



Lithium insertion in graphite from ternary ionic liquid–lithium salt electrolytes: II. Evaluation of specific capacity and cycling efficiency and stability at room temperature

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ABSTRACT

In this paper we report the results about the use of ternary room temperature ionic liquid–lithium salt mixtures as electrolytes for lithium-ion battery systems. Mixtures of *N*-methyl-*N*-propyl pyrrolidinium bis(fluorosulfonyl) imide, PYR₁₃FSI, and *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide, PYR₁₄TFSI, with lithium hexafluorophosphate, LiPF₆ and lithium bis(trifluoromethanesulfonyl) imide, LiTFSI, containing 5 wt.% of vinylene carbonate (VC) as additive, have been used in combination with a commercial graphite, KS6 TIMCAL. The performance of the graphite electrodes has been considered in term of specific capacity, cycling efficiency and cycling stability. The results clearly show the advantage of the use of ternary mixtures on the performance of the graphite electrode.

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1. Introduction

Lithium-ion batteries are today the only high-energy density portable power sources commercially available. These electrochemical systems consist of graphite-based electrodes in combination with electrolytes commonly based on organic carbonates (e.g. propylene carbonate, PC; ethylene carbonate, EC). These devices have several advantages such high-energy density and good cycling stability, however, as the organic carbonates are flammable, the use of such electrolytes poses a serious safety risk and strongly reduces the battery operative temperature range [1,2]. This problem, rather than the electrical performance, represents the main drawback presently holding the lithium-ion technology from a wide deployment in hybrid electric vehicles.

Ionic liquids (ILs) represent a very interesting new class of room temperature fluids. The main advantages of ILs towards organic solvents are: non-flammability, negligible vapor pressure, high chemical and thermal stability and, in some cases, hydrophobic-

ity. Therefore, ILs have attracted a large attention for use as “green” solvents and recently have been intensively investigated as electrolytes (or electrolyte components) for various electrochemical devices due to their high ionic conductivity and electrochemical stability [3–16].

So far, different types of ILs have been already used in combination with several cathodic and anodic materials for lithium-ion batteries and the results of these studies have shown that ILs can be successfully used as alternative electrolytes in these systems [17–23]. Since carbon anodes are today the “state of the art” in the lithium batteries technology, particular attention has been dedicated to these anodic materials and the obtained results appear quite promising [21–23].

Recently, we investigated the use of two different ultrapure ionic liquids, *N*-butyl-*N*-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR₁₄TFSI) and *N*-methyl-*N*-propylpyrrolidinium bis(fluorosulfonyl)imide (PYR₁₃FSI) in combination with graphite electrodes [24]. PYR₁₄TFSI and its mixtures with lithium salts were found to have a good room temperature ionic conductivity (>1 mS cm⁻¹) and a cathodic stability window extending below the lithium plating/stripping potential and an overall stability window exceeding 5.5 V [25]. *N*-methyl-*N*-propyl pyrrolidinium bis(fluorosulfonyl) imide, PYR₁₃FSI, is characterized by a lower viscosity because of the reduced steric hindrance of the (PYR₁₃)⁺ cation

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and, especially, the $(\text{FSI})^-$ anion. In addition, $\text{PYR}_{13}\text{FSI}$ exhibits a lower melting point thus resulting in its high conductivity values (1.8 mS cm^{-1}) also at low temperatures (-5°C). Nevertheless, the $\text{PYR}_{13}\text{FSI}$ shows a lower electrochemical stability window than $\text{PYR}_{14}\text{TFSI}$ and, also important, a much higher cost due to the more difficult purification of the FSI^- anion. The results of our studies indicated that when ultrapure ILs are used as electrolytes in combination with graphite electrodes, the need of additives (vinylene carbonate, VC) in the electrolyte solution is strictly related to the film-forming ability of the ILs themselves. For instance, in electrolyte solutions based on the ultrapure $\text{PYR}_{14}\text{TFSI}$ the use of VC appears to be indispensable because such IL does not display film-forming ability. To the contrary, in electrolyte solutions based on $\text{PYR}_{13}\text{FSI}$ the presence of VC was not strictly required because this IL displayed film-forming ability [24]. In order to verify if the favorable properties of these two ILs could be combined, blends of $\text{PYR}_{13}\text{FSI}$ and $\text{PYR}_{14}\text{TFSI}$ were prepared and, in order to increase the performance of the investigated electrolytic solutions, VC was always used as additive.

Since it is well known that the selection of the lithium salt strongly influences the performance of lithium-ion batteries, the role of two suitable lithium salts, LiTFSI and LiPF_6 was also considered. LiTFSI was selected because the anion TFSI^- was already present in one of the two ionic liquids. LiPF_6 was selected because it is the most common lithium salt employed in lithium-ion batteries [26] since it offers good electrolyte conductivity [27,28], good film-forming ability and, finally, stabilize the cathodic (aluminum) current collector toward oxidation [29].

