Short communication

Properties of the graphite-lithium anode in *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl) imide as an electrolyte

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Abstract

The ternary $[Li^+][MPPip^+][NTf_2{}^-]$ ionic liquid, obtained by dissolution of solid lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$) in liquid *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($MPPipNTf_2$), was used as an electrolyte, and stable at the lithium or graphite-lithium anodes. The graphite-lithium (C_6Li) anode showed good cyclability and Coulombic efficiency in the presence of a molecular additive (10 wt.% of vinylene carbonate, VC) to the ionic liquid. The electrode showed ca. 90% of its initial discharge capacity after 100 cycles. The addition of ethylene carbonate (EC) does not improve the cyclability of the anode to the same degree as that observed in the case of vinylene carbonate.

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1. Introduction

Graphite (G) is now the most popular anode material for lithium-ion batteries, while the cathode is usually based on a transition metal oxide, such as NiO_2, CoO_2 or MnO_2 [1,2]. All these materials are lithium-host (insertion or intercalation) compounds, and during the discharging process, the lithium ion which is released from the carbon anode (LiC_n), migrates across the electrolyte to the opposite electrode where it is inserted into its crystal structure (LiM_xO_y). As the lithium ion migrates during charging and discharging between the electrodes, the electrolyte is an important element determining the properties of the device. The electrolyte is usually applied as a lithium salt ($LiPF_6$ solution in a mixture of organic solvents (cyclic carbonates). Another type of electrolyte for lithium-ion batteries is a polymer electrolyte, formed by dissolution of a lithium salt in a polymer network (for example, poly(ethylene)oxide) [3]. The polymer electrolyte may also be applied in the form of the polymer network swollen in a solution of the lithium salt in an organic solvent (gel-type polymer electrolyte). Both types of polymer electrolytes may be prepared in the form of thin foils, and therefore, no separator is necessary in the system. The main advantage of the solvent-free polymer electrolyte is its non-volatility, which is very important from the point of view of safety. However, such electrolytes suffer from low specific conductivity. In practical applications gel-type systems may be considered as electrolytes, owing to their acceptable conductivity, but they contain volatile organic solvents. Instead of salt solutions in volatile organic solvents (or molecular liquids), molten salts may be applied in electrochemical devices. Cells filled with such kind of electrolytes do not contain any volatile components and are not flammable. Salts having a low melting point, and therefore liquid at room temperature, or even below, form a new class of liquids usually called room temperature ionic liquids (RTIL). Their general physical and chemical properties are the same as those characteristics for high temperature ionic liquids, though the practical aspects

