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Lithium electrochemistry and cycling behaviour of ionic liquids using cyano based anions†

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Lithium based battery technologies are increasingly being considered for large-scale energy storage applications such as grid storage associated with wind and solar power installations. Safety and cost are very significant factors in these large scale devices. Ionic liquid (IL) electrolytes that are inherently non-volatile and non-flammable offer a safer alternative to mainstream lithium battery electrolytes, which are typically based on volatile and flammable organic carbonates. Hence, in recent years there have been many investigations of ionic liquid electrolytes in lithium batteries with some highly promising results to date, however in most cases cost of the anion remains a significant impediment to widespread application. Amongst the various possible combinations the dicyanamide (DCA) anion based ionic liquids offer exceptionally low viscosities and high conductivities – highly desirable characteristics for Li electrolyte solvents. DCA ILs can be manufactured relatively inexpensively because DCA is already a commodity anion, containing only carbon and nitrogen, which is produced in large amounts for the pharmaceutical industry. In this study we use the non-fluorinated ionic liquid *N*-methyl-*N*-butylpyrrolidinium dicyanamide to form non-volatile lithium battery electrolytes. We demonstrate good capacity retention for lithium metal and LiFePO₄ in such electrolytes and discharge capacities above 130 mAh.g⁻¹ at 50 °C. We show that it is important to control moisture contents in this electrolyte system in order to reduce capacity fade and rationalise this observation using cyclic voltammetry and lithium symmetrical cell cycling. Having approximately 200 ppm of moisture content produces the optimum cycling ability. We also describe plastic crystal solid state electrolytes based on the DCA anion in the lithium metal–LiFePO₄ battery configuration and demonstrate over 150 mAh.g⁻¹ discharge capacity without any significant capacity fading at 80 °C.

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Broader context

Lithium battery technologies have applications in large-scale energy storage such as grid storage and electric vehicles. Safety, energy density, and cost are very crucial factors in the choice of large scale devices. Currently, mainstream lithium-ion battery electrolytes are based on volatile and flammable organic carbonates which introduce significant safety issues. Ionic liquid (IL) electrolytes, which are inherently non-volatile and non-flammable, offer a safer alternative. Additionally, ILs offer the promise of enabling a rechargeable lithium metal electrode to deliver significant increases in energy. Amongst the various possible cation and anion combinations, ILs using the dicyanamide (DCA) anion, which contain no fluorine reducing cost, offer exceptionally low viscosities and high conductivities – highly desirable characteristics for Li electrolyte solvents. We have investigated the ionic liquid *N*-methyl-*N*-butylpyrrolidinium dicyanamide to form lithium battery electrolytes which enable good capacity retention for a lithium metal–LiFePO₄ battery with discharge capacities above 130 mAh.g⁻¹ at 50 °C. We also describe solid state electrolytes, based on plastic crystals with the DCA anion, in a lithium metal–LiFePO₄ battery and demonstrate over 150 mAh.g⁻¹ discharge capacity without any significant capacity fading at 80 °C.

Introduction

Ionic liquid (IL) electrolytes, which are inherently non-volatile in nature,¹ offer a potentially safer alternative to mainstream lithium battery electrolytes which are based on volatile and flammable organic carbonates.^{2,3} Hence, in recent years there have been many investigations of ionic liquid electrolytes in lithium batteries with some highly promising results to date.^{4–8}

The suitability of any particular ionic liquid for use in a lithium battery is heavily dependent on the type of anode and

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cathode materials used.⁹ One anode material that is of particular interest to researchers is lithium metal. Lithium has an enormous specific capacity (3860 mAh.g^{-1})¹⁰ compared to graphite (380 mAh.g^{-1}) which is commonly used in commercial lithium-ion devices. However lithium metal exhibits high reactivity in the presence of electrolytes based on aprotic organic solvents, leading to excessive electrode–electrolyte side reactions. Dendrite formation and excessive electrolyte degradation eventually stifles the proper functioning of the battery, and as yet a rechargeable lithium metal battery has not been successfully commercialised.^{11,12}

An early study by Sakaebe and Matsumoto demonstrated successful cycling, albeit with some capacity fade, of lithium metal– LiCoO_2 batteries in ionic liquids based on the bis(trifluoromethanesulfonyl)imide (TFSI) anion.¹³ Howlett *et al.* studied the lithium metal electrode in isolation using the IL *N*-methyl-*N*-propylpyrrolidinium TFSI ($\text{C}_3\text{mpyr TFSI}$) and reported excellent cycling behaviour,¹⁴ thus concluding that the limited capacity fade observed by Sakaebe probably resulted from the cathode (LiCoO_2) side of the battery. Despite this, LiCoO_2 , and its derivatives, continue to be used in many battery studies involving TFSI type ILs due to the need for high energy batteries.^{15–17}

