer electrolyte was developed by mixing [N2222][FSI] and poly(diallyldimethylammonium) bis(trifluoromethanesulfonylimide (PDADMA NTf2)/LiNTf2, which achieved good mechanical properties, high conductivity (2 × 10−4 S cm−1 at 30 °C) and good electrochemical stability. However, analysis of the electrolyte mixture of [N2222][FSI] and lithium bis(trifluorosulfonylimide) without polymer was not reported. Moreover, in the body of recent studies, none has tried to delineate the key factors that determine electrolyte performance by systematically making stepwise variations in cation-anion composition.

To address this situation, and in the process pursue a deeper understanding of this promising family of OIPCs, we herein report the synthesis of six different ammonium salts (Fig. 1) formed from small ammonium cations paired with [FSI]− and [NTf2]− anions. Five OIPCs and one high melting salt was obtained. Comparison of the chemical and physical properties of the six salts has been made by thermal analysis (DSC and TGA) and ion conductivity, to investigate the influence of cation chain length and the nature of the anion. Comparison of the ionic conductivity has also been made with other, previously reported, FSI-based OIPCs (N-ethyl-N-methylpyrroolidinium bis[fluorosulfonylimide ([C3mpyr][FSI]), [C2epyr][FSI] and [HMG][FSI]). PALS analysis has been performed on these six salts for the first time, to determine the size and concentration of vacancies and compare these to the free volume within other OIPCs.

Solid-state NMR was used to investigate the effect of anion and cation alkyl chain length on the ion dynamics. Finally, the efficacy of these materials as quasi-solid-state electrolytes has been demonstrated by addition of lithium salts to [N1222][FSI] and [N2222][NTf2], utilising a common anion, to make electrolytes with either 10 mol% lithium salt as “lithium salt in OIPC” or 90 mol% lithium salt as “OIPC in lithium salt.” The thermal, transport and electrochemical properties of these mixtures demonstrate their promise as electrolytes for next generation solid-state lithium batteries.

Experimental

Materials and methods.—Tetramethylammonium bromide ([N1111][Br]) (98%, Sigma Aldrich, Australia), triethylmethylammonium chloride ([N1222][Cl]) (97%, Sigma Aldrich, Australia), tetraethylammonium bromide ([N2222][Br]) (99%, Sigma Aldrich, Australia), lithium bis(trifluoromethanesulfonylimide) (LiNTf2) (99.9%, Solvay, Canada), potassium bis(trifluorosulfonylimide) (KFSI) (99.9%, Suzhou Fluolyte Co, China), potassium bromide (KBr) (99%, Sigma Aldrich, Australia), potassium chloride (KCl) (99%, Sigma Aldrich, Australia) and dichloromethane (CH2Cl2) (HPLC grade, lab supply) were used without further purification. The structures and abbreviations were shown in Fig. 1.

[1H, 13C and 19F NMR spectra were collected on a Bruker Avance III instrument operating at 400 MHz, 100 MHz and 375 MHz respectively, in (CD3)2CO or CD3OD by referencing the solvent peak. Mass spectrometry was performed on an Agilent 1200 series HPLC system. All samples were dried for at least 72 h on a Schlenk line at 50 °C. All samples were sent to the Campbell Microanalytical Laboratory, New Zealand for elemental analysis.

Ion selective electrodes (ISE).—The residual chloride and bromide content were determined by means of an Ionode IJ-Cl or IJ-Br ion-selective electrode, after calibration with 10 and 100 ppm solutions of the chloride (potassium chloride) or bromide (sodium bromide) solutions. Potassium nitrate was used as an ion strength adjuster (ISA) and was added to both standards and samples. A known dried amount of OIPC (50–100 mg) was added to known amount of distilled water and the same ratio of ISA was used in the calibration step.

Figure 1. The structures of the cations and anions used for the development of OIPCs and OIPC-based electrolytes. For all the OIPCs discussed here, the subscript number denotes the number of carbons on each alkyl chain on the cation.
Inductively coupled plasma-mass spectroscopy (ICP-MS).—
Quantification of lithium and potassium was carried out using an inductively coupled plasma-mass spectrometer (ICP-MS; NexION 350X, PerkinElmer, USA). The internal standards Sc (200 ppb) and Rh (20 ppb) in 1% aqua regia were used for correction of matrix effects. The internal standard solution was mixed prior to the nebulizer using a T-piece in a 1:1 ratio. Calibration standards for lithium and potassium (Perkin Elmer, Lithium or Potassium standard 1000 ppm in 2% HNO3) were prepared at 0.1, 1, 10, 50, 100 and 500 ppb with 2% suprapur nitric acid (HNO3) in each. The mass spectrometer was operated in kinetic energy discrimination mode (KED) with 90 ms dwell times, 20 sweeps, one reading and three replicates. The plasma source conditions were: nebulizer gas (KED) with 50 ms dwell times, 20 sweeps, one reading and three replicates. The spectra were recorded with 4 scan rate was used for all measurements.