of their handling are quite different. Moisture sensitive ionic liquids based on the imidazolium cation and chloroaluminate anion has been extensively studied since the last three decades. Recently, an increasing number of new non-haloaluminate ionic liquids have been prepared and used as solvents and electrolytes in electrochemical capacitors and in lithium-ion batteries [4,5]. Ionic liquids, being usually quaternary ammonium salts, are characterized by negligible vapour pressure, which makes them non-flammable. In addition, RTILs show a broad electrochemical stability window, usually >4 V. However, quaternary ammonium cations, cannot be applied directly in any known kind of primary or secondary batteries, due to their incompatibility with any electrode. On the other hand, it is possible to dissolve a metal salt ($[M^+][X^-]$), solid in room temperature, in an ionic liquid ($[A^+][X^-]$), with the formation of a new ionic liquid, consisting of two cations: $[M^+]_m[A^+]_n[X^-]_z$. During the last few years there has been increasing interest in such ternary ionic liquids as electrolytes for lithium or lithium-ion batteries [6–37]. One of these ionic liquids, *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($[MPPip^+][NTf_2^-]$), shows exceptionally broad electrochemical stability range of ca. 5.6 V. It has been shown that the $LiCoO_2$ cathode has good electrochemical properties when combined with the ionic liquid prepared by dissolution of lithium bis(trifluoromethanesulfonyl)imide ($[Li^+][NTf_2^-]$), which is solid in room temperature, in the $[MPPip^+][NTf_2^-]$ ionic liquid [6,15]. Lithium or graphite-lithium electrodes lose their discharge capacity in ionic liquids after a couple of charge-discharge cycles, and molecular additives, such as ethylene carbonate (EC), vinylene carbonate (VC), ethylene sulphite, or vinylene acetate, have been used to improve the electrodes properties [7,10,13,23,32]. The most popular ionic liquids, based on the 1-ethyl-3-methyl-imidazolium cation ($[EMIm^+]$), do not efficiently show the negative limit of the electrolyte cathodic decomposition. Replacing the lithium-graphite anode by such a material as Mo_6S_8, makes the reversible cycling of the battery possible [30]. However, the graphite anode may be reversibly intercalated from the ionic liquid $[Li^+][EMIm^+][NTf_2^-]$ at the presence of the VC [7]. Another ionic liquid, based on the diethyl-3-methylpyrazolium imide has been used in a cell based on $LiFePO_4$ and $Li_4Ti_5O_{12}$ electrodes [29]. On the other hand, tetralkylammonium cations ($[R_4N^+]$) show good stability, and electrolytes based on such cations may be used in batteries [15,21,24,25]. The present work reports, for the first time, properties of the graphite-lithium anode working together with an ionic liquid $[Li^+]_m[MPPip^+]_n[NTf_2^-]_z$. The performance of the graphite electrode was also studied in the presence of additives (molecular solvents).

2. Experimental

2.1. Materials

Cryptand 222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo-[8.8.8]hexacosane) was used as received from Merck. Acetonitrile (Aldrich) was distilled and kept over A3 molecular sieves. Graphite SL-20 was obtained from Superior Graphite

(USA), carbon black (CB) and poly(vinylidene fluoride) (PVdF) from Fluka, lithium foil from Aldrich (0.75 mm thick) and lithium bis(trifluoromethanesulfonyl)imide ($LiNTf_2$) from Fluka. *N*-Methyl-*N*-propyl-piperidinium bromide (MPPipBr) was obtained from *N*-methyl piperidine (Aldrich) and bromo-propane (Aldrich), dissolved in 2-propanol (P.O.Ch., Poland) and after an addition of tetrahydrofurane (P.O.Ch., Poland) white crystals of MPPipBr were precipitated. *N*-Methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($MPPipNTf_2$) was obtained from MPPipBr by metathesis with lithium bis(trifluoromethanesulfonyl)imide (Fluka) in an aqueous medium. The ionic liquid was dried by evaporation in a vacuum at 50 °C for 10 h and kept over A3 molecular sieves. The electrolyte (0.4 M solution of $LiNTf_2$ in $MPPipNTf_2$) was obtained by dissolution of solid $LiNTf_2$ in $MPPipNTf_2$. The water content in ionic liquids, analysed with a standard Karl-Fisher titrant (Aldrich, Cat. No: 22,120-1), was below the detection limit ($<4.5\,mg\,H_2O\,ml^{-1}$). Carbon electrodes were prepared by casting a slurry of the graphite, carbon black and PVdF in *N*-methyl-2-pyrrolidone (NMP, Fluka) on a copper foil (Hohsen, Japan). The ratio (G):(CB):(PVdF) was 85:5:10 (by weight). The layer of the carbon electrode, containing G, CB and the binder (PVdF) was formed by evaporation of the solvent (NMP) at 120 °C in a vacuum.