With the demonstrated excellent stability of lithium metal in some TFSI ILs, many researchers have since reported on the cycling of lithium metal batteries using TFSI based ILs for a range of cathode materials. More recently, another sulfonyl type anion, bis(fluoromethanesulfonyl)imide (FSI) has been the subject of investigation in lithium battery studies.^{18–21} The FSI ILs, which are more fluid and conductive than their TFSI counterparts, have become favoured over TFSI ILs due to the excellent battery cycling behaviour at high rates that can be obtained using FSI IL electrolytes.^{18,20,22} However, there are some concerns about the thermal stability of FSI.^{23,24}

The relative expense (currently) of TFSI and FSI ILs compared to organic carbonate-based electrolytes detracts from their attractiveness as commercial electrolytes. Therefore, the investigation of alternative ILs based on less expensive anions, especially non-fluorinated anions, is of significance. To our knowledge there are no publications in the scientific literature which report lithium metal battery cycling using a non-fluorinated ionic liquid. In fact, in lithium metal systems using TFSI ILs, LiF has been identified as a major component of the solid electrolyte interphase (SEI) that acts to prevent ongoing degradation of the electrolyte.⁴ Stable cycling behaviour of a fluorine free system would prove that LiF is not an indispensable SEI component in IL systems, and may promote the study of fluorine free ILs in the ongoing research effort.

Ionic liquids based on the dicyanamide (DCA) anion have exceptionally low viscosities,^{25,26} a highly desirable characteristic for potential electrolyte solvents. DCA ILs can be manufactured relatively inexpensively as DCA is already a commodity anion produced in large amounts for the pharmaceutical industry. However, for lithium batteries, the DCA anodic stability is below that of TFSI, by at least 1 V,^{25,26} therefore the lithium ion insertion potential of cathode, such as LiCoO_2 , would be likely to exceed the anodic breakdown potential of a

DCA type ionic liquid. This potential problem may explain the lack of investigation of these ILs in lithium batteries.

In this article we report on the use of IL electrolytes using DCA and two other related anions based on the cyano-moiety. In particular we will focus on ionic liquids and plastic crystals based on *N*-methyl-*N*-alkyl-pyrrolidinium dicyanamide ($\text{C}_x\text{mpyr DCA}$) in lithium batteries. We include investigations of lithium metal, $\text{Li}_4\text{Ti}_5\text{O}_{12}$, and LiFePO_4 electrode materials, with particular attention paid to batteries using a lithium metal anode and LiFePO_4 (LFP) cathode.

Experimental

Materials

N-Methyl-*N*-butylpyrrolidinium dicyanamide ($\text{C}_4\text{mpyr DCA}$ with 90 ppm of H_2O) and *N*-methyl-*N*-butylpyrrolidinium tetracyanoborate ($\text{C}_4\text{mpyr TCB}$ with 34 ppm of H_2O) were both sourced from Merck™, Germany. *N*-Methyl-*N*-butylpyrrolidinium tricyanomethanide ($\text{C}_4\text{mpyr TCM}$) was synthesized from *N*-methyl-*N*-butylpyrrolidinium bromide from Merck™, Germany and potassium tricyanomethanide from Alfa Aesar™, USA in dry acetonitrile. Lithium dicyanamide (LiDCA) was synthesized from sodium dicyanamide with LiCl in dry acetone in our laboratories.²⁷ *N*-*N*-Dimethylpyrrolidinium dicyanamide ($\text{C}_1\text{mpyr DCA}$) was synthesized following the previously reported method by MacFarlane *et al.*²⁶ Moisture contents were determined *via* a Karl Fisher titration 756KF coulometer.

Cyclic voltammetry

For cyclic voltammetric studies, a 500 μm dia. Pt working electrode and a Pt wire counter electrode were employed. The reference electrode consisted of a silver wire immersed in a solution of 10 mM silver triflate in *N*-methyl, *N*-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($\text{C}_4\text{mpyr TFSI}$) and separated from the main solution by a glass frit as reported by Snook *et al.*²⁸ The scan rate was 20 mV s^{-1} . Measurements were obtained at ambient temperature. Potentiostatic control was provided by an Autolab pgstat302 (Eco Chemie, Netherlands) controlled with GPES (Version 4.9.005) software.

Coin cells

LiFePO_4 electrodes consisted of 75 wt% LiFePO_4 coated with carbon [1.6 wt%] (Phostech), 15 wt% carbon black (Shawinigan) and 10 wt% PVDF binder. Dry ingredients were milled together for 72 h, prior to the addition of the binder (dissolved in *N*-methylpyrrolidone) to form a slurry. The slurry was milled for a further 72 h prior to being spread on aluminium foil using a 100 μm graded roller giving its loading of 2.5 mg.cm^{-2} . Foils for the plastic crystal $\text{C}_1\text{mpyr DCA}$ used a 60 μm graded roller giving its loading of 1.5 mg.cm^{-2} . All coated foils were allowed to dry overnight in a fume hood prior to being dried in a vacuum oven at $100 \text{ }^\circ\text{C}$ for 72 h.