Differential scanning calorimetry (DSC).—Before performing DSC, the melting points were determined visually using a Gallenkamp melting point apparatus. Before measurement the heat flow and temperature for DSC was calibrated using cyclohexane. DSC was measured on a Mettler Toledo TGA/DSC 1 STArE System over a range of 25 °C to 550 °C under N2 (30 ml min⁻¹), at a heating rate of 10 °C min⁻¹. The samples (5 to 10 mg) were held in aluminium pans. Heating rate was 10 °C min⁻¹.

Electrochemical measurements.—A Biologic SP-200 potentiostat was used to perform the electrochemical plating and stripping of lithium. Cyclic voltammetry was performed in a three-electrode cell at 50 °C in an Argon filled glove box. The cell contained a platinum disk working electrode with surface area of 2.0 mm², a lithium metal coil and a lithium metal strip as counter and reference electrodes respectively. Lithium metal was brushed with cyclohexane prior to use. 20 mV s⁻¹ scan rate was used for all measurements.

Synthesis.—Tetramethylammonium bis(trifluoromethanesulfonyl)imide, [N1111][NTf2].—Tetramethylammonium bromide (10.6473 g, 69 mmol) and lithium bis(trifluoromethanesulfonyl)imide (20.0345 g, 70 mmol) were dissolved separately in 50 ml of water each to get clear solutions. Upon mixing the solutions, a white precipitate formed instantly, and the solution was left to stir for an hour at room temperature. The solution was then filtered and the filtrate was washed with water (7 × 50 ml). The white solid was dried in vacuo for 72 h at 50 °C to get [N1111][NTf2] (18 g, 75%). This sample was recrystallized from hot water to get colourless single crystals. ¹H NMR (400 MHz, CD3OD): 3.20 (s, C(NTf2)), 1.3 C NMR (100 MHz, CD3OD): 55.89 (N(CH3)), 121.21 (CF), δcr = 320 Hz. ¹⁹F NMR (375 MHz, CD3OD): −80.71 (CF3) ppm. ES− m/z 73.9 ([CH3(N)+), ES− m/z 279.9 (NTf2)−. Anal. Calculated for C10H25F3N4O2S2: C, 40.54; H, 7.38; N, 11.93. Found: C, 40.54; H, 7.37; N, 11.95.

Tetramethylammonium bis(trifluorourosulfonyl)imide, [N1111][FSI].—Tetramethylammonium bromide (6.0767 g, 39 mmol) and potassium bis(trifluorourosulfonyl)imide (8.735 g, 40 mmol) were dissolved separately in 50 ml of water each to get clear solutions. Upon mixing the above solutions, a white precipitate formed instantly, and the solution was left to stir for an hour at room temperature. The solution was then filtered, the filtrate was washed with water (7 × 50 ml). The white solid was dissolved in hot water and cooled down slowly at room temperature to get colourless needle-like crystals. These crystals were filtered and dried in vacuo at 50 °C for 72 h to get [N1111][FSI] (8 g, 45%). ¹H NMR (400 MHz, CD3OD): 3.21 (s, C(NTf2)). ¹³C NMR (100 MHz, CD3OD): 55.89 (N(CH3)), 121.21 (CF), δcr = 320 Hz. ¹⁹F NMR (375 MHz, CD3OD): 3.20 (s, C(NTf2)), 121.21 (CF) ppm. ES− m/z 73.9 ([CH3(N)+), ES− m/z 279.9 (NTf2)−. Anal. Calculated for C4H12F3N4O2S: C, 48.36; H, 12.40; N, 11.49. Found: C, 48.36; H, 12.46; N, 11.49.

Positron annihilation lifetime spectroscopy.—Positron annihilation lifetime spectroscopy (PALS) was performed on EG&G Ortec spectrometers using nitrogen airflow in the sample cell during analysis. The 3.5 MBq positron source (²²NaCl) was heat sealed in a Mylar envelope and placed in the middle of two OIPC pellets (1 mm thickness each) and placed between the spectrometers. A minimum of 1 × 10⁶ integrated counts was collected for each file with five or more files collected for each sample. The spectra was fitted using LT-v9 software, using a 3 component fit and a source correction (1.501 ns and 3.48%). The first component was attributed to para-positronium (p-PS) annihilation with the bound state of the positron and electron with opposite spins and fixed to 0.125 ns. The second component (~0.36 ns) was due to the annihilation of the positrons with free electrons within the sample. The final component was due to ortho-positronium (o-PS) annihilation where the positron forms a bound state with an electron of the same spin. This longer lifetime for τ₃ was used to calculate the average pore radius (R₀) within the OIPC sample using the Tao-Eldrup quantum based empirical equation31,32 where R₀ is the thickness of the electron layer within the potential well;