2.2. Measurements

The cycling efficiency of the lithium-graphite electrode was measured against a counter electrode consisting of the lithium foil, separated by the glass micro-fibre GF/A separator (Whatmann), placed in an adapted 0.5 in. Swagelok® connecting tube. The $G/[Li^+][MPPip^+][NTf_2^-]/Li$ cells were assembled in a dry argon atmosphere in a glove box. The measurements were done with the use of an ATLAS 0461MBI multichannel electrochemical system (Atlas-Sollich, Poland) at a constant current of $10\,mA\,g^{-1}$ of graphite. Cyclic voltammetric curves were recorded with the μAutolab electrochemical system (EcoChemie, The Netherlands). The glassy carbon electrode (Mineral Poland) had a surface of $0.070\,cm^2$. The $Ag/(Ag^+222, AN)$ reference electrode was prepared by placing an Ag wire into a solution of $AgNTf_2$ (0.01 M) and cryptand 222 (0.1 M) in acetonitrile. The tube containing the solution (obtained from a conventional calomel electrodes producer, Euro-Sensor, Poland), was separated from the tested ionic liquid by a glass frit at the tube end. Such a reference was much more stable than the Ag/Ag^+ reference commonly used in aprotic media [38]. Density of the electrolytes was measured with Anton Paar MA 35N meter.

3. Results and discussion

The solubility of the $LiNTf_2$ solid salt in liquid $[MPPip^+][NTf_2^-]$ salt was at the level of ca. 0.4 M in room temperature, with a density of ca. $1.576\,g\,cm^{-3}$. This leads to the $[Li^+][NTf_2^-]/[MPPip^+][NTf_2^-]$ mole ratio of 0.096/0.904, and the ionic liquid composition: $[Li^+]_{0.04}[MPPip^+]_{0.73}[NTf_2^-]_{0.23}$. In comparison to classical solutions of lithium salts in organic
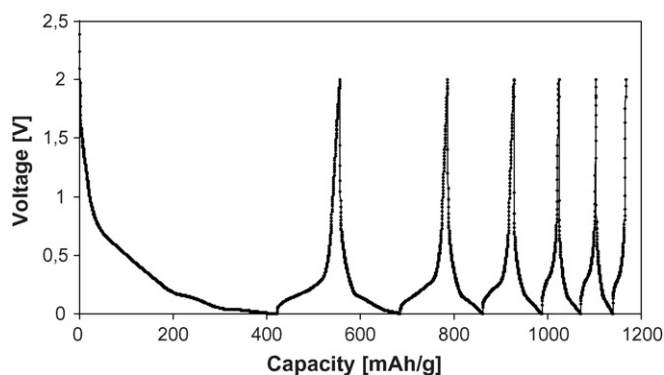
Fig. 1. Galvanostatic charging/discharging of the lithium-graphite anode. Electrolyte: 0.4 M LiNTf$_2$ in MPPipNTf$_2$. $I = 10$ mA g^{-1}. Graphite mass: 4.1 mg.