Coin cells consisted of a CR2032 stainless steel coin cell case, a 10 mm diameter disc cathode, a 10 mm diameter disc of lithium foil (China Energy Lithium, 0.33 mm thick, cleaned with *n*-pentane) anode, and 30 μm thick Separion® (Evonik

Industries, Germany, dried under vacuum at 100 °C) separator. An internal spring and spacer provided uniform pressure inside the cells. Cells were assembled in an argon filled glove box (<5 ppm H₂O, 10 ppm O₂).

Cells were cycled on a Maccor series 4000 battery tester. The test temperature was 50 °C unless stated otherwise.

Results and discussion

Electrochemical windows

In order to determine the electrochemical stability of the cyano-based anions, we have chosen to use the pyrrolidinium cation for these experiments. Whilst ionic liquids using these cations do not have the highest conductivity or lowest viscosity, they have superior electrochemical stability when compared to imidazolium-based ionic liquids.^{29,30}

We have checked the solubility of various lithium salts in C₄mpyr DCA, C₄mpyr TCM and C₄mpyr TCB (whose structures are shown in Fig. 1) to determine their possible application as lithium battery electrolytes. LiDCA salts could be dissolved into C₄mpyr DCA to approximately 0.75 mol.kg⁻¹, and up to 1.5 mol.kg⁻¹ into C₄mpyr TCM. We have tried to solubilise a range of lithium salts (*e.g.*, LiDCA, LiTFSI, LiFSI, LiPF₆ and LiBF₄) into C₄mpyr TCB with no success above a concentration of 0.3 mol.kg⁻¹, which limits the viability of C₄mpyr TCB for use as a lithium battery electrolyte. Scheers *et al.*³¹ have reported the same issue for TCB based ILs; in order to overcome this, they introduced glycol dimethyl ether to dissolve the Li salts in the mixture, which is similar to the approach of Watanabe and co-workers.^{32–35} For C₄mpyr DCA, we have chosen to use a salt concentration of 0.5 mol.kg⁻¹ LiDCA as this was found to exhibit the optimum Li|Li⁺ behaviour in solution.

Fig. 2 shows the electrochemical windows of the ionic liquids chosen for this study. For the DCA, TCB and reference NTf₂ (or TFSI) ILs, the CV started at 0 V scanning reductively first. After completion of the scan, the working electrode was polished before starting at 0 V and scanning in the oxidative direction. Only in the TCM case did this change; the CV started at 0 V for reductive direction and –2 V in the oxidative direction. In this

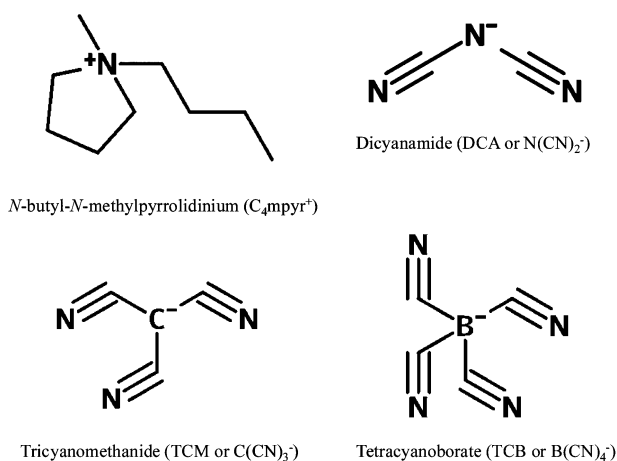


Fig. 1 Structures of ions examined in this study.

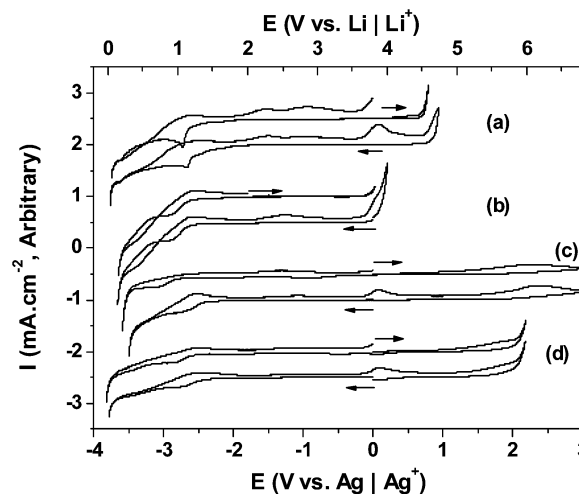


Fig. 2 Comparison of the electrochemical window of three cyano-based ionic liquids with a pyrrolidinium cation (scan rate: 20 mV s⁻¹ at r.t.); where (a) C₄mpyr DCA, (b) C₄mpyr TCM, (c) C₄mpyr TCB, (d) C₄mpyr NTf₂ (added for comparative purposes).²⁸ Note values in the top x-axis are converted from Ag|Ag⁺ to Li|Li⁺ for comparative purpose. The moisture content of each IL was 90 ppm, 40 ppm, 28 ppm and 21 ppm for (a) to (d) respectively.

way, we sought to isolate the products generated as a result of the scan direction.