\[
\tau_3 = \frac{1}{2} \left[ 1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin \left( \frac{2\pi R}{R_0} \right) \right]^{-1}
\]
Triethylmethylylammonium bis( trifluoromethanesulfonyl)imide, \([\text{[N}_{1222}]\text{[FSI]}\).—Triethylmethylylammonium chloride (5.060 g, 33 mmol) and lithium bis(trifluoromethanesulfonyl)imide (9.6663 g, 34 mmol) were dissolved separately in 50 ml of water each to get clear solutions. Upon mixing the above solutions, a white precipitate formed instantly, and the solution was left to stir for one hour at room temperature after the addition of \(\text{CH}_2\text{Cl}_2\) (100 ml). The organic layer was separated and dried in \(\text{vacuo}\) for 72 h at 50 °C to get \([\text{[N}_{1222}]\text{[NTf}_2]\) (8 g, 61%). This sample was crystallized from hot water to get colourless single crystals. \(^1\)H NMR (400 MHz, ((CD3)2CO): 1.43 (tt, \(\text{CH}_2\text{CH}_3\), 9H), 3.16 (s, \(\text{NCH}_3\), 3H), 3.55 (q, \(\text{NCH}_2\text{CH}_3\), 6H). \(^1\)C NMR (100 MHz, ((CD3)2CO): 7.89 (NCH2CH3), 46.31 (NCH3), 55.89 (NCH2), 119.20 (CF3, \(\delta_{\text{CF}} = 320\) Hz). \(^19\)F NMR (375 MHz, ((CD3)2CO): −79.99 (CF3) ppm. ES+ m/z 116.2 ([CH3CH2CH3)N]+, ES− m/z 279.9 (FSI)−. Anal. Calculated for \(\text{C}_2\text{H}_5\text{N}_2\text{F}_6\text{O}_4\text{S}_2\); C, 29.26; H, 4.91; N, 6.82. Found: C, 29.18; H, 5.11; N, 6.92. Chloride content measured by ISE was below 10 ppm. Potassium content measured by ICP-MS was 370 ppm. Visual melting point was 102 °C.

Results and Discussion

Thermal properties.—The ammonium salts were synthesized by anion metathesis between commercially available ammonium halides and lithium bis(trifluoromethanesulfonyl)imide (LiNTf2) or potassium bis(fluorosulfonyl)imide (KFSI). The synthesis of all six ammonium salts are very amenable to scale-up as they are synthesised in one step from commercially available, relatively low-cost starting materials, which is a significant benefit to their widespread utility. The purity of the salts was confirmed by \(^1\)H, \(^13\)C, \(^19\)F NMR, mass spectroscopy, residual halide content by ion selective electrode, residual Li+ or K+ content by ICP-MS and microanalysis. The onset decomposition temperature \(T_{\text{d(onset)}}\) was determined by rising temperature TGA (Fig. 2). This technique can result in an overestimate of long-term thermal stability compared to an isothermal measurement\(^{33}\) but is nevertheless a valuable initial assessment of the impact of different cations and anions on the thermal properties of ionic liquids or OIPCs.

For all the FSI-based ammonium salts the \(T_{\text{d(onset)}}\) is above 300 °C, which is in the same range as other FSI salts with cations such as pyrrolidinium (\(\text{N,N-diethylpyrrolidinium bis(fluorosulfonyl)imide (}[\text{C,N,N}_{\text{pyr}}]\text{[FSI]},>[\text{C,N,N}_{\text{pyr}}]\text{[FSI]}\) and \([\text{C,N,N}_{\text{pyr}}]\text{[FSI]}\) and guanidinium (HMGF][FSI]). Notably, they also have a higher decomposition temperature than analogous phosphonium based salts (isobutyl(diethyl)methylphosphonium bis(fluorosulfonyl)imide ([P_{1224}][FSI]) \(T_{\text{d(onset)}} = 250 °C\), isobutyl(triethyl)phosphonium bis(fluorosulfonyl)imide ([P_{1224}][FSI]) \(T_{\text{d(onset)}} = 250 °C\), triethyl(methyl)phosphonium bis(fluorosulfonyl)imide ([P_{1222}][FSI]) \(T_{\text{d(onset)}} = 220 °C\) and tri(isobutyl)methylphosphonium bis(fluorosulfonyl)imide ([P_{1444}][FSI]) \(T_{\text{d(onset)}} = 220 °C\) at a similar heating rate (10 °C min\(^{-1}\)).\(^{34}\) The NFT2 salts have onset decomposition temperatures approximately 100 °C higher than the corresponding FSI salts. This is consistent with previous reported thermal decomposition behaviour of other FSI and NFT2 salts. The impact of the nature of the anion on the decomposition temperature is also much more significant than the effect of changing the length of the alkyl chain on the cation.

Figure 2. Thermogravimetric analysis of the ammonium salts.
The NTf$_2$-based salts display a one-step decomposition compared to a two-step decomposition for the FSI-based salts, from room temperature to 550 °C. Similar behaviour has been observed in hexamethyguanidinium ([HMG][FSI]) and [HMG][NTf$_2$] and pyrrolidinium-based ([C$_1$mpyr][FSI], [C$_2$mpyr][FSI] and [C$_2$epyr][FSI]) salts. However, phosphonium-based salts ([P$_{1222}$]$^+$, [P$_{1222}$]$^+$ and [P$_{1i444}$]$^+$) with [FSI]$^-$ and [NTf$_2$]$^-$ displayed one-step decomposition.

In-depth characterisation by, for example, TGA-MS would be required to elucidate fully the decomposition mechanisms. Nevertheless, and despite the lower onset decomposition temperature for FSI salts, the thermal stability of all of the reported ammonium salts is high enough for most electrochemical applications.