In the present work we focused the investigation on the use of LiTFSI and LiPF_6 as lithium salts in combination with the ionic liquids $\text{PYR}_{14}\text{TFSI}$, $\text{PYR}_{13}\text{FSI}$ and their mixtures (containing VC as additive) as electrolytes for lithium-ion battery systems. The considered mixtures were used in combination with commercial KS-6 TIMCAL[®] graphite. KS-6 TIMCAL[®] graphite displays high crystallinity and specific area ($20 \text{ m}^2 \text{ g}^{-1}$) and, most importantly, it is very sensitive to the electrolyte properties. This latter characteristic makes it as an appropriate candidate for the investigation of the SEI formation mechanism at the electrode/electrolyte (IL) interface.

The influences of the considered mixtures on the specific capacity, the cycling efficiency and the cycling stability of the electrodes have been investigated at RT. The results are reported in this paper.

2. Experimental

2.1. Synthesis of ionic liquids and preparation of the ternary mixtures

The $\text{PYR}_{14}\text{TFSI}$ and $\text{PYR}_{13}\text{FSI}$ room temperature ionic liquids and their mixtures were synthesized and dried as previously reported [30,31].

2.2. Preparation of electrode and electrochemical tests

The composite electrodes consisted of commercial graphite (TIMCAL[®] KS-6), conductive carbon additive (Super-P) and polyvinylidene fluoride (PVdF) binder (Kynar[®]7 61). The graphite electrodes contained 90 wt.% TIMCAL[®] KS-6, 7 wt.% Super-P and 3 wt.% PVdF. The mass loading of the prepared electrodes was approximately 1 mg cm^{-2} . Three-electrode cells assembled under dry Argon in a glove box were used for all the electrochemical tests. Li metal was used for both counter and reference electrode. As separator a polypropylene Freudenberg fleeces (FS2190) discs were used, drenched in $80 \mu\text{L}$ of electrolyte solution.

Cyclic voltammetry (CV) has been performed with a laboratory made potentiostat (Adesys[®]) at a scan rate of $50 \mu\text{V s}^{-1}$ in the

potential range between 3000 and 0 mV vs. Li/Li^+ in the first cycle and between 1500 and 0 mV vs. Li/Li^+ in the following cycles. The constant current cycling (CC) was performed with a Maccor Series 4000 battery tester with a C-rate of 1.

All the experiments have been carried out at room temperature.

3. Results and discussion

Fig. 1 shows the cyclic voltammogram (CV) of a KS-6 graphite electrode in the electrolyte solution containing 0.3 M LiTFSI in $\text{PYR}_{14}\text{TFSI}$ without (a) and with (b) VC as additive electrolyte. As shown in the figure, the KS6 graphite electrode in absence of VC displayed poor electrochemical performance and high irreversibility of the Li intercalation–deintercalation process. On the contrary, when VC was present in the electrolyte, the system showed better electrochemical performance and stability during prolonged