Fig. 2(a) shows that C₄mpyr DCA has wider electrochemical window than C₄mpyr TCM but narrower electrochemical window than C₄mpyr TCB. On the reverse (cathodic) scan, a noticeable peak is present at –2.7 V, which may be due to an unknown impurity or potential cation reduction. Using a threshold current density of 0.014 mA.cm⁻² above background, the reductive breakdown of the IL is underway by –3.62 V, and the oxidative breakdown by +0.59 V, giving an electrochemical window of 4.2 V. C₄mpyr TCM in Fig. 2(b) exhibits the narrowest electrochemical window of the cyano-based ILs. The rapid oxidation behaviour at the electrochemical limit is not observed in the case of C₄mpyr TCB (Fig. 2(c)); it is unclear why this is the case.

The TCM and DCA ILs are at least 1 V (*vs.* Ag|Ag⁺) less electrochemically stable than the NTf₂ ILs, limiting the scope for using these materials with common cathodes such as LiCoO₂ or LiMn₂O₄. For this reason in the battery cycling work described later, we have focused on LiFePO₄ (LFP) cathodes. Whilst the TCB based IL appears to have an equivalent electrochemical window to C₄mpyr NTf₂ (or TFSI) and FSI based ILs, the very limited Li salt solubility precludes its further study in this work. Consequently, we focused the further investigation described below on the DCA-based ionic liquids.

Cycling stability of C₄mpyr DCA with different moisture content

We have found that cyano based ionic liquids have a strong affinity for moisture and it is therefore very difficult to remove all moisture from the solution. Electrolytes composed of fluorine based anions or salts in the presence of moisture may have an unfavourable effect on the lithium plating process and SEI

formation.^{36,37} There are few reports on the role of trace amounts of H₂O in non-fluorinated ionic liquid based electrolytes, however, Scheers *et al.* investigated the role of relatively large amount of H₂O in 4,5-dicyano-(2-trifluoromethyl)imidazolium based ionic liquids on lithium ion co-ordination behaviour.³⁸ Hence, we have conducted a number of experiments to understand the role of H₂O on the lithium electrochemistry in the electrolyte of C₄mpyr DCA + 0.5 mol.kg⁻¹ LiDCA. We have systematically increased the moisture content of the electrolyte from 36 ppm up to 630 ppm. The electrolyte with 36 ppm of H₂O was prepared by eliminating moisture from the solution *via* contacting it with lithium metal for up to three months. The CV of this electrolyte, shown in Fig. 3(a), indicates

that no lithium dissolution was possible following a strong reduction peak at ~ -3.7 V *vs.* Ag|Ag⁺. We ascribe this peak to be related to ionic liquid decomposition, more specifically C_xmpyr reduction, due to insufficient moisture to form an SEI. We do note that the electrolyte was slightly discoloured after being exposed to the Li metal for the extended period of time.

Fig. 3(b) shows the cyclic voltammetry for the 0.5 mol.kg⁻¹ LiDCA solution with 97 ppm H₂O. The Li⁺ reduction peak, beginning at -3.9 V *vs.* Ag|Ag⁺, reaches a maximum current density of 4 mA.cm⁻² on the first scan. On the reverse scan a clear bulk lithium metal stripping is present at -3.95 V *vs.* Ag|Ag⁺, along with some smaller peaks which are due to the stripping of Li from Li-Pt alloys.^{14,39,40} The Li stripping peak of the 2nd scan is bigger than the first scan and then reduces in subsequent scans. We attribute this change to the formation of a passivation layer that grows with continued cycling. The tendency of decreasing peak currents for Li⁺ deposition and Li stripping during cycles are commonly observed in all samples with different H₂O amount but, the highest peak current value was observed when the water content is 97 ppm. In all instances we have not found it possible to clearly resolve the deposition peak; it appears that bulk electrolyte decomposition is almost co-incident with lithium deposition. Of note is the increase in current density for the peak at -2.5 V *vs.* Ag|Ag⁺ which can be attributed to the increasing presence of moisture in the electrolyte.