Of the six ammonium salts synthesized, only five display one or more solid-solid phase transitions in the temperature range from −120 °C to melting (Fig. 3, Table I), which is a key indicator of plasticity. By convention, the highest temperature solid phase is termed phase I, while the lower temperature phases are termed phase II, III and so on. There is a clear dependence of both cation and anion on thermal behaviour. Generally, FSI-based OIPCs display more disorder than those with NTf$_2$ anions, as evidenced by smaller entropies of fusion, and this is also observed in the current study. Only one of the salts shows no evidence of plasticity: the [N$_{1111}$][NTf$_2$] displays only a melting point at 134 °C (previously reported 130 °C–134 °C) and can simply be classified as a crystalline solid.

The [N$_{1222}$][FSI] and [N$_{1222}$][NTf$_2$] have higher melting points than their NTf$_2$-based analogues. Similar behaviour has been seen in salts with the pyrrolidinium ([C$_2$epyr]$^+$ and [C$_2$mpyr]$^+$) and phosphonium ([P$_{1222}$]$^+$) cations. However, here the opposite behaviour is displayed in salts with the larger ammonium cation ([N$_{2222}$]$^+$), highlighting the fact that the nature of both the cation and anion can be important in determining the crystal packing and lattice energy.

[N$_{1111}$][FSI] displays one solid-solid phase transition before melting and the onset of decomposition above 300 °C (Fig. 1 and Fig. S1). This high melting point was confirmed visually, and is consistent with the previously reported solid-solid phase transition at 71 °C and a melting at 294 °C (the previously reported $T_m$ of 70 °C is, we suggest, a solid-solid transition). The entropy of melt agrees with Timmerman’s suggested criterion for plasticity of $\Delta S_f \leq 20$ J K$^{-1}$ mol$^{-1}$, indicating significant disorder in phase I.

[N$_{1222}$][NTf$_2$] melts at 98 °C with an entropy of fusion of 25 J K$^{-1}$ mol$^{-1}$. This entropy slightly exceeds Timmerman’s criterion for plasticity, but the material nonetheless has a very advantageous temperature range for phase I, starting from −4 °C and spanning the temperature range of relevance for most electrochemical device applications.

[N$_{2222}$][FSI] gives the lowest entropy of fusion, but unfortunately, the temperature range of phase I is very narrow. On the other hand, [N$_{1222}$][FSI] has the second lowest entropy of melt but the phase I window is much wider, making it particularly promising for electrolyte development. The physical appearance of [N$_{1222}$][FSI] is a soft solid, similar to [C$_2$mpyr][FSI] and [C$_2$epyr][FSI].

The thermal behaviour for [N$_{1222}$][FSI] has previously been reported by Yang et al. ($T_x$ = −16.06 and $T_m$ = 124.9 °C) and Yoshizawa-Fujita et al. ($T_x$ = −13 and $T_m$ = 130 °C).

The entropy of melt for [N$_{1222}$][FSI] is similar to other OIPCs with this anion: [C$_2$mpyr][FSI] (9 J K$^{-1}$ mol$^{-1}$), [HMG][FSI] (7 J K$^{-1}$ mol$^{-1}$) and [C$_2$epyr][FSI] (10 J K$^{-1}$ mol$^{-1}$). However, it is lower than for the small phosphonium salts [P$_{1222}$][FSI] (23 J K$^{-1}$ mol$^{-1}$) and [P$_{1i444}$][FSI] (23 J K$^{-1}$ mol$^{-1}$).

[N$_{2222}$][NTf$_2$] has two solid-solid transitions before melting at 105 °C, consistent with prior literature, and has an entropy of fusion of 25 J K$^{-1}$ mol$^{-1}$. This salt is much less disordered than [N$_{1222}$][FSI], and this anion trend is also observed in [HMG][NTf$_2$] vs [HMG][FSI]. However, as noted above, it is more common for [FSI]$^-$ salts to have higher melting points than their NTf$_2$ analogues, as seen in [C$_2$mpyr]$^+$ and [C$_2$epyr]$^+$ and the other ammonium salts investigated here.

**Transport properties.**—The ionic conductivity of OIPCs is one of the most important parameters that determine their suitability for electrochemical applications. A wide phase I temperature range is also very valuable (Fig. 4 and Table II). Overall, the FSI-based ammonium salts display higher conductivity in phase I than the NTf$_2$-based ammonium salts. Of the different ammonium-based OIPCs studied here, [N$_{1222}$][FSI] displays the highest conductivity of 9.9 × 10$^{-4}$ Sc m$^{-1}$ at 30 °C (consistent with the previous report), indicating an advantageous increase in disorder as a result of use of the less symmetrical cation. The conductivity of [N$_{1222}$][FSI] at 30 °C is slightly lower than that of [C$_2$mpyr][FSI], but higher than [HMG][FSI] or [C$_2$epyr][FSI] (Fig. 4b). The entropy of melt is a very similar to [N$_{1222}$][FSI] (8 J K$^{-1}$ mol$^{-1}$) and [C$_2$epyr][FSI] (9 J K$^{-1}$ mol$^{-1}$).

