

Ionic liquid and plastic crystalline phases of pyrazolium imide salts as electrolytes for rechargeable lithium-ion batteries

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Abstract

A new member of the plastic crystal, pyrazolium imide family, *N,N'*-diethyl-3-methylpyrazolium bis-(trifluoromethanesulfonyl)imide (DEMPyr123) was prepared. It showed a single, plastic crystalline phase that extends from 4.2 °C to its melting at 11.3 °C. When 10 mol% LiTFSI salt was added, the mixture showed ionic conductivities reaching $1.7 \times 10^{-3} \text{ S cm}^{-1}$ at 20 °C, in the liquid state and $6.9 \times 10^{-4} \text{ S cm}^{-1}$ at 5 °C, in the solid, plastic phase. A wide electrochemical stability window's of 5.5 V was observed by cyclic voltammetry of the molten salt mixture. Batteries were assembled with LiFePO₄/Li₄Ti₅O₁₂ electrodes and the salt mixture as an electrolyte. They showed a charge/discharge efficiency of 93% and 87% in the liquid and the plastic phase, respectively. The capacity retention was very good in both states with 90% of the initial capacity still available after 40 cycles. In general, the batteries showed good rate capability and cycle life performance in the ionic liquid phase that were sustained when the electrolyte transformed to the plastic phase. Comparison of the battery results with those of a classic (non-plastic crystal) ionic liquid has proven the advantage of the dual state of matter character in this electrolyte.

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1. Introduction

In recent years, room temperature ionic liquids (RTIL) have been applied as electrolytes to rechargeable lithium batteries, due to their non-flammability, non-volatility, wide electrochemical window, thermal and chemical stabilities [1–3]. Those based on salts of the 1-ethyl-3-methylimidazolium (EMI) cation, were widely studied because of its low viscosity, high conductivities and ability to dissolve lithium salts [4]. Like most organic salts of heterocyclic cations, they are reactive towards metallic lithium [5,6], therefore current research is focused on either modifying the cathodic stability

of the salts [7] or assembling Li-ion batteries with lower output voltages (2.5 V) [8] instead. It is worth mentioning that salts based on the quaternary ammonium cation can still be applied to lithium metal batteries [9].

Due to safety concerns and the possibility of obtaining high energy density, solid-state electrolytes are more desirable for lithium batteries than their liquid counterparts with most of the development being focused on polymer electrolytes [10]. However, despite their good mechanical properties, compatibility with lithium, conductivities higher than $10^{-5} \text{ S cm}^{-1}$ at room temperature could not be reached [11]. In present commercial batteries, this problem is circumvented by the use of polymer–gel electrolytes (liquid electrolyte solution/polymer mixtures) [12].

Timmermans has identified a new metastable state of matter, became known as, plastic crystal [13]. He noticed that molecular crystals with an overall globular (spherical) shape

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show this behavior due to their ability to rotate or tumble over preferred orientations (disorientation) within a crystalline lattice. The plastic crystalline phase is characterized by a great degree of structural disorder that renders enhanced diffusivity and plasticity (giving soft materials) and in general exhibit low entropies of fusion and dielectric constant, resembling in this sense the liquid state [14].

Solid materials based on the plastic crystalline phase of certain organic salts (organic plastic crystal electrolytes, OPCEs) are a promising new type of electrolytes for electrochemical applications [15–18]. They are mainly based on cations of aliphatic or heterocyclic amines, showing room temperature conductivities reaching $10^{-3} \text{ S cm}^{-1}$ in the solid, plastic state, either in the neat form or when mixed with lithium salts such as LiTFSI. Most recently, we have prepared pyrazolium salts that show only one plastic crystalline phase, which allowed for better understanding of their properties and facilitated their application in electrochemical devices [19,20].

In principle, OPCEs are able to deliver high Li^+ ion transport numbers [21] and plastic mechanical properties [22], both ensure fast kinetics and good electrode–electrolyte contact, that will accommodate volume changes during charge/discharge cycling, both are vital to the performance of the battery. First batteries based on the plastic crystalline phase were developed in our laboratories incorporating either Li^+ -doped OPCEs [23] or succinonitrile [24], a non-polar molecular plastic crystal. The performance of the batteries has revealed the potential of this new type of solid materials to seriously compete with currently used solid conductors. A typical example is the Pyr6m-TFSI salt, 5-methyl-5,6,7,8-tetrahydro-pyrazolo [1,2] pyridazin-4-ium TFSI salt (Fig. 1) [23]. It has a wide plastic crystalline phase that starts at 20°C , well below its melting at 65°C . Its mixture with 20 mol% LiTFSI, showed an ionic conductivity of $1 \times 10^{-4} \text{ S cm}^{-1}$ at 20°C . When employed in a $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$ battery, at 40°C , in the solid state, it showed a real capacity of 137 mAh g^{-1} .

