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ORIGINAL PAPER

$LiFePO_4$ cathode in *N*-methyl-*N*-propylpiperidinium and *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide

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Abstract Ternary $[Li^+][MePrPip^+][NTf_2^-]$ and $[Li^+][MePrPyrr^+][NTf_2^-]$ room temperature ionic liquids (ILs) were obtained by dissolution of solid lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$) in liquid *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide and *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide, respectively, and studied as electrolytes for the use in $Li/LiFePO_4$ or $C(Li)/LiFePO_4$ batteries. The cell worked properly in the presence of 10 wt% of vinylene carbonate (VC). Impedance-spectroscopy studies showed that the additive (VC) forms a protective coating on the anode. The $LiFePO_4$ cathode shows good efficiency (135 mAh g^{-1}) working together with $[Li^+][MePrPip^+][NTf_2^-]$ + VC and $[Li^+][MePrPyrr^+][NTf_2^-]$ + VC ionic liquid electrolytes. The flash point of ionic liquid electrolytes containing 10 wt% of VC is above 300 °C, which makes them practically non-flammable.

Keywords Ionic liquid · Lithium · $LiFePO_4$ · Lithium-ion battery · Cathode · SEI

1 Introduction

Conventional organic solvents (e.g. ethylene carbonate, propylene carbonate, dimethyl carbonate, etc.) used in Li ion cells are flammable due to the relatively high vapor pressure. However, conventional electrolytes may be replaced by practically nonvolatile and hence, nonflammable solvent-free ionic liquids (ILs) [1–8]. Dissolution of a solid lithium salt LiX in a room temperature ionic liquid $[A^+][X^-]$ leads to a liquid $[Li^+][A^+][X^-]$ ternary system containing the lithium cation, which may be applied as an electrolyte. Among ILs two of them (*N*-methyl-*N*-propylpiperidinium and *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulphonyl)imides) seem to be promising electrolytes for Li-ion batteries due to their exceptionally negative reduction potential [3, 9, 10]. These new electrolytes need examination of their compatibility with potential electrodes. It was shown that a graphite anode works properly with both ILs [11–14]. There are many possible cathode materials for application in Li-ion batteries. During the past few years considerable interest has been observed in $LiFePO_4$ as a promising cathode material for low-cost lithium batteries, because it is inexpensive, non-toxic, thermally stable and has high specific capacity (170 mAh g^{-1}) [7]. However, the Li^+ diffusion coefficient (about 10^{-16} cm s^{-1}) and electronic conductivity (about 10^{-10} S cm^{-1} at room temperature) are low [15–17]. The latter property may be improved by coupling with powders of noble metals [18, 19], conducting carbons [20–22], or by doping with an alien ion [23–25]. In this article, we report properties of a carbon coated $LiFePO_4$ cathode working together with two non-flammable ILs.

2 Experimental

2.1 Materials

Lithium iron phosphate (carbon coated, 99.5+%, $LiFePO_4$, battery grade), particles size in the range 1–4 μm (determined with Zetasizer Nano ZS, Malvern Instruments Ltd., UK) was received from Aldrich. Lithium foil (0.75 mm thick, Aldrich), graphite KS-15 (G) (Lonza),

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poly(vinylidene fluoride) (PVdF, Fluka), vinylene carbonate (VC, Aldrich), ethylene carbonate (EC, Aldrich), dimethyl carbonate (DMC, Aldrich), and lithium bis(trifluoromethanesulphonyl)imide ($LiNTf_2$, Fluka) were used as received from suppliers. *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulphonyl)imide ($[MePrPip^+][NTf_2^-]$) and *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulphonyl)imide ($[MePrPyrr^+][NTf_2^-]$) were prepared by reacting *N*-methylpiperidine (Aldrich) or *N*-methylpyrrolidine (Aldrich), with propylbromide (Aldrich) [11], followed by metathesis with lithium bis(trifluoromethanesulphonyl)-imide. Ionic liquids were dried in a rotor evaporator under vacuum at 60 °C for 10 h. Water content in ionic liquids, analyzed with a standard Karl-Fisher titrant (HYDRANAL® Composite 1), was below 0.1%. Liquid ternary $[Li^+]_m[MePrPip^+]_n[NTf_2^-]_z$ and $[Li^+]_m[MePrPyrr^+]_n[NTf_2^-]_z$ electrolytes were obtained by dissolution of solid $LiNTf_2$ (0.7 M) in ionic liquids. The tested cathode was prepared by casting $LiFePO_4 + G + PVdF$ (ratio 85:5:10) slurry in *N*-methyl-2-pyrrolidone (NMP, Fluka) on golden current collector (diameter 12 mm). The solvent (NMP) was evaporated in vacuum at 120 °C.