[N$_{2222}$][FSI] and [N$_{1111}$][FSI] are present in phase II at 30 °C and an increase in conductivity is seen as they transition from phase II to phase I with heating. The thermal properties of the salts, determined by DSC (Fig. 3), suggest that [N$_{2222}$][FSI] is the most disordered of the materials in phase I—reflected in the lowest entropy of fusion—and the material has the highest conductivity (5 × 10$^{-4}$ Sc m$^{-1}$ at 50 °C) of all the salts studied here. [N$_{2222}$][FSI] is also the most conductive of all the salts at 60 °C, when all six ammonium OIPCs are in phase I. However, the narrow temperature domain for phase I is a disadvantage. The conductivity measured for [N$_{2222}$][NTf$_2$] here is lower than in the prior report, which is attributed to differences in experimental setup and material preparation. The lowest conductivity is displayed by [N$_{1111}$][NTf$_2$] because it is a crystalline solid with no solid-solid phase transitions and no evidence of plasticity.

**Positron annihilation lifetime spectroscopy (PALS) of the neat OIPCs.**—The six ammonium salts were characterized by PALS analysis at room temperature, to study the impact of different anions and the cation chain length. This technique allows investigation of the defects / free volume size (τ$_f$) and relative abundance of the vacancies in a material. The investigation of vacancy concentration in OIPCs is highly valuable as they are intrinsically involved in the mechanism of ionic conductivity. The measured positronium lifetimes (which are correlated to defect size), intensities (which give a measure of relative defect concentration), the calculated pore size and volume for the six ammonium salts at room temperature are shown in Table II.

An important point to note when comparing the salts is the influence of the thermal phase—at room temperature, the [N$_{1222}$] salts are in phase I, whereas the other salts are in phase II or are crystalline solids. The phase I of OIPCs is normally the most conductive and disordered, but when comparing different OIPCs, the size and shape of the ions will also impact defect number and volume.
Table I. Phase transition temperatures (taken from the onset, ±1 °C) and entropy change (±10%) for the ammonium salts.

|                  | Phase IV-III | Phase III-II | Phase II-I | I-Melt |
|------------------|--------------|--------------|------------|--------|
|                  | $T_s$ (°C)   | $\Delta S$ (J K$^{-1}$ mol$^{-1}$) | $T_s$ (°C) | $\Delta S$ (J K$^{-1}$ mol$^{-1}$) | $T_m$ (°C) | $\Delta S$ (J K$^{-1}$ mol$^{-1}$) | $T_{d(onset)}$ (°C) |
| $[\text{N}_{1111}]^+\text{NTf}_2^- $ | 135 | 35 | 415 |
| $[\text{N}_{1111}]^+\text{FSI}^- $ | 71 | 45 | 301$^a$ | 17 | 339 |
| $[\text{N}_{1222}]^+\text{NTf}_2^- $ | −50 | 20 | 98 | 25 | 409 |
| $[\text{N}_{1222}]^+\text{FSI}^- $ | −61 | 2 | −8 | 19 | 133 | 8 | 324 |
| $[\text{N}_{2222}]^+\text{NTf}_2^- $ | 5 | 67 | 53 | 3 | 105 | 25 | 407 |
| $[\text{N}_{2222}]^+\text{FSI}^- $ | −27 | 14 | −1 | 15 | 68 | 5 | 324 |

$^a$ melt and onset of decomposition overlap. Illustrated in Fig. S1.
Overall, larger PALS volumes are consistently evident for NTf$_2$-based salts than the FSI ones, which reflects the influence of the larger anion on the crystal packing. There appears to be a general correlation between the fractional free volume (FFV = Average Pore Volume $\times$ Intensity) and conductivity across the NTf$_2$ salt series (Fig. 5a).

When comparing the [NTf$_2$] salts, the intensity and conductivity for the [N$_{1111}$][NTf$_2$] (crystalline solid) is the lowest at room temperature. While, the free volume and conductivity for [N$_{1222}$][NTf$_2$] and [N$_{2222}$][NTf$_2$] are much higher compared to the [N$_{1111}$][NTf$_2$]. Comparison of [N$_{1222}$][NTf$_2$] (phase I) with the previously reported OIPC [C$_2$mppy][NTf$_2$] (phase II),$^{37}$ shows similar free volume (2.38 ns, 12.0%) and higher conductivity ($1.45 \times 10^{-8}$ S cm$^{-1}$ at 30 °C).$^{37}$ Conversely, previous studies on [HMG][NTf$_2$] (phase II)$^3$ had higher conductivity ($2.3 \times 10^{-8}$ S cm$^{-1}$ at 30 °C), potentially due to significantly higher defect concentration of 31% intensity (from I$_3$) than [N$_{1222}$][NTf$_2$]. This confirms again the role of free volume in conductivity of OIPCs.