In this work, we extend the work to OPCEs with melting points below room temperature, i.e., in the ionic liquid state, and showed that their biphasic character is advantageous when employed in Li-ion batteries. We report on the thermal and electrochemical performance of DEMPy123 and its mixture with 10 mol% LiTFSI. We also report on its use in a lithium-ion battery in both the liquid and solid states. Comparison was conducted with conventional ionic liquids

in order to show the greater advantage of the dual-state of matter for an electrolyte.

2. Experimental

2.1. Synthesis of *N,N'*-ringed pyrazolium trifluoromethanesulfonimide (DEMPyr)

2.1.1. *N*-ethyl-3-methylpyrazole

3-Methyl-pyrazole (6.808 g, 100 mmol) was dissolved in 100 mL of dry tetrahydrofuran, under argon. Ninety-five percentage of dry sodium hydride (2.526 g, 100 mmol) was slowly added, to the stirred solution. The solution was left to cool, and iodoethane (15.597 g, 100 mmol) was added drop wise over 10 min. The reaction mixture was then refluxed for 10 h. The resulting solution was evaporated under vacuum, and the resultant *N*-ethyl-3-methylpyrazole was purified by distillation (85% yield).

2.1.2. 1,2-Diethyl-3-methylpyrazolium trifluoromethanesulfonimide

The *N*-ethyl-3-methylpyrazole (9.613 g, 100 mmol) was dissolved in dichloromethane and a 1.0 M solution of tri-ethyloxonium tetrafluoroborate in dichloromethane (105 mL, 105 mmol) was added drop wise. The mixture is stirred 2 h at room temperature, and then evaporated under vacuum to yield 1,2-diethyl-3-methylpyrazolium tetrafluoroborate as a nearly colorless oil (95% yield). Aqueous solutions, of the tetrafluoroborate salt (2.120 g, 10 mmol) and of KTFSI (3.192 g, 10 mmol) were mixed, causing the plastic crystal salt to separate out of solution. The pyrazolium salt was dissolved in dichloromethane and washed several times with distilled water. The organic phase was dried with Na_2SO_4 and evaporated under vacuum to give a colorless oil (typical yield 90% of DEMPyr).

2.2. Electrochemical characterization

Battery investigations were carried out with coin-type cells. Cathode (LiFePO_4) and anode ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel) materials were prepared by mixing 85:5:10 (w/w) ratios of active material, carbon black and polyvinylidene fluoride binder, respectively, in *N*-methyl pyrrolidinone. The resulting paste was applied to a carbon coated aluminum (Rexam[®]) film current-collector. A Celgard[®] separator (30 μm thickness)

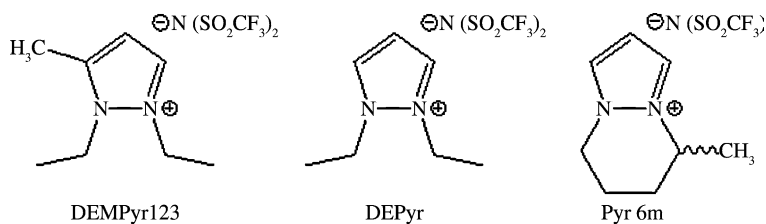


Fig. 1. Structures of the pyrazolium imide salts.