Lithium-metal foil protected with SEI film was prepared in the way proposed by Ue [26]. Two Li foils were separated by two separator layers soaked with the conventional 1 M $LiPF_6$ in EC + DMC 1:1 electrolyte. After polarisation with a constant current (1 mA cm^{-2}) for 1 h and for the next 1 h in the opposite direction, the cell was disassembled into two Li/SEI + separator pieces. The Li/SEI + separator system was washed with acetonitrile (P.O.Ch., Poland) and dried and further used in some experiments as a lithium counter electrode.

2.2 Measurements

Test Li/electrolyte/$LiFePO_4$ cells were assembled in a dry argon atmosphere in a glove box. Electrodes were separated by a glass micro-fibre GF/A separator (Whatman), placed in an adopted 0.5" Swagelok® connecting tube. Cycling measurements were taken with the use of the ATLAS 0461 MBI multichannel electrochemical system (Atlas-Solich, Poland) at different current rates (C/10–C/5). Constant current charging/discharging cycles were conducted between 2.5 and 4.0 V versus the lithium-metal reference electrode. The surface of the lithium counter electrode was 1.265 cm^2. Resistance at the electrode/electrolyte interface was measured using an ac impedance analyzer (Atlas–Solich system, Poland). Flash point of electrolytes was measured with the use of an open-cup (1.5 ml) apparatus, based on the Cleveland instrument. The cup was heated electrically through a sand bath, and the temperature of the electrolyte was measured with the Fluke 52 (Fluke, USA) digital thermometer. The apparatus was scaled with a number of organic compounds of known flash points.

3 Results and discussion

3.1 SEI formation

Anodes characterized by low potential, such as lithium-metal or lithiated graphite, react spontaneously with electrolyte. The performance of the test $LiFePO_4$/electrolyte/Li cell may be affected by an inefficient work of the lithium counter electrode. Although metallic lithium is not a part of lithium-ion batteries, in laboratory test cells of the cathode, lithium-metal was used as the counter electrode. Moreover, it has been shown that lithiated graphite needs the formation of a protective coating similarly to lithium [11]. Consequently, the electrolyte for a Li-ion battery, including that working with the $LiFePO_4$ cathode, is expected to form SEI, protecting the graphite anode. Therefore, properties of the cathode should be examined in an electrolyte working properly with the anode. The passivation of both the $LiFePO_4$ cathode and the lithium anode was observed using impedance spectroscopy.

Figure 1 shows impedance of the $Li|[Li^+][MePrPip^+][NTf_2^-]$ + 10 wt% $VC|LiFePO_4$ unsymmetrical cell just after its assembling (Fig. 1a) and after 100 charging/discharging (C/5) cycles (Fig. 1b). Impedance, after electrochemical SEI formation was lower in comparison to that characteristic to a fresh system. On the other hand, if the cell is left under open circuit conditions, impedance increases considerably (Fig. 2). This indicates that the electrochemical process is necessary for the formation of the protective SEI coating in the system under study. Figure 3 shows the impedance spectrum of the $LiFePO_4|[Li^+][MePrPip^+][NTf_2^-]$ + 10 wt% $VC|LiFePO_4$ symmetrical cell. The spectrum shape differs from that shown in Fig. 1 for the unsymmetrical cell, and impedance is much lower—the abscissa with the real axis suggests ohmic resistance of ca. 50 Ω cm^2. Taking into account that the cathode mass and real surface in the unsymmetrical cell was much lower in comparison to the lithium mass and surface, this suggests that resistance of the cathode, expressed versus its surface, is much lower than that characteristic for the Li/SEI system. The SEI layer on the lithium surface may also be formed in the Li/Li cell using the classical electrolyte (Li salt in cyclic carbonates) [26]. The cell after the charging and discharging process may be described as a Li/SEI/electrolyte/SEI/Li system. Figure 4 shows impedance spectra of the Li/Li cell just after its assembling and Li/SEI//SEI/Li after electrochemical SEI deposition on lithium surface ($LiPF_6$ or $LiNTf_2$ in EC + DMC). It can be seen that impedance decreases due