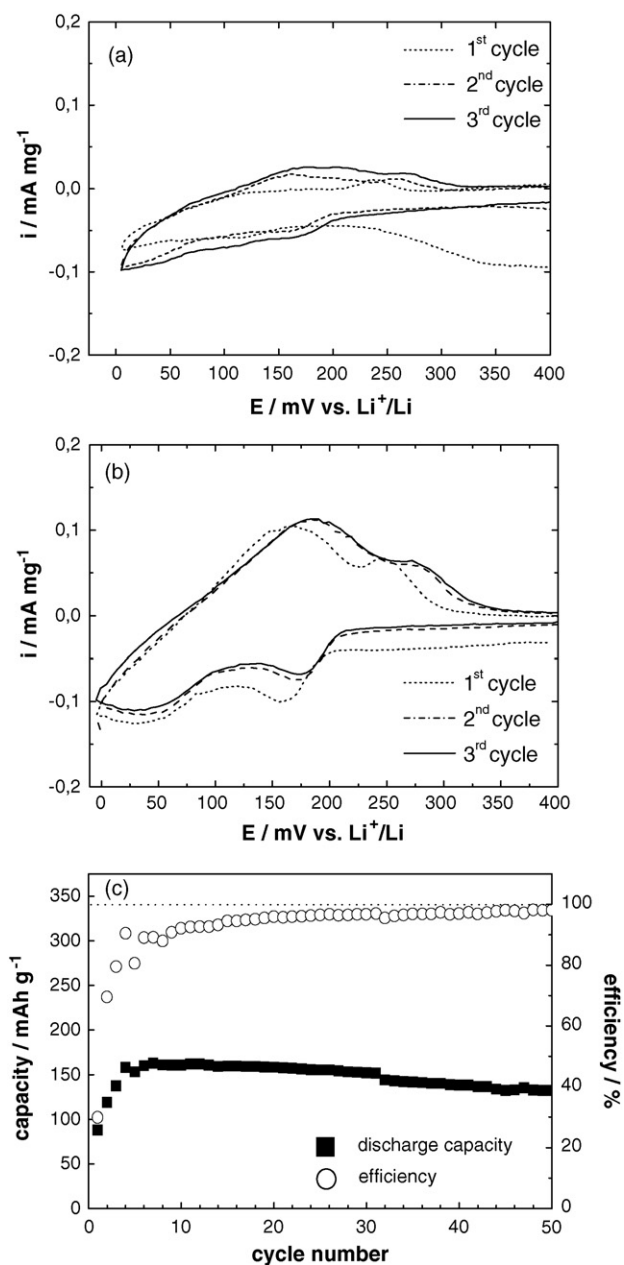


Fig. 1. KS-6 graphite electrode in 0.3 M LiTFSI in $\text{PYR}_{14}\text{TFSI}$: (a) CVs at $50 \mu\text{V s}^{-1}$ without VC as additive electrolyte; (b) CVs at $50 \mu\text{V s}^{-1}$ with VC as additive electrolyte; (c) CC at 1 C with VC as additive electrolyte.

charge–discharge galvanostatic cycles with a specific capacity of ca. 130 mAh g^{-1} (Fig. 1c). Therefore, the VC additive seems to be indispensable for the formation of the SEI layer on the KS6-based electrodes immersed in $\text{PYR}_{14}\text{TFSI}$ -based electrolytes.

In situ FTIR studies showed that the absence of film formation in the VC-free, $\text{PYR}_{14}\text{TFSI}$ -based electrolyte is obviously related with the high cathodic stability of this IL. In the considered range of potential $\text{PYR}_{14}\text{TFSI}$ does not decompose thus leaving the decomposition of VC as the only source of reactive chemicals for an effective SEI formation at the electrolyte/electrode interface [24].

When the electrolyte based on $\text{PYR}_{13}\text{FSI}$ was considered, the observed behavior was different. In fact, KS-6 graphite electrode in combination with 0.3 M LiTFSI in $\text{PYR}_{13}\text{FSI}$ electrolyte showed cycling stability and specific capacitance (during charge–discharge galvanostatic tests) comparable to those observed in 0.3 M LiTFSI in $\text{PYR}_{14}\text{TFSI} + 5 \text{ wt.}\% \text{ VC}$. When VC was added into the electrolyte solution, the irreversibility of the Li intercalation–deintercalation process was slightly decreased, but cycling stability and specific capacitance (during charge–discharge galvanostatic tests) were comparable to that of the solution without VC (ca. 130 mAh g^{-1}) (Fig. 2). Therefore, in the case of electrolyte solution based on $\text{PYR}_{13}\text{FSI}$ the use of additive is not strictly necessary because the $\text{PYR}_{13}\text{FSI}$ displays an intrinsic film-forming ability. In situ FTIR studies showed that intrinsic film-forming ability of $\text{PYR}_{13}\text{FSI}$ is given by the decomposition of the FSI^- anion that leads to the formation of an effective SEI. Considering the irreversibility of the Li intercalation–deintercalation process, the cycling stability and the values of specific capacity, the SEI formed by the decomposition of the FSI^- anion seems to display stability comparable with that of the electrolytic solutions containing $\text{PYR}_{14}\text{TFSI}$ and VC.

It is well known that the selection of the Li-salt plays a crucial role in electrolyte solutions based on organic carbonates since it may strongly affect the SEI formation process as well as the performance of the lithium-ion batteries. LiPF_6 is today the most common lithium salt employed in lithium-ion batteries and display good performances in contact with carbonaceous anodes. For these reasons, in order to evaluate the influence of the Li-salt in ILs-based electrolyte, we considered the LiPF_6 in combination with $\text{PYR}_{14}\text{TFSI}$ and $\text{PYR}_{13}\text{FSI}$.

Fig. 3 shows the CV of a KS-6 graphite electrode in combination with the electrolytic solution containing 0.3 M LiPF_6 in $\text{PYR}_{14}\text{TFSI}$ without (a) and with (b) VC as electrolyte additive. Like in the case of the system with LiTFSI , the use of VC seems to be indispensable for the formation of the SEI layer on the KS6-based electrodes immersed in $\text{PYR}_{14}\text{TFSI}$ -based electrolytes. When VC was used the specific capacity of the system increased of nearly 30% (180 mAh g^{-1} , Fig. 3c) with respect to that obtained with LiTFSI , but the stability during prolonged charge–discharge galvanostatic cycles was reduced (results not shown).