was put between electrodes and imbibed with 10 mol% LiTFSI-doped DEMPy. The active material loading was about 4.5 mg cm^{-2} and the geometric surface area of the cathode was always 1.5 cm^2 . The cells were assembled in a helium-filled dry box (dew point -95°C ; $\text{O}_2 < 1 \text{ Vpm}$), at room temperature. Cell performance was evaluated by slow scan voltammetry and galvanostatic experiments carried out on a multichannel potentiostats (VMP[®], Biologic, Claix, France). The cells were first charged and then discharged at constant current density between the potential limit of 1.2 V for discharge and 2.5 V for charge. Cyclic voltammograms were realised with platinum electrode ($\text{Ø}100 \mu\text{m}$) and a silver wire as pseudo reference. The true potential was established with butyl-ferrocene (Aldrich) and was found around 3.2 V versus Li/Li^+ . Conductivity measurements were performed using the impedance spectroscopy technique. The sample was sandwiched between two stainless steel electrodes with a 1 cm diameter. The frequency was swept between 5 Hz and 13 MHz using an HP frequency analyzers. The temperature was varied between -20 and 25°C allowing 20 min for thermal equilibration. Differential scanning calorimetric analysis was performed using a Perkin-Elmer Pyris 1. All the samples were sealed in aluminum pans in a dry box and then scanned from -150 to 160°C at 2°C min^{-1} . All experiments were performed in a He-filled glove box.

3. Results and discussion

3.1. Differential scanning calorimetry

We have previously reported that, in the pyrazolium imide family we generally found that only N,N' -ringed derivatives, bis-annular, display plastic crystal behavior [18]. We suggested that the disc-like shape of the cations could be responsible for this behavior based on the assumption that disks are, to some extent, free to rotate along the plane of the cationic ring or able to tumble over preferred orientations. Supporting this observation, is the fact that none of the unsubstituted N,N' -dialkylpyrazolium imides studied are plastic crystals. However, with a methyl group on the ring, DEMPy123 is a plastic crystal, as its DSC scan shows a characteristic endothermic peak at 4.2°C preceding that of melting at 11.3°C (Fig. 2). This first order transition corresponds to the normal crystal–plastic crystal transition (T_{pc}). The figure also shows the scan for DEPy, the unmethylated equivalent of DEMPy123. It exhibited a single peak corresponding to melting at -2.6°C and no extra peaks that might correspond to any plastic crystalline phase. This, we suggest, might be attributed to the dissymmetric structure of the cation where the skewed position of its center of gravity relative to the charge distribution in the methylated equivalent.

The melting entropy ($\Delta S_{\text{m}}^\circ$) of DEMPy123 is $29.5 \text{ J K}^{-1} \text{ mol}^{-1}$, a value higher than Timmermans' criterion ($\Delta S_{\text{m}}^\circ \leq 20 \text{ J K}^{-1} \text{ mol}^{-1}$), which is common in OPCEs [16]. Although the plastic phase is relatively narrow

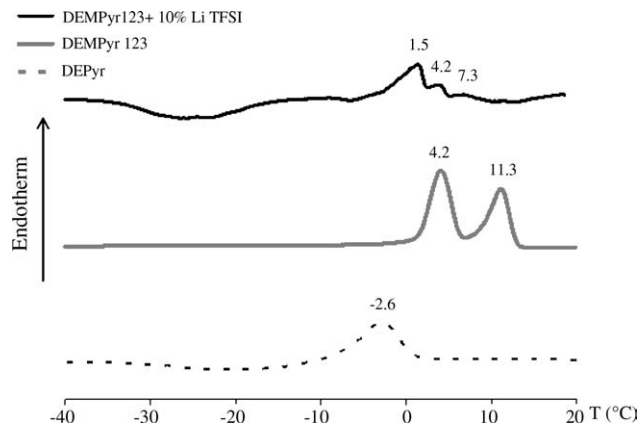


Fig. 2. DSC scans of the studied electrolytes.

ΔT : 7.1°C , it is still considered applicable to support a good performance in the solid state, provided enough time were allowed for equilibration at the operating temperature, in our case at 5°C .

In order to introduce a Li-ion contribution to the electrolyte, a 10 mol% of LiTFSI salt was added to the pyrazolium salt. The resultant mixture showed an expected depression in melting point to $T_{\text{m}} = 7.3^\circ\text{C}$ and an additional transition at 1.5°C (Fig. 2), with the original plastic transition still unaffected at ($T_{\text{pc}} = 4.2^\circ\text{C}$). This method of mixing a lithium salt and an OPCE was introduced by MacFarlane et al. [25,26] who showed that adding doping levels (up to 9% LiTFSI) to OPCEs, in their case being the pyrrolidinium family, results in the formation of solid solutions. They observed that upon the addition of LiTFSI no extra peaks were emerged in the DSC up to the 9.3 mol% composition, beyond which, a new peak appears at 35°C , which they attributed to an eutectic with a 33 mol% composition. This, however, was challenged by Hederson and Passerini [27] who constructed a complete phase diagram of LiTFSI and N -alkyl- N -methyl-pyrrolidinium-TFSI mixtures. They suggested that the peak corresponds, rather, to a 2:1 crystalline solid. We tend to agree with this finding as in our case, although the 1.5°C event could still be, simply, interpreted as a eutectic, its hard to explain the enhanced conductivity found at temperatures well below a possible “melting point”. Also, the degree of (dis)order in the plastic crystalline phase may vary considerably. In either case, the salt mixture was investigated visually at 5°C , and a plastic appearance was observed. Moreover, we have suggested in the case of mixtures of LiTFSI-succinonitrile, that even if a eutectic or pseudo-eutectic is formed, it will be most probably nanodispersed within the extensive dislocation networks known to exist in plastic crystalline phases [28,29].