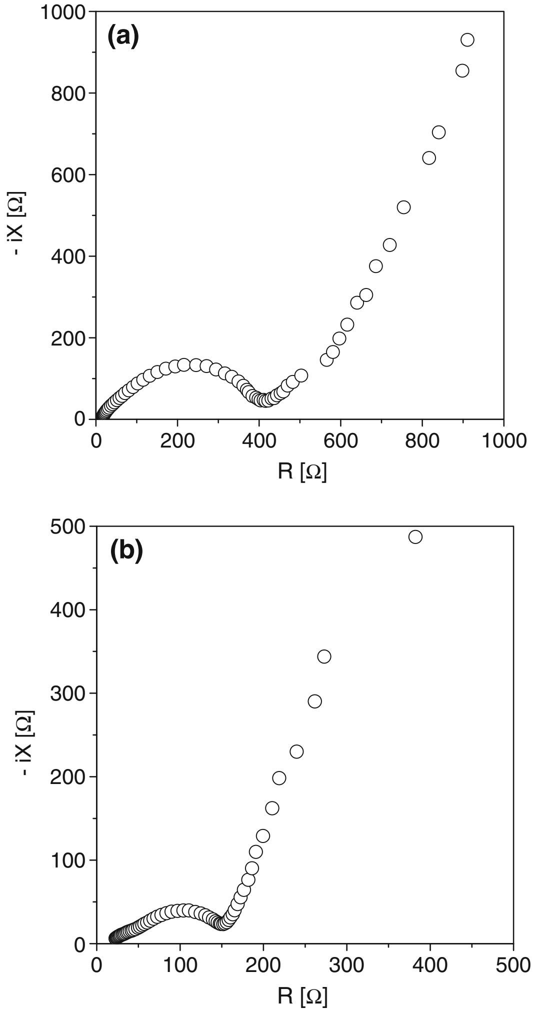

Fig. 1 Impedance spectroscopy of $\mathrm{LiFePO_4}$ $|[\mathrm{Li}^+][\mathrm{MePrPip}^+][\mathrm{NTf}_2^-]$ + 10 wt% VC|Li system (**a**) fresh cell (**b**) after 100 cycles of galvanostatic charging/discharging. Frequency range 10^5–10^{-2} Hz

to the SEI formation. The Li/SEI electrodes, after Li/SEI//SEI/Li disassembling were used to construct a number of $\mathrm{Li/LiFePO_4}$ cells.

3.2 Galvanostatic charging/discharging

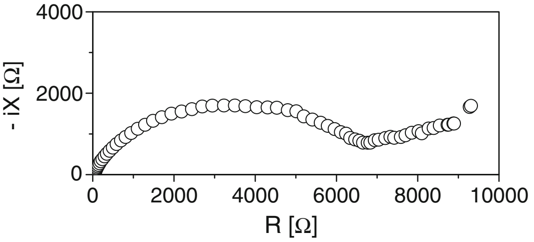

Fig. 2 Impedance spectroscopy of $\mathrm{LiFePO_4}|[\mathrm{Li}^+][\mathrm{MePrPip}^+][\mathrm{NTf}_2^-]$ +10 wt% VC|Li system kept under open circuit conditions for 24 h. Frequency range 10^5–10^{-2} Hz

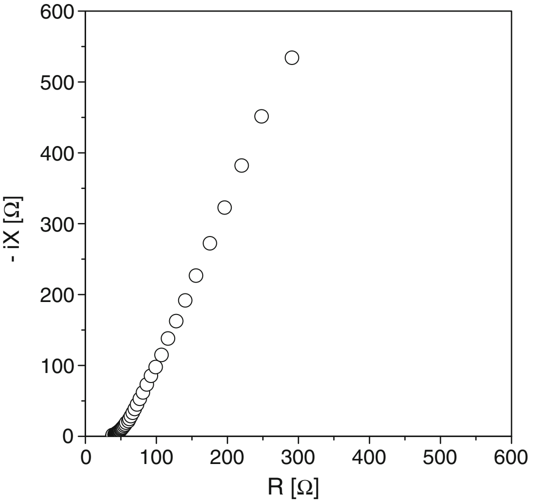

Fig. 3 Impedance spectroscopy of $\mathrm{LiFePO_4}|[\mathrm{Li}^+][\mathrm{MePrPip}^+][\mathrm{NTf}_2^-]$ +10 wt% VC|$\mathrm{LiFePO_4}$ system. Frequency range 10^5–10^{-2} Hz