The increase in performance was even higher when 0.3 M LiPF_6 in $\text{PYR}_{13}\text{FSI}$ was used as the electrolyte. In fact, in this electrolytic solution the irreversibility of the Li intercalation–deintercalation process decreased and the specific capacity considerably increased to reach 300 mAh g^{-1} , a value more than two times higher than that of the electrolyte solution containing LiTFSI (Fig. 4). When VC was added into the electrolyte based on $\text{PYR}_{13}\text{FSI}$ the irreversibility of the Li intercalation–deintercalation process slightly decreased while the specific capacitance was comparable to that of the solution without VC (like in the case of the system containing LiTFSI). However, both the systems displayed much lower cycling stability with respect to the systems containing LiTFSI (results not shown).

These results clearly show the strong influence of the couple IL/Li-salt on the performance of the graphite electrodes. For example, using the couple $\text{PYR}_{13}\text{FSI}$ – LiPF_6 and VC as additive it is possible to achieve the best performance in terms of reversibility of the Li intercalation–deintercalation process and specific capacity, but

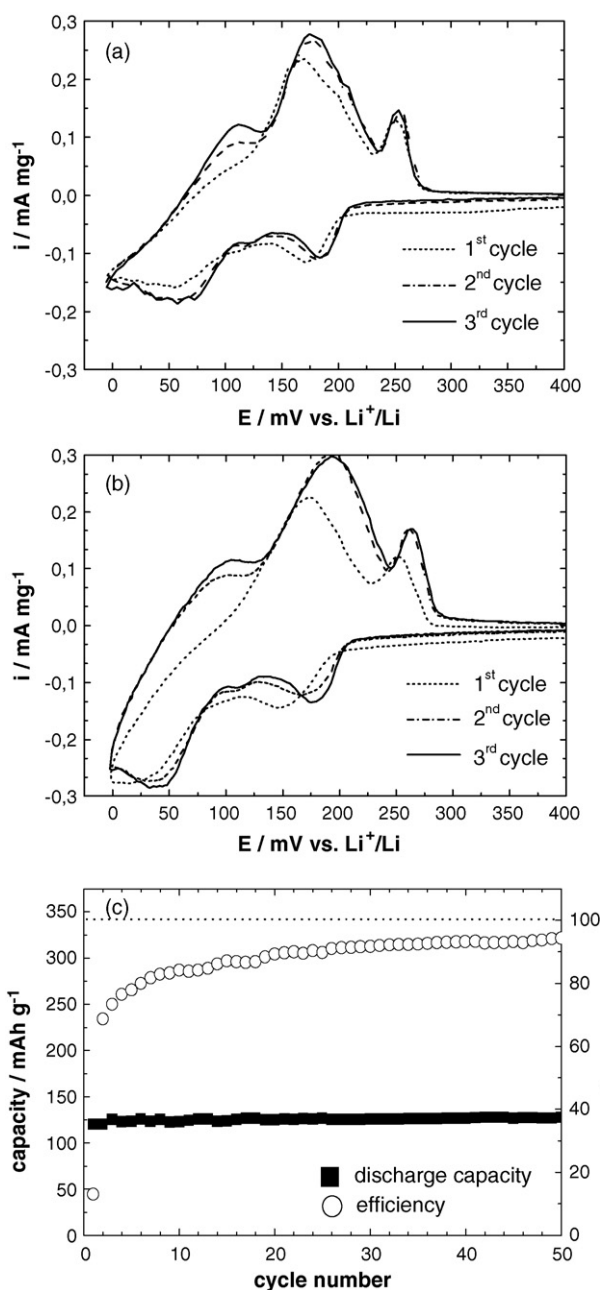


Fig. 2. KS-6 graphite electrode in 0.3 M LiTFSI in $\text{PYR}_{13}\text{FSI}$: (a) CVs at $50 \mu\text{V s}^{-1}$ without VC as additive electrolyte; (b) CVs at $50 \mu\text{V s}^{-1}$ with VC as additive electrolyte; (c) CC at 1 C with VC as additive electrolyte.

not a sufficient cycling stability. To the contrary, using the couple $\text{PYR}_{14}\text{TFSI}$ – LiTFSI and VC as additive is possible to obtain very good cycling stability but low performance in term of the reversibility of the Li intercalation–deintercalation process and specific capacity. These differences are related with the characteristics of the ILs. As reported, $\text{PYR}_{14}\text{TFSI}$ displays a wide electrochemical stability window (exceeding 5 V), while $\text{PYR}_{13}\text{FSI}$ displays high conductivity (1.8 mS cm^{-1}) at low temperature ($-5 \text{ }^\circ\text{C}$) and film-forming ability.