3.2. Conductivity measurements

The DEMPy123 compound displays significant conductivity in the neat form, when molten or in the solid, plastic crystal states. In the molten state, at 20°C the conductivity

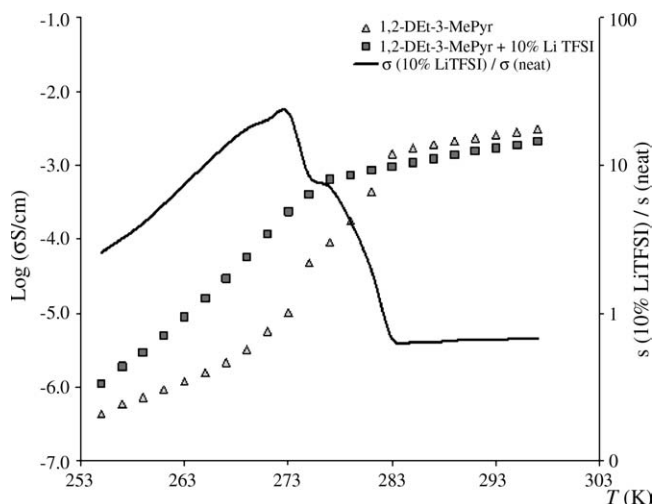


Fig. 3. Temperature dependence of the conductivity of DEMPyr 123.

is $2.6 \times 10^{-3} \text{ S cm}^{-1}$ while within the plastic crystal phase (from 5 to 10°C), the conductivity values ranged from 1.3×10^{-4} to $1.4 \times 10^{-3} \text{ S cm}^{-1}$, respectively. Upon doping with 10 mol% of LiTFS salt, the conductivity decreased slightly at 20°C to $1.7 \times 10^{-3} \text{ S cm}^{-1}$ as expected from increased viscosity or the formation of less-mobile species. Conversely, within the plastic phase, doping increases the conductivity by five folds throughout the temperature range ($6.9 \times 10^{-4} \text{ S cm}^{-1}$ at 5°C , Fig. 3). The conductivity variation, as a function of temperature, is characteristic of plastic crystal electrolytes. Within the plastic crystalline phase ($T_{pc} < T < T_m$), the variation of conductivity as a function of temperature fits neither Arrhenius nor VTF (free volume) plots. Rather, the conductivity varies as a binomial (parabolic) function of temperature. The rationale for this observation involves pipe diffusion mechanism as discussed previously [18].

3.3. Electrochemical stability window

Fig. 4 shows a cyclic voltammogram of the 10 mol% LiTFSI DEMPyr123 electrolyte at 20°C . The electrolyte's stability spans from -3.7 to 1.8 V (versus Ag/Ag^+ pseudo-reference) (from -2.2 to 3.3 V versus Li/Li^+). Within this 5.5 V operating window both $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (negative electrode) and LiFePO_4 (positive) are stable and this combination provides a 2.5 V lithium battery suitable for the study of the electrolyte response at the phase changes.

3.4. $\text{Li}_4\text{Ti}_5\text{O}_{12}/10\% \text{ LiTFSI-DEMPyr 123}/\text{LiFePO}_4$ battery system

3.4.1. Slow scan voltammetry

At 20°C , in the molten state, the tested batteries typically yielded a discharge capacity of 141 mAh g^{-1} (over 83% of the theoretical capacity based on LiFePO_4 ($\text{Li}_4\text{Ti}_5\text{O}_{12}$ in excess)) with 93% charge/discharge efficiency (Fig. 5).