solvents, the ionic liquid contains less lithium cation versus the mass of the electrolyte. For example, the 1 M LiPF$_6$ solution in the mixture of dimethyl carbonate (DMC) and EC, has the density of ca. 1.282 g cm^{-3}, and the composition [Li$^+$]$_{0.07}$[PF$_6$]$_{0.07}$[DMC]$_{0.43}$[EC]$_{0.43}$. However, at higher Li$^+$ content in the ternary [Li$^+$][MPPip$^+$][NTf$_2^-$] ionic liquid, the system showed a tendency to form a crystalline solid phase. Fig. 1 shows the charging/discharging curve for the G/[Li$^+$][MPPip$^+$][NTf$_2^-$]/Li cell (without any additive to the ionic liquid electrolyte). It can be seen that in this case the system G/IL/Li is not reversible. This effect may be caused by destruction of the tested graphite anode or passivation of the metal-lithium counter electrode. Fig. 2 illustrates charging/discharging curves, for a number of cycles, for the graphite anode with the electrolyte containing 10 wt.% of VC as an additive. After the first cycle, the capacity of the graphite is at the level of ca. 340 mAh g^{-1}, close to its maximum theoretical value (ca. 370 mAh g^{-1}). The electrode showed ca. 90% of its initial discharge capacity after 100 cycles, at charge/discharge current at the level of 10 mA g^{-1} of graphite. The addition of a smaller amount of VC (5 wt.%) somewhat improves the cyclability, in comparison to the ionic liquid without any additive, but a systematic decrease of Coulombic efficiency can be seen (Fig. 3).
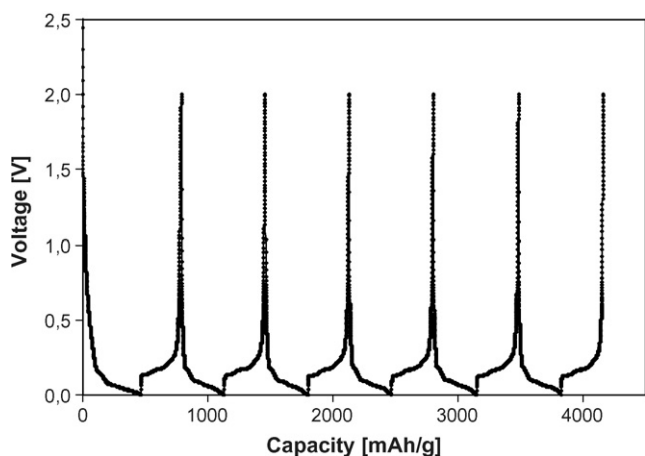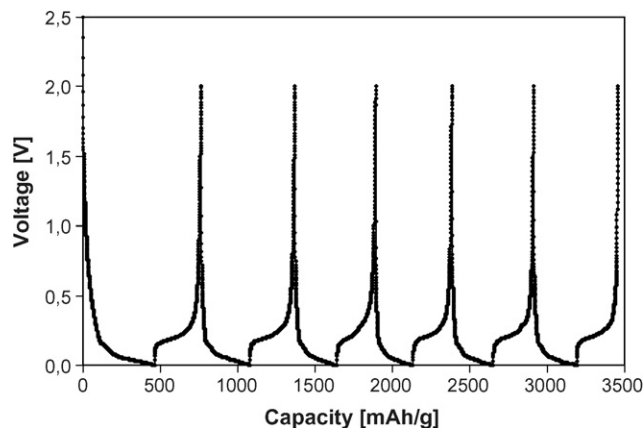

Fig. 3. Galvanostatic charging/discharging of the lithium-graphite anode. Electrolyte: 0.4 M LiNTf$_2$ in MPPipNTf$_2$ + 5 wt.% VC. $I = 10$ mA g^{-1}. Graphite mass: 4.0 mg.

However, ethylene carbonate as an additive does not stabilize the graphite anode (Fig. 4). Comparison of the Coulombic efficiency for the graphite anode working together with the neat ionic liquid, as well as with different additives is shown in Fig. 5. The discharge capacity of the graphite working together with the ionic liquid containing 10 wt.% of VC is close to the maximum theoretical value (Fig. 6). The problem of the limited efficiency is characteristic not only for the graphite-ionic liquid system. The carbon anode has a limited cycle-life due to graphite exfoliation during its continuous intercalation and de-intercalation processes, which leads to the degradation of the electrode structure. It has been suggested that in the case of electrolytes based on cyclic carbonates the capacity lost is mainly, or even solely, caused by the solvent reduction at the electrode with the formation of ROCO$_2$Li, ROLi or lithium carbonates [40–42]. The performance of the electrode may be improved by an addition of Li$_2$CO$_3$ (or CO$_2$ with further formation of Li$_2$CO$_3$) in the case of dioxalane as molecular solvent [39]. Generally, the electrochemical reaction of the electrolyte additive (for example, lithium carbonate or salicyloborate, vinylene carbonate, etc.) at the graphite electrode may result in the formation of a coating, and the modification of the electrode surface. Vinylene carbonate seems to be one of the most effective additives to the electrolyte.
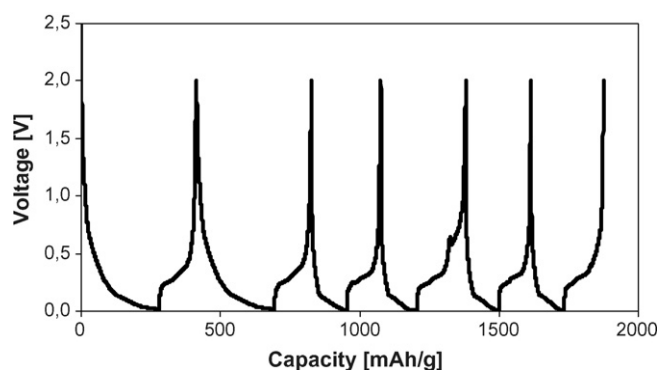