Fig. 3(c) shows a trend for the peak current density of the plating of lithium decreasing as increasing amounts of H₂O are added to the electrolyte. Comparing the sample which has 97 ppm H₂O and the sample which has 630 ppm of H₂O, a significant decrease in the current density for both Li⁺ deposition and stripping can be seen, suggesting increasing amounts of moisture are detrimental to electrochemical kinetics. Cyclic voltammetry experiments clearly show the feasibility and stability of lithium cycling in the C₄mpyr DCA ionic liquid with non-fluorinated lithium salt and an optimum moisture content contributes to higher current densities and efficiencies.

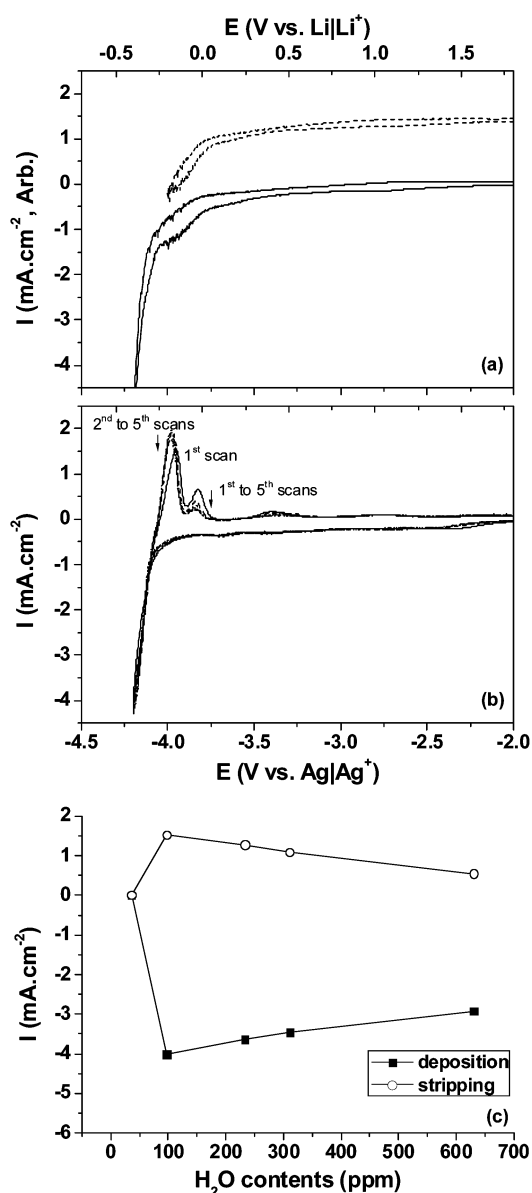


Fig. 3 (a) CVs of 0.5 mol.kg⁻¹ LiDCA in C₄mpyr DCA with 36 ppm H₂O showing 5 cycles at ambient temperature (scan rate is 20 mV s⁻¹). (b) CV with 97 ppm H₂O. (c) Li deposition and dissolution peak current at the first cycle with different amount of H₂O. Note: CVs for electrolytes with different H₂O content are presented in the ESI†

Cyclic performance of C₄mpyr DCA lithium symmetrical cells

Lithium symmetrical cells, with 0.5 mol.kg⁻¹ LiDCA in C₄mpyr DCA and different moisture contents, were prepared and cycled 100 times at 50 °C and at a current density of 0.1 mA.cm⁻² for 16 min (0.1 C cm⁻²) for each polarisation. Fig. 4(b)–(d) show the cycling results using electrolytes and Fig. 4(f)–(h) show the EIS before and after the cycling with 226 ppm, 291 ppm and 443 ppm moisture respectively. In all cases, the over-potentials of the symmetrical cells start at approximately the same point; however, with continued cycling the cells exhibit increasing over-potentials, which vary dramatically with moisture content. We have ascribed this change to unrestrained growth of the SEI on the lithium metal electrode, leading to increased impedance and hence, the over-potential. The cell impedance of the electrolyte containing 36 ppm water increases most rapidly with cycling leading to the high over-potentials recorded here (Fig. 4a and e). From this experiment, it appears that a certain amount of moisture is required to form and stabilise an SEI layer in