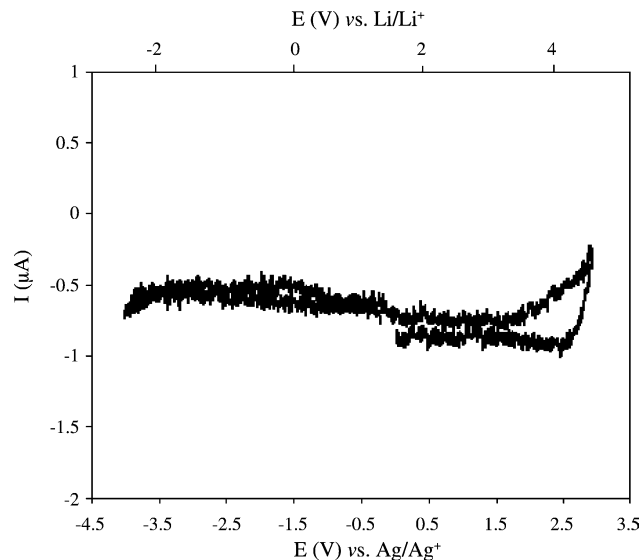


Fig. 4. Cyclic voltammogram scan of 10% LiTFSI-DEMPyr 123, using 0.1 mm Pt electrode, and a Ag wire as a counter and reference electrodes.

At 5°C , within the plastic crystalline phase, the batteries yielded 81% of the initial discharge capacity (114 mAh g^{-1}), with 87% charge/discharge efficiency. The oxidation and reduction peaks were observed at 1.98 and 1.77 V , respectively, at 20°C , in the liquid state. At 5°C within the solid-state, plastic crystalline phase and we found that the position of the peaks remained unaffected. This suggests that when crossing from the liquid to the plastic crystal state the salt mixture is able to provide similar performances in terms of electrolyte properties and electrode/electrolyte interface.

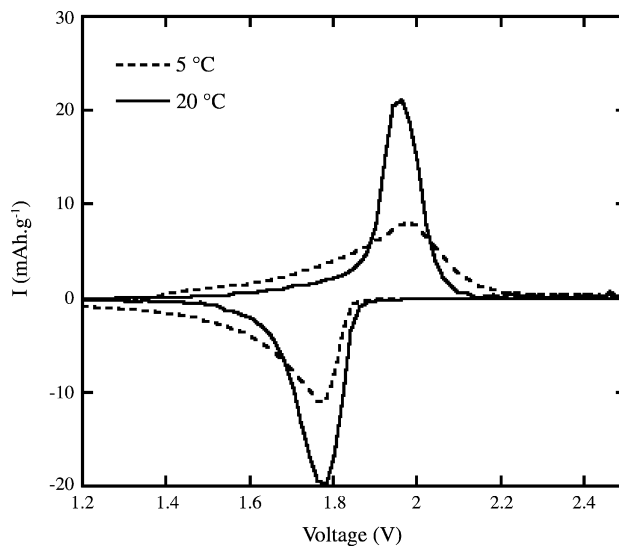


Fig. 5. Slow scan voltammetry (20 mV h^{-1}) for the $\text{Li}_4\text{Ti}_5\text{O}_{12}/10\% \text{ LiTFSI-DEMPyr123}/\text{LiFePO}_4$ system.

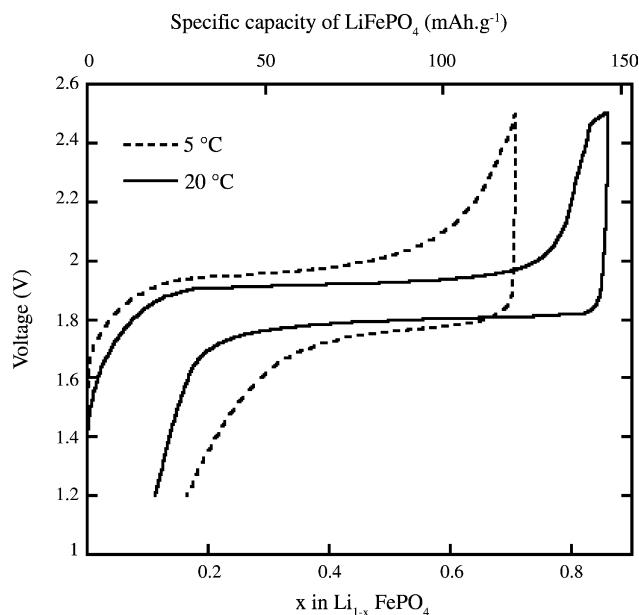


Fig. 6. Capacity retention with temperature variation at $C/12$ current.