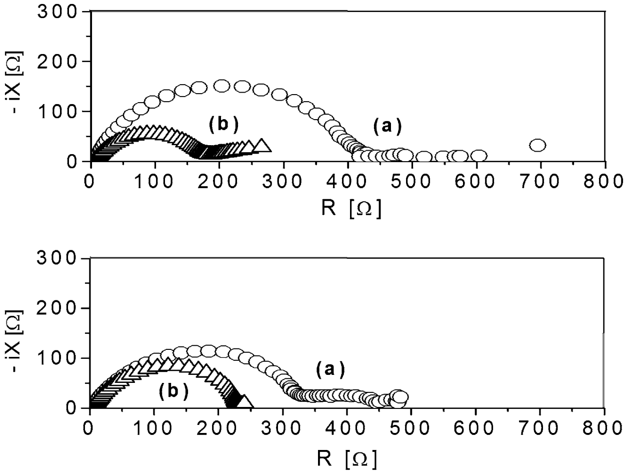

Fig. 4 Impedance spectroscopy of Li|EC + DMC + $\mathrm{LiNTf_2}$|Li and Li|EC + DMC + $\mathrm{LiPF_6}$|Li system (*a*) fresh cell (*b*) after galvanostatic SEI formation. Frequency range 10^5–10^{-2} Hz

Galvanostatic charging/discharging of the $\mathrm{Li}|[\mathrm{Li}^+][\mathrm{MePrPip}^+][\mathrm{NTf}_2^-]|\mathrm{LiFePO_4}$ cell (the electrolyte did not contain any SEI forming additive) showed that the initial charging capacity of the $\mathrm{LiFePO_4}$ cathode was only ca. 50 mAh g^{-1} to systematically decrease during the next cycles (below 10 mAh g^{-1} after 80 cycles). The low charging/discharging capacity was due to the poor performance of the lithium counter-electrode, which was discussed in the previous section. In the case of the lithium counter-electrode, electrochemically covered with the SEI protective coating before the $\mathrm{Li|SEI}/[\mathrm{Li}^+][\mathrm{MePrPip}^+][\mathrm{NTf}_2^-]|\mathrm{LiFePO_4}$ cell was assembled, the charging and discharging efficiency was much better. The initial charging capacity was ca. 150 mAh g^{-1} to stabilize at the level of ca. 85 mAh g^{-1} after four cycles. However, the charging or discharging capacity of ca. 80–90 mAh g^{-1} is much lower in comparison to the theoretical value (170 mAh g^{-1}). Much better performance is achieved after an addition of VC to the electrolyte. The charging/discharging process of the $Li|[Li^+][MePrPip^+][NTf_2^-]$ + 10 wt% $VC|LiFePO_4$, with the lithium-metal counter-electrode not initially covered with the SEI film, but formed during the charging and discharging of the cell (with the help of the VC additive) was also examined. The capacity of the initial charging and discharging was 135 and 125 mAh g^{-1}, respectively. During the next five cycles, the discharging capacity increased to an approximately constant value of 137 mAh g^{-1}. Potential versus specific capacity curves (1st, 5th and 100th cycles) for the cell with the VC additive are shown in Fig. 5. The summary of discharge capacity for cells with the piperidinium based ionic liquid electrolyte is shown in Fig. 6. The gradual decrease of the capacity of cells without VC, as well as the corresponding increase in the case of the cell containing VC, is probably due to the inefficient work of the lithium-metal counter-electrode. The procedure of SEI electrochemical pre-formation on the lithium electrode before cell assembling is not sufficient. A similar behavior was found in the case of cells filled with pyrrolidinium-based ionic liquid electrolytes. Figure 7 shows discharge capacity of the $Li|[Li^+][MePrPyrr^+][NTf_2^-]$ + 10 wt% $VC|LiFePO_4$ cell. Again, discharging capacity increased during the first five cycles to 138 mAh g^{-1}, probably due to SEI formation, to stabilize after 20 cycles at a slightly lower level (ca. 135 mAh g^{-1}).