Fig. 2. Galvanostatic charging/discharging of the lithium-graphite anode. Electrolyte: 0.4 M LiNTf$_2$ in MPPipNTf$_2$ + 10 wt.% VC. $I = 10$ mA g^{-1}. Graphite mass: 4.1 mg.

Fig. 4. Galvanostatic charging/discharging of the lithium-graphite anode. Electrolyte: 0.4 M LiNTf$_2$ in MPPipNTf$_2$ + 5 wt.% EC. $I = 10$ mA g^{-1}. Graphite mass: 4.2 mg.
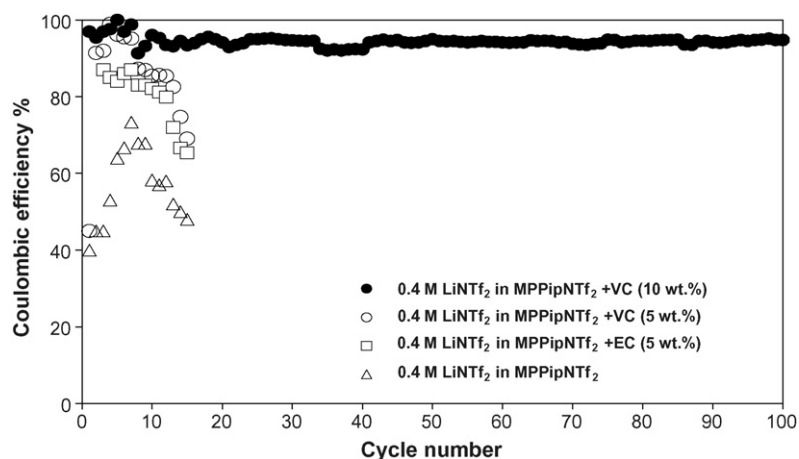
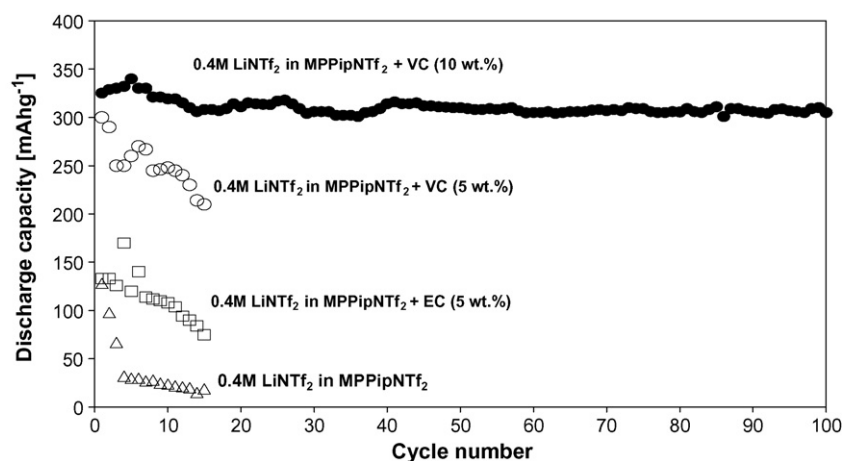Fig. 5. Coulombic efficiency of the lithium-graphite anode working with different electrolytes.