3.5. Rate capability

In order to establish the relative performance of the system at 5 and 20 °C, the variation of the cell voltage against composition and capacity during the first discharge–charge cycle, with a rate of $C_{\text{exp}}/12$ ($C_{\text{exp}(5^\circ\text{C})} = 114 \text{ mAh g}^{-1}$ and $C_{\text{exp}(20^\circ\text{C})} = 141 \text{ mAh g}^{-1}$) was examined (Fig. 6). At 20 °C, the delivered discharge capacity was 127 mAh g^{-1} , with 88% charge/discharge efficiency. At 5 °C, under the same conditions, a discharge capacity of 92 mAh g^{-1} was obtained, with 77% charge/discharge efficiency. On going from the liquid to the solid, plastic crystal state, over 72% of the battery's performance was preserved.

Furthermore, the effect of the discharge rate on the capacity of the batteries was considered over a rate range of $C/12$ to C , at the studied temperatures (Fig. 7). At 20 °C, 81% of the capacity was available at rates up to $C/6$. The capacity retention remained satisfactory at 5 °C, with 62% of the initial capacity still available at $C/6$ rate. In general, the slight decrease in capacity and charge/discharge efficiency on going from liquid to plastic phase, could be attributed mainly to the distortion of the interfacial contact between the electrode and turned-solid electrolyte. In order to further demonstrate the advantage of having an electrolyte with a dual state of matter, a comparative study was carried out, under exactly the same conditions with 1,2-diethyl-3-methylpyrazolium TFSI (DEPyr, Fig. 1). DEPyr is a conventional ionic liquid ($T_m = 2.6^\circ\text{C}$) at room temperature with no plastic crystalline phase. A battery electrolyte was prepared by adding 10 mol% LiTFSI to DEPyr and batteries were assembled and further tested at various temperatures.

As shown in the Ragone plots, for both electrolytes, the behavior of DEPyr differs markedly from that of DEMPyr123

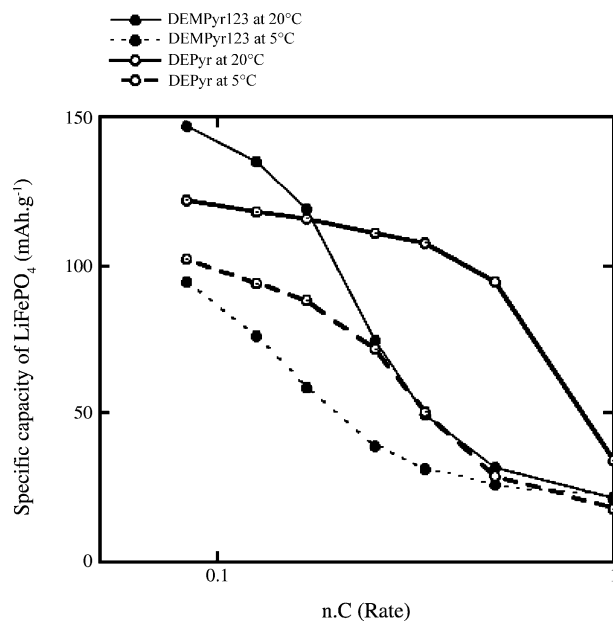


Fig. 7. Rate capability for DEMPyr123 and DEPyr based electrolyte at 20 and 5 °C.

(Fig. 7): The capacity loss decreased with increasing discharge rates for DEMPyr123; on the contrary, to the ionic liquid DEPyr, that showed an increase in capacity loss with increasing rates, with less than 50% capacity retention at $C/3$ rate. At low discharge rates, DEMPyr123 at 20 °C, showed the highest capacity, which at intermediate rates decreased to values that compare well with that of DEPyr at 5 °C, leaving the DEPyr at 20 °C with the highest capacity, a behavior that holds at higher rates. Although at the higher temperature and higher rates, the ionic liquid DEPyr is superior, at lower temperatures, the solid DEMPyr123 electrolyte showed similar behavior to DEPyr. This is because the latter suffer from a decrease in conductivity due to an increase in viscosity which is detrimental to the function of the battery. This is more evident when the battery incorporating the DEPyr electrolyte was tested at -10°C , below the melting point of the electrolyte. In this case, it was not possible to obtain significant capacity from DEPyr when it crosses to the solid state (normal crystal phase), which underlines the advantage of the dual state of matter character exhibited by DEMPyr123. Also, as important, is the fact that the efficiency of its plastic crystalline phases in sustaining a battery performance to a level similar to that of liquids at both extremes of discharge rates. As we pointed earlier, this is a result of not only the liquid-like ion conducting ability of the plastic crystalline solid phase, but also, to its flexible structure during cycling.