Figure 4. (a) The ionic conductivity for ammonium salts and (b) Comparison of ionic conductivity for different FSI-based OIPCs.
Table II. Conductivities and PALS analysis data for ammonium-based salts

| Conductivity (S cm\(^{-1}\)) (±5%) 30 °C | PALS analysis |
|------------------------------------------|---------------|
|                                          | Lifetimes \(\tau_3\) (ns) | Intensities I_3 (%) | Pore Size Diameter (nm) | PALS Volume (Å\(^3\)) |
| [N\(_{1111}\)][NTf\(_2\)] (crystalline solid) | \(1.2 \times 10^{-10}\) | 1.824 ± 0.017 | 9.3 ± 0.1 | 0.537 ± 0.003 | 81 ± 1 |
| [N\(_{1111}\)][FSI] (phase II) | \(1.0 \times 10^{-10}\) | 1.325 ± 0.023 | 8.7 ± 0.3 | 0.426 ± 0.006 | 40 ± 1 |
| [N\(_{1222}\)][NTf\(_2\)] (phase I) | \(4.3 \times 10^{-9}\) | 2.214 ± 0.019 | 12.0 ± 0.1 | 0.608 ± 0.003 | 118 ± 1 |
| [N\(_{1222}\)][FSI] (phase I) | \(9.9 \times 10^{-6}\) | 1.744 ± 0.023 | 12.5 ± 0.2 | 0.521 ± 0.005 | 74 ± 1 |
| [N\(_{2222}\)][NTf\(_2\)] (phase II) | \(1.7 \times 10^{-9}\) | 2.171 ± 0.017 | 12.8 ± 0.2 | 0.601 ± 0.003 | 114 ± 1 |
| [N\(_{2222}\)][FSI] (phase II) | \(1.4 \times 10^{-8}\) | 2.074 ± 0.021 | 11.8 ± 0.2 | 0.584 ± 0.004 | 104 ± 1 |
Figure 5. The relationship between the average fractional free volume (FFV) as determined with PALS and the conductivity of the OIPCs (a) NTf₂ salts and (b) FSI salts. Square data points are taken from previous studies. Except for [C2mepy][FSI] and [C2mepy][NTf₂], the conductivity for the OIPCs in Figs. 5a and 5b were measured at 30 °C and the PALS analysis at room temperature. The effect of this small difference in temperature is assumed to be minor as none of the materials have a phase transition between 25 °C and 30 °C and are thus in the same phase during both measurements.

Figure 5b indicates that the free volume is not the limiting factor for conductivity for the FSI salts. Salts with the [N1111] cation again had very low free volume, as with the NTf₂ counterpart, and has a correspondingly low conductivity. However the [N1222][FSI] and [N2222][FSI] did not show a consistent trend with conductivities, which is also highlighted when compared to previously studied FSI salts: [C2mepy][FSI] (1.921 ± 0.013 ns at room temperature in phase I) and [C2epy][FSI] (1.956 ± 0.019 ns at room temperature in phase I) had comparable free volumes but conductivities which varied by orders of magnitude (note the log scale in Fig. 5b). It therefore appears that the free volume is not the controlling variable for conductivity of the FSI salts.

Solid-state NMR analysis of the neat plastic crystals. —Solid state NMR can be highly insightful for elucidating the chemical environment and molecular motions of the materials at a molecular level. While NMR spectra of solutions normally have very sharp peaks, and a static NMR spectra of a solid powder sample would be relatively broad, OIPCs are often sufficiently disordered to give either relatively narrow lines or a combination of broad and narrow lines that reflect the presence of both mobile and less mobile components. Thus, in static NMR spectra, the linewidths may provide information about the relative mobility of the nuclei; in this case, the cation and anion by ¹H and ¹⁹F respectively. Further, the spectra can indicate the presence of residual dipole-dipole couplings and/or chemical shift anisotropy (CSA), which relates to the orientation dependent electron shielding environment of the nuclei. For example, for the NTf₂ anion the ¹⁹F CSA was observed but with significant distortion in the broad component of the spectra. This distortion is often observed for broad CSA patterns and is caused by the extremely fast T₂ relaxation, and as a consequence the loss of a few initial data points in the time domain. Therefore, in this study, only MAS NMR data is shown for ¹⁹F NMR spectra.

For the [N1222][NTf₂] (top spectra, green), the static ¹⁹F spectrum (Figs. 6e and 6f) is broad but almost symmetrical, indicating very little chemical shift anisotropy (CSA). This is relatively unusual for NTf₂ salts and suggests tumbling of the anion, but not significant translational motion as the conductivity is relatively low. The static ¹H NMR (Figs. 6b and 6c) indicates that this cation has similar dynamics to the [N1111][FSI] (blue) and to the less mobile component (the broad peak) in [N2222][FSI] (Fig. 2b, pink). This suggests that there was a similar entropy of melt and the relatively low conductivity, suggests that in [N1222][NTf₂], the [N1222] cation does not have significant rotational or translational motion at either 20 °C or 70 °C. For [N1222][FSI] (pink spectra), the static ¹H NMR (Fig. 6b) spectrum at 20 °C indicates that there is a fraction of cations that are mobile and fraction that are relatively static. The ¹H static NMR linewidths of the different OIPCs indicates that apart from the quite mobile cation in [N1222][FSI], the other cations seem to have similar dynamics. At 70 °C (Fig. 6c), the [N1222][FSI] is in the melt and the cation gives much sharper peaks. Interestingly, the peaks from the molten [N2222][FSI] are only slightly sharper than for [N1222][FSI] (purple spectra), which is still solid but very disordered. For clarity, only the ¹H and ¹⁹F static NMR data at 20 °C and 70 °C are shown (Fig. 6). The spectra recorded with increasing temperature from 30 °C to 60 °C are shown in Fig. S5. The [N1222][FSI] (purple spectra) is a much more disordered OIPC and thus no CSA is observed. This OIPC gives significantly narrower ¹H (Fig. 6b) and ¹⁹F (Fig. 6c) static NMR line widths than the other OIPCs studied, suggesting faster dynamics of the cation and anion. In particular, the ¹⁹F shows an extremely narrow (liquid-like) line, suggesting fast isotropic rotation/reorientation motion of the FSI anion. This almost liquid-like behaviour is consistent with the high conductivity at room temperature.