It is obvious that an electrolyte able to display the favorable characteristics of $\text{PYR}_{14}\text{TFSI}$ and $\text{PYR}_{13}\text{FSI}$ at the same time would be a very promising candidate. For that, in order to verify if the favorable properties of the two ILs could be combined, mixtures of $\text{PYR}_{14}\text{TFSI}$ and $\text{PYR}_{13}\text{FSI}$ were prepared. In a previous manuscript several ternary $(x)\text{PYR}_{13}\text{FSI}/(1-x)\text{PYR}_{14}\text{TFSI}/\text{LiTFSI}$ and $(x)\text{PYR}_{13}\text{FSI}/(1-x)\text{PYR}_{14}\text{TFSI}/\text{LiPF}_6$ mixtures were prepared and

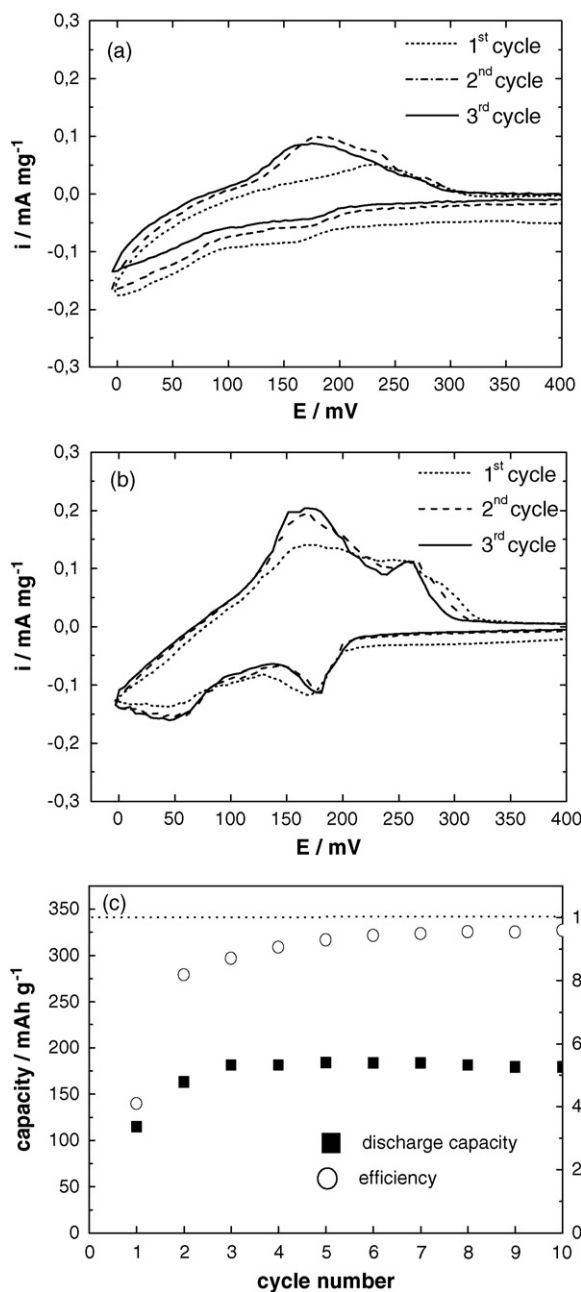


Fig. 3. KS-6 graphite electrode in 0.3 M LiPF₆ in PYR₁₄TFSI: (a) CVs at 50 μV s⁻¹ without VC as additive electrolyte; (b) CVs at 50 μV s⁻¹ with VC as additive electrolyte; (c) CC at 1 C with VC as additive electrolyte.

their electrochemical stability window and ionic conductivity were evaluated [30].

In this paper, two ternary (*x*)PYR₁₃FSI/(1 - *x*)PYR₁₄TFSI/Li-salt (described in Table 1 and indicated as A and B) have been selected on the base on their electrochemical properties and used as electrolyte solutions in combination with KS-6 graphite electrodes (see Table 1). VC was added since it is a necessary component in electrolytic solutions containing PYR₁₄TFSI and it is able to increase the efficiency of the Li intercalation–deintercalation in electrolytic solutions containing PYR₁₃FSI.