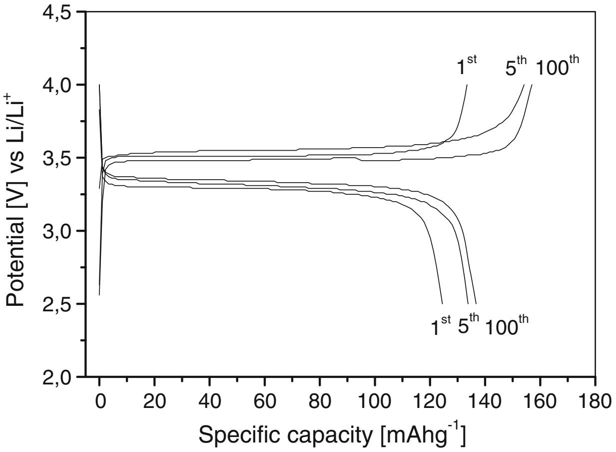

Fig. 5 Galvanostatic charging and discharging of $Li|[Li^+][MePrPip^+][NTf_2^-]$ +10 wt% $VC|LiFePO_4$ system (1st, 5th and 100th cycles) at 0.2 C rate

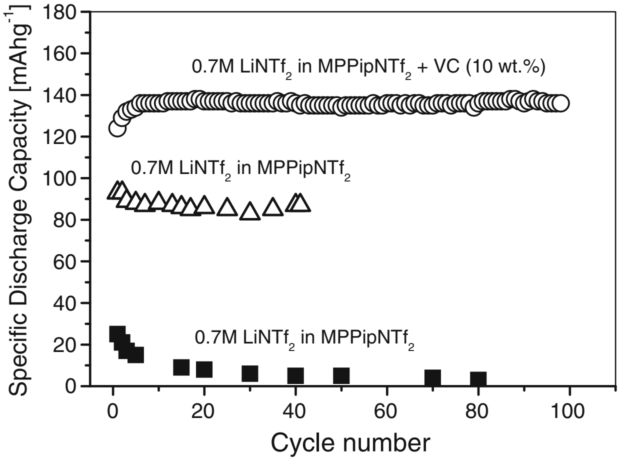

Fig. 6 Discharge specific capacity of $Li/electrolyte/LiFePO_4$ cell working with different electrolytes and lithium counter electrode (*open circle*) $Li|[Li^+][MePrPip^+][NTf_2^-]$ +10 wt% $VC|LiFePO_4$, (*open triangle*) $Li/SEI|[Li^+][MePrPip^+][NTf_2^-]|LiFePO_4$, (*filled square*) $Li|[Li^+][MePrPip^+][NTf_2^-]|LiFePO_4$; 0.2 C rate

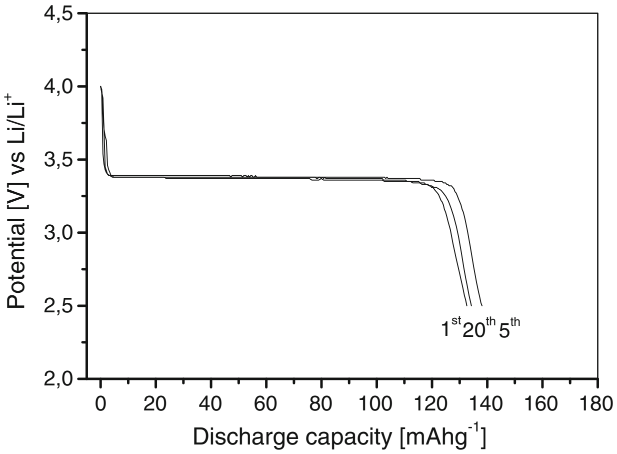

Fig. 7 Galvanostatic discharging of $Li|[Li^+][MePrPyrr^+][NTf_2^-]$ +10 wt% $VC|LiFePO_4$ cell (1st, 5th and 20th cycles) at 0.1 C rate