Fig. 6. Discharge capacity of the lithium-graphite anode working with different electrolytes.

It was used in the case of such an electrolyte as $LiPF_3(CF_2CF_3)_3$ (a salt that may replace $LiPF_6$) [42] or ionic liquids [7,10,13]. The problem is more complicated due to the fact that the rate and degree of the electrode degradation, and hence, the capacity decrease, depends not only on the electrolyte, but also on the graphite. The carbon material, used for the anode preparation, may be produced from different precursors and under different conditions, which results in a variety of final products. In each case there is a specific carbon/electrolyte electrochemical system. Taking into account the fact that a variety of carbon types, as well as different electrolytes (including ionic liquids) may be assembled together and tested, the number of possible carbon/electrolyte systems seems to be high. Lithium intercalation into the graphite anode takes places at quite negative potentials, and therefore, the electrolyte must be stable at these potentials. On the other hand, applying high voltage cathodes, such as nickel or cobalt oxides, makes it necessary to use electrolytes characterized by an anodic oxidation limit shifted to quite positive potentials. The electrochemical stability window of the $[MPPip^+][NTf_2^-]$ neat ionic liquid, detected at glassy carbon, is of ca. 5.7 V (Figs. 7 and 8 show CV on glassy carbon for $[MPPip^+][NTf_2^-]$ and $[Li^+][MPPip^+][NTf_2^-]$, respectively). The cathodic reduction of the electrolyte takes place at ca.

-3 V. The potential of the lithium-metal/Li^+ couple is somewhat more positive in comparison to the cathodic stability limit of the electrolyte ($E^o(Li//[Li^+][MPPip^+][NTf_2^-] = -2.62$ V versus the Ag/Ag^+222 in AN reference), which indicates the
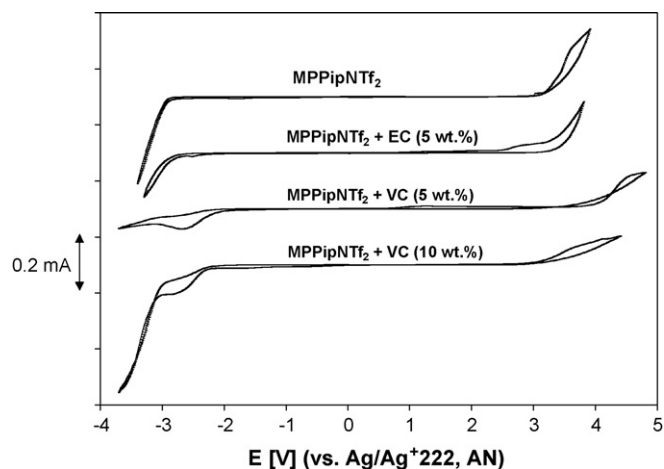
Fig. 7. Ionic liquid stability on glassy carbon. Potentials expressed vs. the $\{Ag/(Ag^+ \ (0.01\,M) + cryptand \ 222 \ (0.1\,M) \ in \ AN)\}$ reference. Scan rate: $5\,mV\,s^{-1}$. Room temperature.
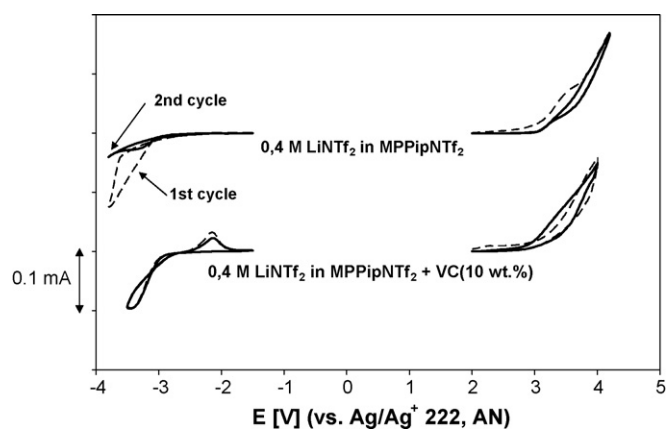
Fig. 8. Cyclic voltammetry of lithium containing ionic liquids on glassy carbon. Potentials expressed vs. the $\{Ag/(Ag^+ (0.01\,M) + \text{cryptand } 222\,(0.1\,M) \text{ in AN})\}$ reference. Scan rate: $5\,mV\,s^{-1}$. Room temperature.