Fig. 5a shows the CV curves of KS-6 graphite electrodes in combination with the ternary mixtures A and B containing 0.3 M LiTFSI and, for comparison, with electrolyte solutions of 0.3 M LiTFSI in PYR₁₄TFSI + 5 wt.% VC and of 0.3 M LiTFSI in PYR₁₃FSI + 5 wt.% VC (indicated as C and D, respectively). In Table 2

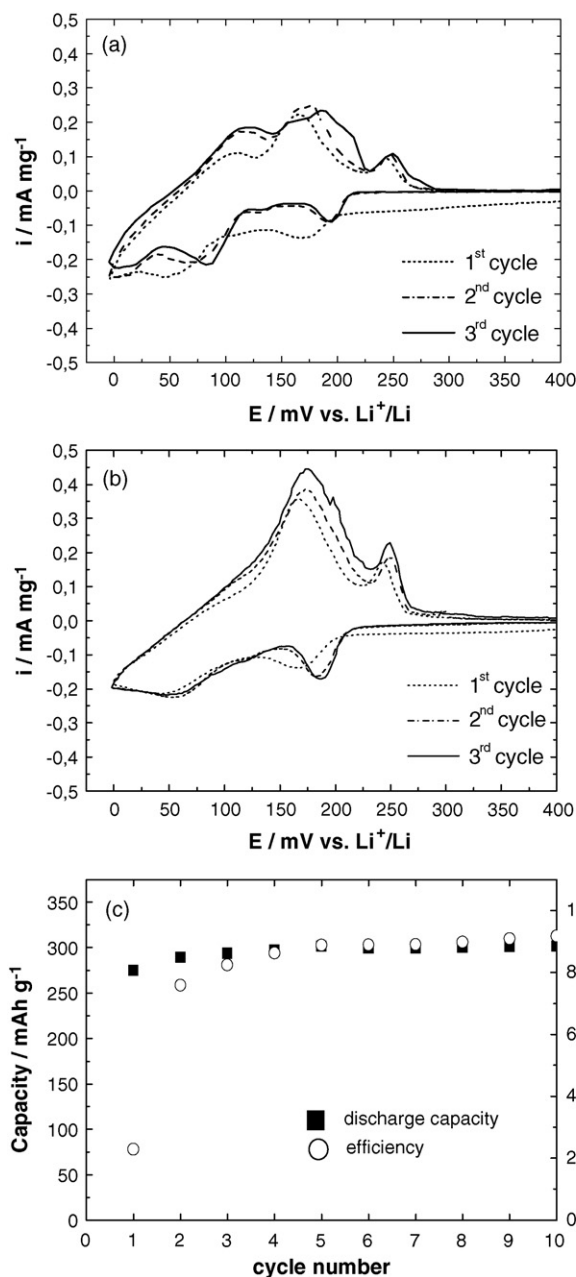


Fig. 4. KS-6 graphite electrode in 0.3 M LiPF₆ in PYR₁₃FSI: (a) CVs at 50 μV s⁻¹ without VC as additive electrolyte; (b) CVs at 50 μV s⁻¹ with VC as additive electrolyte; (c) CC at 1 C with VC as additive electrolyte.

Table 1

Mole composition of (*x*)PYR₁₃FSI/(1 - *x*)PYR₁₄TFSI/(0.3 M)LiTFSI and (*x*)PYR₁₃FSI/(1 - *x*)PYR₁₄TFSI/(0.3 M)LiPF₆ ternary mixtures. The parameters *x* and (1 - *x*) are the mole fractions of PYR₁₃FSI and PYR₁₄TFSI, respectively. The weight fractions of PYR₁₃FSI and PYR₁₄TFSI are reported for comparison purpose. The lithium salt (i.e., LiTFSI and LiPF₆) concentration was fixed to 0.3 M. Also 5 wt.% of VC was added into the mixtures.

Mixture	PYR ₁₃ FSI		PYR ₁₄ TFSI	
	Mole fraction	Weight fraction	Mole fraction	Weight fraction
A	0.25	0.20	0.75	0.80
B	0.58	0.50	0.42	0.50
C	0.00	0.00	1.00	1.00
D	1.00	1.00	0.00	0.00

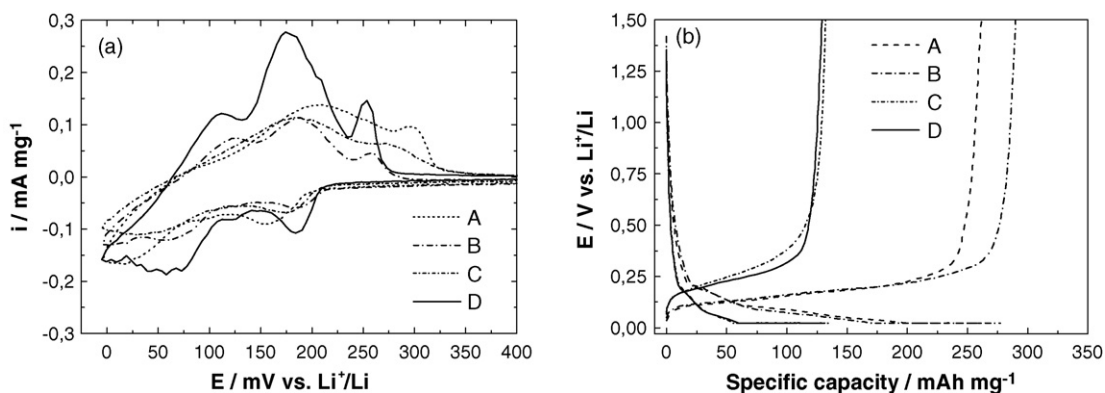


Fig. 5. KS-6 graphite electrode in mixtures of ILs (A and B) and in single IL electrolytic solution (C and D) containing 0.3 M LiTFSI at RT: (a) overlay of the CV curves (3rd cycle) at $50 \mu\text{V s}^{-1}$; (b) overlay of the calculated specific capacity from CC at 1 C.