3.6. Lithium batteries, cyclability

The ability to sustain charge/discharge cycles was assessed, for the $\text{Li}_4\text{Ti}_5\text{O}_{12}/10\% \text{ LiTFSI-DEMPyr123/}$

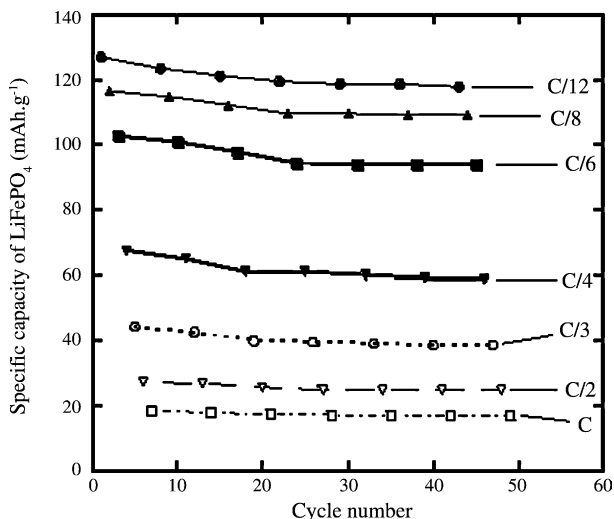


Fig. 8. Cyclability at 20 °C of DEMPy123 based batteries at different currents.

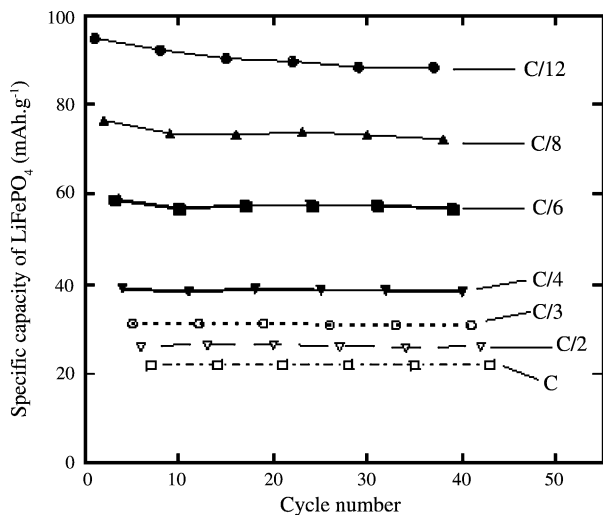


Fig. 9. Cyclability at 5 °C of DEMPy123 based batteries at different currents.

LiFePO₄ system, at 5 and 20 °C. The behavior in the solid, plastic crystalline state, and the molten state was similar (Figs. 8 and 9): The capacity retention was very good, both at 5 and 20 °C, as over 90% of the initial capacity was still available after 40 cycles; The capacity retention was also the same regardless of the discharge rate (from C/12 to C).

These observations undoubtedly show that DEMPy is a good candidate as a dual state of matter electrolyte matrix, for lithium battery applications. Moreover, the results demonstrate the viability of a system, able to switch from liquid to solid and solid to liquid states, without impeding the batteries' efficiency.

4. Conclusions

An ionic liquid that shows a plastic crystalline phase below its melting point has the advantage of sustaining most of its electrolyte properties and hence support battery performance at temperatures below melting. The DEMPy123 salt and its LiTFSI mixture show high conductivities, in the solid state and when the latter was incorporated into lithium-ion batteries of 2.5 V, it was able to support a performance in the liquid and solid (plastic crystalline) states giving 83% and 67% of the theoretical capacity, respectively. We have also conducted a comparative study of the performance of the electrolyte with conventional ionic liquid DEPy which does not show a plastic crystalline phase and crosses to its normal crystalline phase below melting. We found that it gives high performance at high temperatures that decreases rapidly at with temperatures, to disappear completely below melting point being not able to show any capacity. With the ability to reach low operating temperatures, the present work underlines the growing ability of pyrazolium imide OPCEs to compete with classic solid and liquid systems.

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