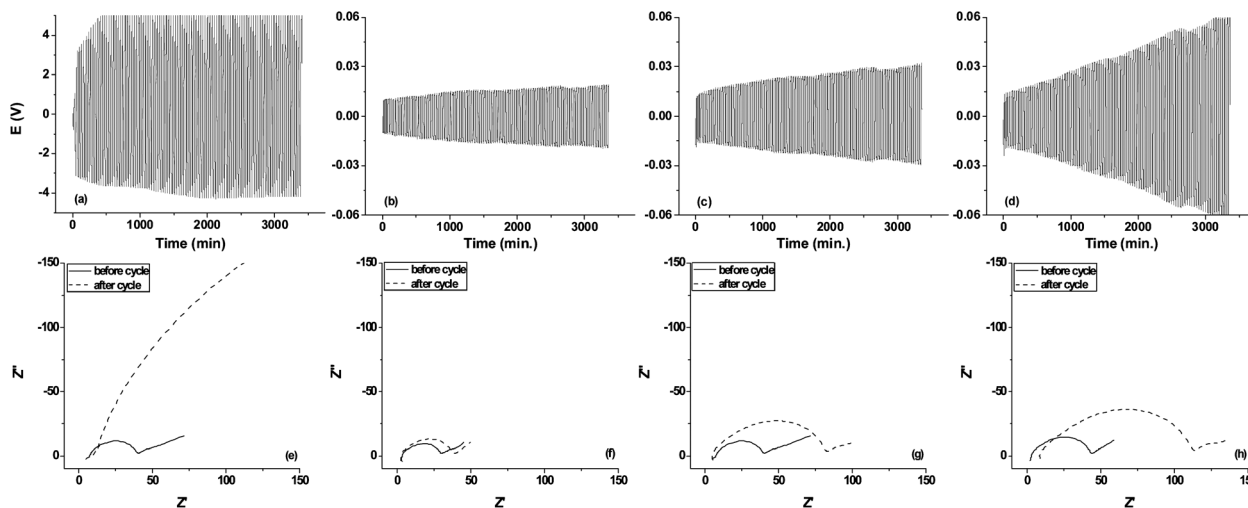


Fig. 4 Li symmetrical cell cycling and EIS results: 10 mm Li disc, $0.1 \text{ mA}\cdot\text{cm}^{-2}$ constant current for 16 minutes, 100 cycles at 50°C using $0.5 \text{ mol}\cdot\text{kg}^{-1}$ LiDCA in C_4mpyr DCA with different H_2O contents; (a) and (e) 36 ppm, (b) and (f) 226 ppm, (c) and (g) 291 ppm, (d) and (h) 443 ppm.

presence of the DCA anion during lithium cycling. This indicates that the moisture content of the electrolyte has a significant effect on the SEI that forms on the lithium surface in DCA electrolyte systems; however, this can be managed to allow effective cycling of the cell.

In support of this assertion, we prepared a lithium symmetrical cell doped with 223 ppm of water and cycled the cell 100 times at 50°C , with a 15 h, 1 h and 24 h interval after the 10th, 30th and 50th cycles, respectively. During the cycling interval, the cell was maintained at 50°C and open circuit. Fig. 5 shows that even when no current is applied to the cell the impedance continues to increase during the storage period at 50°C . This implies that the increasing cell impedance is not driven by a potential dependant thermodynamic reaction but rather by a temperature and time dependant kinetic reaction.

Li|LiFePO₄ cells

Li|LiFePO₄ cells were constructed using cathodes with a loading of $2.5 \text{ mg}\cdot\text{cm}^{-2}$ and LiDCA salt ($0.5 \text{ mol}\cdot\text{kg}^{-1}$) in C_4mpyr DCA

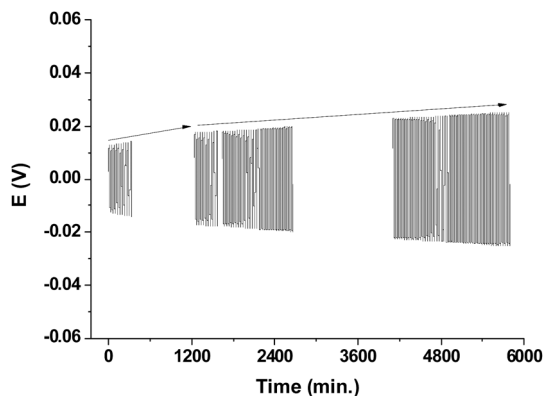


Fig. 5 Li symmetrical cell cycling results: $0.1 \text{ mA}\cdot\text{cm}^{-2}$ constant current for 16 minutes, 100 cycles at 50°C using $0.5 \text{ mol}\cdot\text{kg}^{-1}$ LiDCA in C_4mpyr DCA at 223 ppm H_2O . Cycling procedure were 10 cycles, 15 hours at OCV or "rest", 10 cycles, 1 hour at OCV or "rest", 30 cycles, 24 hours at OCV or "rest", and 50 cycles.

with 226 ppm and 443 ppm of moisture. These cells were cycled between 3.0 V and 3.8 V with $0.35 \text{ mA}\cdot\text{cm}^{-2}$ constant current (about 1 C rate) at 50°C . For each cell, we observed an initial capacity of more than $130 \text{ mAh}\cdot\text{g}^{-1}$ discharging capacity as shown in Fig. 6. The cell with 443 ppm of H_2O shows a larger initial irreversible capacity, lower efficiency (93–95% over 20 cycles) and more rapid capacity fade (93% of initial discharge capacity after 10th cycles) than the cell containing 226 ppm of H_2O , which has $137 \text{ mAh}\cdot\text{g}^{-1}$ maximum discharge capacity at the 2nd cycle, over 97% efficiency and over 97% discharge capacity remaining after 10 cycles. We ascribe the difference in the cycling efficiency and capacity fade to be due to the different amounts of moisture in the cell and the evolution of the SEI on the lithium metal electrode. Importantly, these results show that good performance in a real battery at a relatively high C rate can be achieved with this non-fluorinated electrolyte system.