Finally, the [N1111][FSI] (blue spectra) is the least conductive at room temperature. Chemical shift anisotropy is evident in the MAS NMR (Fig. 6d), which shows an asymmetric signal even with spinning. This suggests that the electron shielding of the ¹⁹F nuclei is less symmetric compared to [N2222][FSI] (pink), and this limited rotation is consistent with the low conductivity.

Development of ammonium OIPCs as electrolytes for lithium batteries. — Thermal properties of OIPCs with lithium salts. — On the basis of the characterization of the neat ammonium OIPCs described above, the most conductive OIPCs [N1222][FSI] and [N1222][NTf₂]
were selected for further investigation as electrolytes for lithium batteries. This choice was based on the high conductivity of these two salts and a strategy of investigating the influence of the anion while keeping the cation constant. To develop these salts as electrolytes, they were mixed with LiFSI and LiNTf₂ respectively, thereby introducing the target ion (Li⁺) while keeping the anion consistent.

Thermal analysis of the neat salts and the 10 and 90 mol% lithium salt compositions are shown in Fig. 7 and Table SI. Addition of 10 mol% LiFSI to [N₁₂₂₂][FSI] forms a composition described as “lithium salt in OIPC.” Compared to the neat OIPC (T_m = 133 °C), the melting transition of this electrolyte is broader and decreased, and a very small and broad peak appears around 66 °C (more visible in Figs. S2 and S3). A broadening and melting point decrease is a common observation upon introduction of a second component to an OIPC. VISually, this material appears as a quasi-solid state electrolyte that does not flow under gravity, but with the presence of a small amount of liquid phase. Thus, as a result of the
heterogeneous nature, the melting peak is very broad. However, the electrolyte mixture still displays three solid-solid transitions consistent with the presence of a plastic phase.

Addition of 90 mol% LiFSI to [N1222][FSI], to form a composition described as an “OIPC in lithium salt,” produces a high lithium concentration quasi-solid state electrolyte as a soft solid. This mixture displays a glass transition (−76 °C), a solid-solid transition (−53 °C) and a broad melting (102 °C). The solid-solid transition in the 90 mol% LiFSI mixture indicates the presence of a LiFSI solid phase in the electrolyte, as neat LiFSI also undergoes a solid-solid phase transition at this temperature, before melting at 140 °C (Fig. 7a).

Similar electrolyte compositions were investigated with the NTf₂ OIPC and Li salt analogues, to assess the influence of the anion (Fig. 7b and Table SI). The NTf₂ anion has been shown to have higher electrochemical and thermal stability compared to FSI and other anions.41−42 In addition, NTf₂ is known to form a stable SEI layer in contact with lithium metal,43,44 and therefore there are significant possible benefits of a high LiNTf₂ salt content electrolyte for prolonged battery cycling.45 Upon addition of 10 mol% LiNTf₂ to [N1222][NTf₂] (forming a soft solid), the DSC trace is different from the neat OIPC, with a large decrease in the onset of melting to 62 °C compared to neat [N1222][NTf₂] (T_	ext{m} = 98 °C). The melting point of this mixture is also more clearly visible in the DSC trace compared to the 10 mol% LiFSI in [N1222][FSI] (Fig. 7a). However, the appearance of new phases were observed in this system, evidenced by a new crystallization and solid-solid phase transition (25 °C). When this sample was held for an hour at −120 °C (Fig. S4) and heated at 2 °C min⁻¹, this crystallization and T_	ext{g} did not appear during the first heating cycle, suggesting that the sample had fully crystallized during the isothermal sequence. However, during the second and third heating run, this solid-solid transition re-appeared even when the sample was kept at −120 °C for an hour. Thus, there is evidence of meta-stability in this particular system, with an impact of thermal history on the phase that is present at around room temperature.

The 90 mol% LiNTf₂ in [N1222][NTf₂] (Fig. 7b) has a higher glass transition temperature (T_	ext{g}) than the 90 mol% FSI-based electrolyte (Fig. 7a). The broad peak at around 149 °C in the NTf₂ system (Fig. 7b) is attributed to a solid-solid phase transition, consistent with the presence of a LiNTf₂ rich phase, and the electrolyte melts at around 200 °C (confirmed visually).