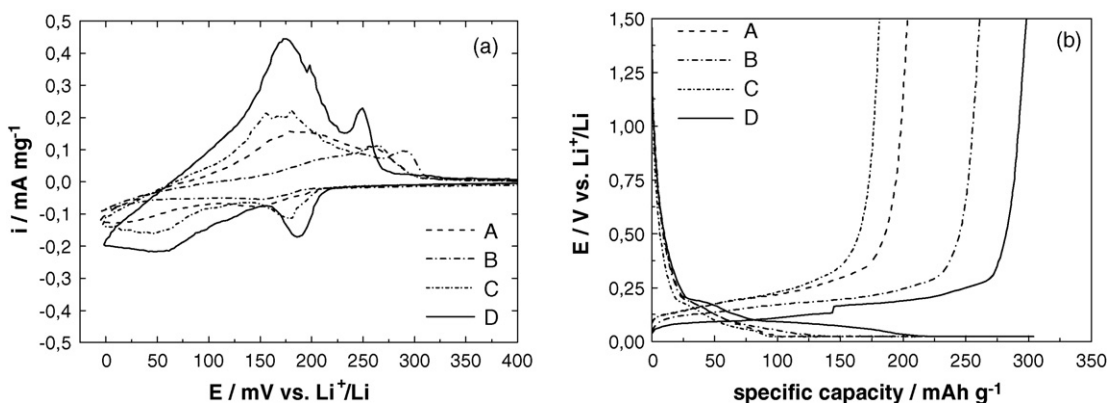


Fig. 6. KS-6 graphite electrode in mixtures of ILs (A and B) and in single IL electrolytic solution (C and D) containing 0.3 M LiPF₆ at RT: (a) overlay of the CV curves (3rd cycle) at $50 \mu\text{V s}^{-1}$; (b) overlay of the calculated specific capacity from CC at 1 C.

are reported the calculated efficiency values (at the 3rd cycle) of the intercalation–deintercalation process of Li in the KS-6 graphite electrodes for the considered mixtures. As shown, the mixtures A and B displayed different efficiency values. In fact, while the solution A displayed efficiency comparable to that of the mixture C, the mixture B showed very low (37.1%) efficiency. These results clearly indicate that this latter ratio of PYR₁₄TFSI and PYR₁₃FSI negatively affects the efficiency of the intercalation–deintercalation process on the KS-6 graphite electrode.

The same mixtures were used to carry out CC tests on the KS-6 graphite electrodes at RT, but the obtained results were surprisingly different. In fact, as shown in Fig. 5b, using the mixtures A and B it was possible to obtain value of specific capacity more than two times higher than that of the single ILs, with a very good stability during prolonged charge–discharge galvanostatic cycles. Particularly promising appears to be solution A, displaying

Table 2

Calculated values for the efficiency of the intercalation–deintercalation process taken at the 3rd cycle and specific capacity for KS-6 graphite electrode in mixtures of ILs (A and B) and in single IL electrolytic solution (C and D) containing 0.3 M LiPF₆ and 0.3 M LiTFSI at RT.

Electrolytic solution	LiTFSI		LiPF ₆	
	$\eta\%$	Spec. capacity (mAh g^{-1})		Spec. capacity (mAh g^{-1})
A	74.9	290	89.0	230
B	37.1	260	47.8	240
C	74.5	130	92.1	180
D	89.8	130	96.5	300

a specific capacity of 290 mAh g^{-1} and a very high cycling stability.

For the ternary mixtures containing LiPF₆ the observed behavior was different, confirming once more the influence of the Li-salt on the electrolytic solutions. Fig. 6a shows the overlay of the CVs of a KS-6 graphite electrode in combination with the ternary mixtures A and B containing 0.3 M LiPF₆ and, for comparison, with 0.3 M LiPF₆ PYR₁₄TFSI + 5 wt.% VC and of 0.3 M LiPF₆ in PYR₁₃FSI + 5 wt.% VC (indicated as C and D, respectively). As shown in the figure and in Table 2, the efficiency of these mixtures was overall higher (ca. 10%) than that of the corresponding mixtures containing LiTFSI, confirming the positive effect of this Li-salt. The trend of the calculated efficiency was comparable and also in this case, the mixture B displayed the lowest efficiency. However, the trend of the specific capacity was completely different. In fact, as shown in Fig. 6b, when ternary $(x)\text{PYR}_{13}\text{FSI}/(1-x)\text{PYR}_{14}\text{TFSI}/\text{LiPF}_6$ mixtures were used, the values of specific capacity was dependent on the concentration of PYR₁₃FSI in the mixture. The interaction between PYR₁₃FSI and LiPF₆ support the formation of an effective SEI layer; the highest is the concentration of PYR₁₃FSI in the electrolyte the highest is the delivered specific capacity. However, also in this case, the mixtures containing LiPF₆ showed a very low cycling stability (results not shown).