Li|Li₄Ti₅O₁₂ cells

Li₄Ti₅O₁₂ is a cheap, high capacity and high cycleability material having zero strain with minimal SEI formation and has been researched vigorously for the application as an alternative anode material.^{41,42} The compatibility of Li₄Ti₅O₁₂ with the C_4mpyr DCA based electrolyte was also investigated. A Li|Li₄Ti₅O₁₂ cell was prepared with a loading of $1.23 \text{ mg}\cdot\text{cm}^{-2}$ and cycled at 50°C . The cell was cycled at 1 C rate at 50°C and displayed a capacity of around $130 \text{ mAh}\cdot\text{g}^{-1}$ (Fig. 7), the theoretical capacity for this material is $175 \text{ mAh}\cdot\text{g}^{-1}$. Clearly Li₄Ti₅O₁₂ is a viable electrode material for C_4mpyr DCA based electrolytes.

Plastic crystal electrolytes based on C_1mpyr DCA

Plastic crystal electrolytes have also been researched widely since they have flexibility and durability during volumetric change.^{43–45} Recently, Adebahr *et al.* have reported the possibility of using C_1mpyr DCA as a plastic crystal electrolyte having

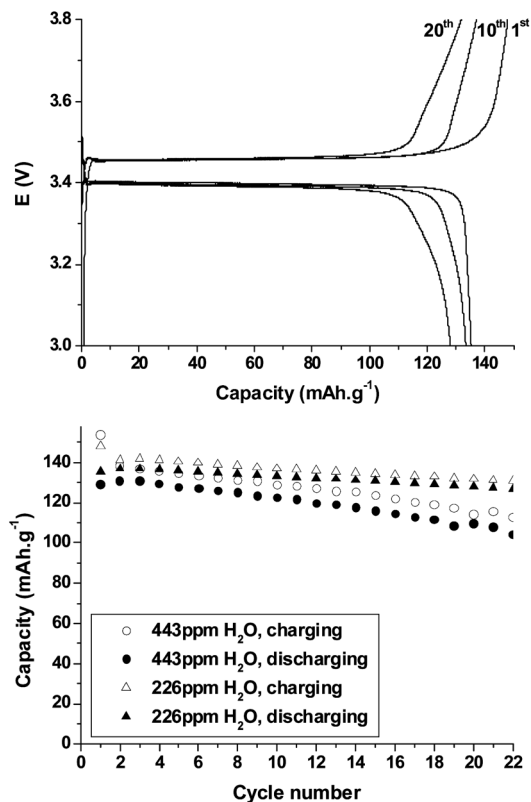


Fig. 6 Coin cell voltage profile of 226 ppm H₂O cell (upper) and the cycling result for a Li|LiFePO₄ using 0.5 mol.kg⁻¹ LiDCA in C₄mpyr DCA with 226 ppm and 443 ppm H₂O (lower). Charging and discharging conditions are from 3.0 V to 3.8 V, with 0.35 mA.cm⁻² constant current (about 1 C rate) at 50 °C.

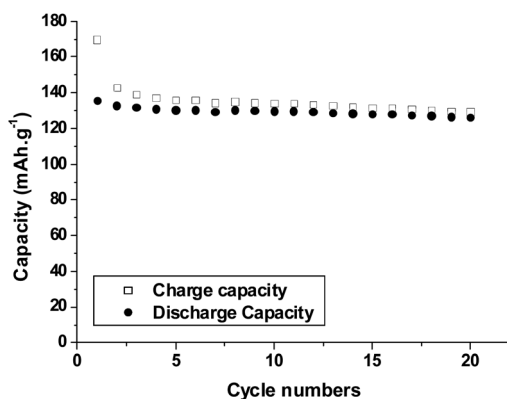


Fig. 7 Li|Li₄Ti₅O₁₂ coin cell cycling at 2/3 C rate at 50 °C using 0.5 mol.kg⁻¹ LiDCA in C₄mpyr DCA with approx. 200 ppm of H₂O.

a high conductivity at elevated temperatures with the addition of lithium salts.⁴⁴

Molten C₁mpyr DCA with 0.5 mol.kg⁻¹ LiDCA binary composite electrolyte, was incorporated in a PVdF separator at 130 °C inside an argon filled glove box. This material was kept at this temperature for more than two hours until the electrolyte was fully absorbed into the separator. The laden separator was then placed on the surface of LiFePO₄, which was already wetted with a thin layer of molten electrolyte at the same temperature.