**Ionic conductivity.**—The ionic conductivities of the four quasi-solid state electrolytes with lithium salt are shown in Fig. 7c. The 10 mol% LiFSI in [N1222][FSI] is predominantly a solid at room temperature but with a small amount of liquid phase present, and thus this shows the highest conductivity of the electrolytes studied. The 10 mol% LiNTf₂ in [N1222][NTf₂] melts at ca. 60 °C, and above this temperature the conductivity is similar to that of the 10 mol% LiFSI in [N1222][FSI]. Similiar significant increases in conductivity upon lithium salt doping has been reported for 10 mol% LiNTf₂ in [N1222][NTf₂].18 The conductivity of 90 mol% LiNTf₂ in [N1222][NTf₂] is around three orders of magnitude higher than neat [N1222][NTf₂], and the conductivity of 90 mol% LiFSI in [N1222][FSI] is an order of magnitude higher than neat [N1222][FSI], which is consistent with the presence of a small amount of liquid phase. It is important to note, however, that the overall physical nature of these materials are quasi-solid state and thus they will significantly reduce electrolyte leakage from a device compared to a liquid electrolyte.

**Electrochemistry.**—For further assessment of the applicability of the new materials for device applications, cyclic voltammetry (CV) was used to investigate the electrochemical stability of the 10 mol% and 90 mol% LiNTf₂ in [N1222][NTf₂] electrolytes as well as the liquid plating/stripping kinetics. Additionally, a preliminary quantification of cycling efficiency was obtained by estimation of the Coulombic efficiency (CE), the percentage of lithium stripped to lithium plating/stripping kinetics. Use of the NTf₂ anion is also believed to be advantageous for long device life. The CV of 10 mol% NTf₂ electrolyte (Fig. 8a) shows distinct lithium plating peak at −0.54 V (vs Li/Li⁺) and stripping peak at 0.95 V with stable current density over six cycles. The

![Figure 7](image-url)
cycle. Given that CE values from cyclic voltammetry typically underestimate significantly the values obtained with more accurate methods, these two electrolytes are promising candidates for battery applications. Future work will investigate symmetrical and full cell cycling of these electrolytes.

Conclusions

In summary, we report here the synthesis of six salts utilising small ammonium-based cations with sulfonylimide anions. Tetramethylammonium bis(fluorosulfonylimide ([N1111][FSI]), triethyl(methyl)ammonium bis(fluorosulfonylimide ([N1222][FSI]), triethyl(methyl)ammonium bis(trifluoromethanesulfonylimide ([N1222][NTf2]), tetraethylammonium bis(fluorosulfonylimide ([N2222][FSI]) and [N2222][NTf2]) are organic ionic plastic crystals, while [N1111][NTf2] is a higher melting salt without any observable solid-solid phase transitions. The thermal stability for NTf2-based salts (ca. 400 °C) is approximately 100 °C higher than the FSI-based salts.

Higher conductivity was observed for the pure FSI-based ammonium salts than the NTf2-based ones. [N1222][FSI] has the highest ionic conductivity at 30 °C (9.9 × 10^{-6} Sc m^{-1}) when it is in phase I, but at 50 °C the conductivity for [N2222][FSI] becomes the highest (5.1 × 10^{-5} Sc m^{-1}), once it is in phase I. However, the temperature range of phase I for [N2222][FSI] is very narrow compared to [N1222][FSI], and thus the latter is more promising candidate for electrolyte applications. The positron annihilation lifetime spectroscopy (PALS) suggested higher lifetimes and volumes for NTf2-based ammonium salts than the FSI salts at room temperature, suggesting less efficient packing (more vacancies) in larger anions. The free volume and conductivity is higher in [N1222][NTf2] and [N2222][NTf2] compared to [N1111][NTf2]. For FSI-based salts, free volume was concluded to be only one of the possible determinants of conductivity, as evidenced in [N1222][FSI] and [N2222][FSI] where no clear trend between FFV and conductivity was seen. The 1H and 19F static NMR line widths in [N1222][FSI] suggests faster dynamics of the cation and anion compared to other ammonium salts at 20 °C and at 70 °C, consistent with higher conductivity. The dynamics of [N1222][FSI] at 70 °C are very liquid-like, despite the fact that it is still in phase I (solid). [N2222][FSI] shows both mobile and less mobile components in the 1H static NMR at 20 °C, while at 70 °C the peak widths of the melted [N2222][FSI] are only slightly narrower than for the solid [N2222][FSI] (phase I). The cation and anion in [N2222][NTf2] do not have significant rotational or translational motion at 20 °C or 70 °C. [N1111][FSI] is least conductive among all the FSI ammonium salts synthesised, with significant CSA observed in the NMR spectra.

From these initial investigations of physical properties, salts with the asymmetric ammonium cation were chosen for further investigation as quasi-solid state electrolytes. [N1222][FSI] and [N1222][NTf2] were mixed with lithium FSI or NTf2 salts, respectively, in two different ratios (10 and 90 mol%) to get quasi-solid state electrolytes. Future work will investigate symmetrical and full cell cycling of these electrolytes.

Acknowledgments

This work was supported by the Australian Research Council (ARC) through Discovery Grant DP170101087. The authors also thank Dr Damien Callahan at Deakin University for his help with the ICP-MS measurements. CMD is supported through a Veski Inspiring Women Fellowship.