stability of the tested anode in the system. However, the graphite anode is not reversible in such a medium. After the addition of ethylene carbonate to the $[Li^+][MPPip^+][NTf_2{}^-]$ electrolyte, the lithium-graphite anode is still not reversible, while after the addition of vinylene carbonate the graphite electrode show reversible intercalation of lithium. For the latter system (90 wt.% $(Li^+][MPPip^+][NTf_2{}^-]$ + 10 wt.% VC) the cathodic limit of the electrolyte oxidation is also shifted to more positive potentials, in comparison to the neat ionic liquid $([Li^+][MPPip^+][NTf_2{}^-])$, and shows the reduction limit comparable to the potential of the metallic lithium electrode (ca. -2.8 V versus the $Ag/Ag^+ 222$, AN reference). The cyclic voltammograms of the $[Li^+][MPPip^+][NTf_2{}^-]$ electrolyte, recorded separately at the cathodic and anodic regions, is shown in Fig. 8, and it is clear that the lithium plating–stripping from the ionic liquid without any additive is not reversible. On the other hand, both stripping as well as plating peaks, can be seen in the electrolyte containing VC. However, the process is driven by a significant overpotential. Ionic liquids based on the piperidinium cation $[Li^+][MPPip^+][NTf_2{}^-]$ with VC as an additive seems to be the next type of RTILs which can form an electrolyte stable at negative potentials, characteristic for the lithium-graphite anode, as well as working together with the $LiCoO_2$ cathode [31,32].

A relatively small energy source (for example, heat of charging or discharging) is sufficient to heat a lithium-ion cell to the temperature above which the solvent vapour pressure may start the release of the electrolyte from the cell, especially near the cathode. Organic electrolytes are highly flammable and they easily ignite. Therefore, for safety reasons, it is of practical significance to look for fire-retardant additives to classical electrolytes, or new non-volatile electrolytes. Ionic liquids are characterized by negligible vapour pressure; however, they are not good electrolytes for lithium-ion batteries. On the other hand, ionic liquids with additives, such as VC, show acceptable electrochemical performance, but they contain some amount of volatile organic compounds. It is interesting to estimate the volatility of such mixtures, consisting of large amount of salts and a low amount of solvent, called salt-in solvent mixtures. In such a system the solvent, due to its low concentration, may

be strongly bound to ions forming the ionic liquid. Studies on the cyclic carbonate–lithium solvato-complexes [43] show that the lithium salvation number is 2–3 (in solution in cyclic carbonates). This indicates that for the lithium concentration at the level of $[Li^+] \approx 0.4\,M$, approximately 5–7 wt.% of VC may be bound to the Li^+ ion. However, the solvation in ionic liquids has not been studied, and a systematic examination of additives vapour pressure over lithium containing ionic liquids, together with flammability tests, is necessary to estimate the safety of such electrolytes.

4. Conclusions

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1. The ternary $[Li^+][MPPip^+][NTf_2{}^-]$ ionic liquid, obtained by dissolution of solid $LiNTf_2$ salt in liquid $MPPipNTf_2$ salt, can be used as an electrolyte, stable against the cathodic reduction at the lithium or graphite-lithium anodes.
2. The graphite-lithium (C_6Li) anode shows good cyclability and Coulombic efficiency in the presence of additives (10 wt.% of VC) to the ionic liquid.
3. The addition of EC does not improve the cyclability of the anode to the same degree as that observed in the case of VC.

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