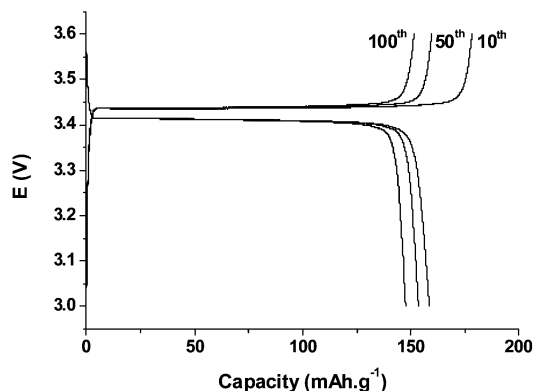


Fig. 8 Charge-discharge profiles at the 10th, 50th, and 100th cycle of a Li|LiFePO₄ cell at C/10 rate using C₁mpyr LiDCA in PVdF at 80 °C.

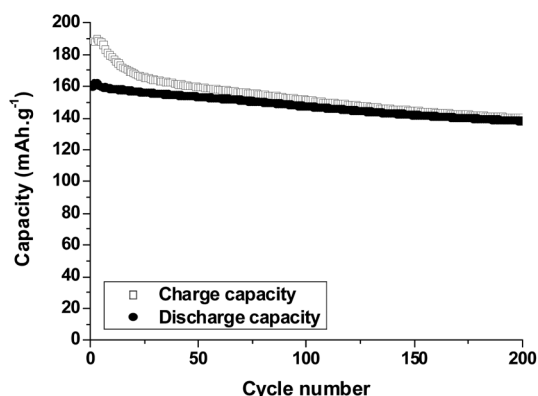


Fig. 9 Li|LiFePO₄ coin cell cycling at C/10 rate using C₁mpyr LiDCA in PVdF at 80 °C.

This combined assembly was then left at 130 °C for a further two hours. The assembly was cooled to room temperature before assembly with a Li metal anode in a battery cell. Cycling performance of the cell was tested at C/10 rate at 80 °C to examine the specific capacity and cycle-ability of this composite in its solid-state phase. Initially, the cell showed a capacity at about 162 mAh.g⁻¹, which was followed a by linear drop reaching 158 mAh.g⁻¹ for the next 10 cycles (Fig. 8). Consequently, the cell showed a slow capacity loss from 158 mAh.g⁻¹ to 140 mAh.g⁻¹ after 200 cycles. Further studies need to be conducted on this composite electrolyte using a separator more suitable for application at higher temperatures.

Fig. 9 shows charge and discharge curves of the 10th, 50th and 100th cycles. The first 20 cycles, shows the cell to have poor efficiency and we ascribe this behaviour to the electrolyte decomposing slowly to form the SEI on Li metal, consistent with our earlier observations. At later cycles (>75), the cell reached and continuously maintained 98% efficiency.

Conclusions

The use of a non-fluorinated anion, as part of an ionic liquid and electrolyte thereof, goes to the heart of the challenge of adopting these exciting materials in lithium battery applications; affordability, availability and electrochemical stability. The

dicyanamide anion is well adopted in a number of different technology areas and is relatively cheap. We have now studied this important family of non-fluorinated ionic liquid electrolytes for potential application in lithium metal batteries. We show that there is promise in the use of these materials for energy storage.

Our studies have shown that the electrochemical stability of DCA is higher than TCM but lower than and TCB analogues. On the other hand, the Li salt solubility shows that the TCM is able to solubilise more salt than DCA and TCB (a very poor solvent for lithium salts). We do note, however, that the electrochemical window of this DCA is still inferior to NTf₂ based ionic liquids.

For the DCA based electrolytes, we have found a strong relationship with the amount of H₂O on the cycle-ability of the lithium anode. When there is less than 100 ppm of H₂O present in the electrolyte, this reduces the lithium cycle-ability significantly, whilst having between 100 and 200 ppm of H₂O provided the best cycling ability in Li|Li symmetrical cells.

Li|LiFePO₄ cells with C₄mpyr DCA ionic liquid showed over 130 mAh.g⁻¹ of discharge capacity without a significant capacity reduction over to 20 cycles. We also demonstrated utility of Li|Li₄Ti₅O₁₂ cells at 50 °C. An organic ionic plastic crystal, C₁mpyr DCA, showed 150 mAh.g⁻¹ discharge capacity in a Li|LiFePO₄ without a significant capacity fade for up to 200 cycles at 80 °C. In conclusion, these non-fluorinated ionic liquids based on cyano-based anions have proved to be a promising base for potentially safer and economical electrolytes for lithium metal batteries.

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