Considering the reported results, the use of ternary mixture of ILs can certainly be considered as a very promising strategy to develop electrolytic solutions able to combine the favorable properties of the two used ILs and consequently increase the performances of the systems. In order to guarantee good performance, the presence of VC appears very important since it is able to increase the efficiency of the Li intercalation–deintercalation in electrolytic solutions. As already mentioned, the selection of the Li-salt appears

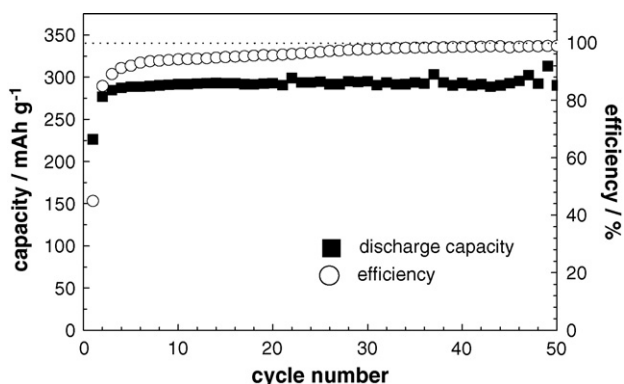


Fig. 7. CC (1C) at RT of KS-6 graphite electrode in the ternary mixture (0.2)PYR₁₃FSI/(0.8)PYR₁₄TFSI/LiTFSI with VC as additive.

crucial because strongly affect the cycling stability of the systems. These results indicated that the nature of the Li-salt as well as the type and the concentration of the used IL are probably able to modify the chemical composition of the SEI and its resistance. These differences in the SEI layer are probably the responsible of the different behavior and performance of the investigated mixtures.

Considering the reported values and the observed cycling stability, it is possible to assert that the ternary mixture (0.2)PYR₁₃FSI/(0.8)PYR₁₄TFSI/LiTFSI + 5 wt.% VC (indicated as A) appears as the most promising electrolyte solution investigated in the present paper. Using this mixture it is possible to obtain high efficiency during the intercalation–deintercalation process of lithium into the KS-6 graphite, high specific capacity (290 mAh g⁻¹) at RT and high rate (1 C) and very good cycling stability (Fig. 7). This good performance is due to the fact that this ternary mixture displays a wide electrochemical stability window (exceeding 5.5 V), high ionic conductivity also at RT and intrinsic film-forming ability due to the presence of PYR₁₃FSI, that help the VC during the SEI formation process.

Work is now in progress to define the charge transfer resistance as well as the SEI resistance of the investigated mixtures. The goal of this work will be to improve the efficiency of the intercalation–deintercalation process into the graphite electrodes during the first cycles when (x)PYR₁₃FSI/(1-x)PYR₁₄TFSI/LiTFSI ternary mixtures are used as electrolyte. Also the use of a different type of graphite is now considered as well as the optimization of the cycling stability in (x)PYR₁₃FSI/(1-x)PYR₁₄TFSI/LiPF₆ ternary mixtures.

4. Conclusions

In this paper we have reported the results of the use of ternary mixtures (x)PYR₁₃FSI/(1-x)PYR₁₄TFSI/LiTFSI and (x)PYR₁₃FSI/(1-x)PYR₁₄TFSI/LiPF₆ containing 5 wt.% of VC in combination with a commercial graphite KS-6 TIMCAL.

The use of these ternary mixtures appears very promising because consents a favorable combination of the properties of the two ionic liquids used. The use of VC seems to be necessary since it is able to increase the efficiency of the Li intercalation–deintercalation in electrolytic solutions.

Particularly interesting is the ternary mixture (0.2)PYR₁₃FSI/(0.8)PYR₁₄TFSI/0.3 M LiTFSI. This mixture displays a wide electrochemical stability window (exceeding 5.5 V), high ionic conductivity also at RT and intrinsic film-forming ability (due of the presence of PYR₁₃FSI) [30]. When used in combination with KS-6 graphite, the investigated system display high performance in term of specific capacity, cycling efficiency and cycling stability at RT and a high C-rate.

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