Results obtained in this study for the $LiFePO_4$ cathode may be compared with the corresponding literature data. The $LiFePO_4$ cathode was studied in a series of ILs or polymer electrolytes based on ILs [5, 13, 27–33]. Ionic liquids were based on pyrazolium, pyrrolidinium, imidazolium and tetraalkylammonium cations as well as bis(trifluoromethanesulphonyl)imide and bis(fluorosulphonyl)imide ($[Nf_2^-]$) anions. The $Li/[Li^+][EtMeIm^+][Nf_2^-]/LiFePO_4$ cell worked with a capacity of 126 mAh g^{-1} at a C/10 rate without any molecular additive to the electrolyte [13]. The bis(fluorosulphonyl)imide anion is probably able to form a SEI film on lithium-metal in the absence of cyclic carbonates. Lithium or lithiated graphite may be replaced by $Li_4Ti_5O_{12}$ as an anode material. It has been shown that the $Li_4Ti_5O_{12}|[Li^+][Et_2MePyrazolium^+][NTf_2^-]|LiFePO_4$ cell may work with charge/discharge efficiency of 93 and 87%, respectively, also without molecular additives [27]. The $[Et_2MePyrazolium^+][NTf_2^-]$ ionic liquid forms a single, plastic crystalline phase from 4.2 °C to its melting point at 11.3 °C [27]. It has been reported that the $Li/LiFePO_4$ cell with a polymer electrolyte based on $[Li^+][MePrPyrr^+][NTf_2^-]$ ionic liquid and poly(ethylene oxide) (PEO) works with a reasonable discharge capacity (ca. 130 mAh g^{-1}) at a moderately increased temperature (40 °C) [5, 28, 29]. Similarly, the temperature effect was found in the case of the Li/$LiFePO_4$ cell working together with polymer electrolytes based on the quaternary ammonium cation, [NTf_2^-] anion and different co-polymers [30, 31]. Charging/discharging of the Li/$LiFePO_4$ cell was also reported for the [Li^+][BuEtPyrr$^+$][NTf_2^-] ionic liquid electrolyte [32]. An increase of the cathode capacity during the cycling (similarly to that shown in Fig. 7 for the [Li^+][MePrPip$^+$][NTf_2^-] + 10% VC electrolyte) was reported.

3.3 Electrolyte flammability

Many ionic liquids, due to strong ion-ion interactions, are characterised by negligible vapour pressure, including [Li^+][MePrPip$^+$][NTf_2^-] and [Li^+][MePrPyrr$^+$][NTf_2^-] systems studied here. However, the SEI forming additive (VC) is a volatile organic compound and it is necessary to estimate the flash point of IL + VC electrolytes. It has been shown previously that the [Li^+][MePrPip$^+$][NTf_2^-] + 10 wt% electrolyte is characterized by a flash point above 300 °C [34]. Measurements with the [Li^+][MePrPyrr$^+$][NTf_2^-] + 10 wt% VC electrolyte showed the same feature: the electrolyte started to decompose at temperatures close to 300 °C, but the decomposition products did not lead to ignition (up to 300 °C). On the other hand, the flash point of the conventional 1 M $LiPF_6$ solution in EC + DMC (1:1) measured with the same apparatus was 35 °C. The difference in flash points is probably due to the fact that VC (molecular solvent) molecules in [Li^+][MePrPip$^+$][NTf_2^-] and [Li^+][MePrPyrr$^+$][NTf_2^-] are involved in ion solvation and hence they are non-volatile. The effect of reduced flammability of an electrolyte was reported recently [35]. Flammability of the $LiPF_6$ + [MePrPip$^+$][NTf_2^-] (50 wt%) + EC + DMC + EMC electrolyte was examined by soaking a glass filter with the electrolyte and exposing it to a flame for 10 s. The high content of the [MePrPip$^+$][NTf_2^-] salt resulted in the non-flammability of the system [35]. This suggests that the dissolution of a salt in a conventional electrolyte leads to a 'solvent in salt' solution of decreased vapour pressure.

4 Conclusions

(1) The $LiFePO_4$ cathode shows good efficiency (135 mAh g^{-1}) working together with [Li^+][MePrPip$^+$][NTf_2^-] and [Li^+][MePrPyrr$^+$][NTf_2^-] ionic liquid electrolytes.
(2) The flash point of ionic liquid electrolytes containing 10 wt% of VC (necessary for the proper work of the graphite or lithium anodes) is above 300 °C, which makes them practically non-flammable.

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