



# The impact of mixtures of protic ionic liquids on the operative temperature range of use of battery systems



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## ABSTRACT

In this work we report for the first time about the mixture of protic ionic liquids, butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr<sub>H4</sub>TFSI) and pyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr<sub>HH</sub>TFSI), as solvent for battery electrolytes. This IL mixture displays a melting point of  $-80\text{ }^{\circ}\text{C}$ , good conductivity and low viscosity at room temperature. We show that its use together with the salt lithium bis(trifluoromethanesulfonyl)imide allows the realization of devices displaying high performance in the temperature range between  $-20\text{ }^{\circ}\text{C}$  and  $80\text{ }^{\circ}\text{C}$ .

## 1. Introduction

In the last years ionic liquids (ILs) have been extensively investigated as electrolytes solvents for battery systems [1]. Mostly, aprotic ionic liquids (AILs) have been considered for these applications [1–2]. Recently, however, also protic ionic liquids (PILs) have been proposed and investigated as alternative electrolytes' solvents for batteries [3–5], showing that PILs-based electrolytes might display conductivities, viscosities and thermal stabilities comparable to those of AILs [3–4], although, due to the presence of the proton in PILs, the ion-ion interactions in the two IL types are markedly different [4,6–7]. It has been shown, for example, that the charge transfer resistance associated to the lithium insertion-extraction (charge-discharge) process in the battery electrode materials (e.g., lithium iron phosphate and lithium vanadium phosphate), is significantly lower in PIL-based electrolytes than in the AIL-based ones [4]. Because of this reduced resistance the performance of PIL-based cells is, during tests carried out at high current densities, significantly higher than that of AIL-based batteries [4]. Thus, PILs can be considered as a new and interesting class of solvents for batteries' electrolytes. Several aspects related to the use of these electrolytes should be, however, further considered. Among them, the investigation about the behavior of PIL-based batteries at high and low temperature appears of importance since no indications about this crucial aspect are presently available.

The use of mixtures of ILs proved to be an effective strategy to realize electrolytes with tailored properties and, also, to expand the

operative temperature range of IL-based devices [8]. Mixtures of AILs have been successfully proposed as electrolytes for supercapacitors and batteries [9–10]. Mixtures of PILs have been proposed as electrolytes for supercapacitors [11]. To the best of our knowledge, however, the use of mixtures of PILs as electrolytes for batteries has not been investigated, so far.

In this work we consider the use of a mixture containing *N*-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr<sub>H4</sub>TFSI) and pyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr<sub>HH</sub>TFSI) as electrolyte solvent for battery systems. Initially, the melting point of this mixture is identified. Afterward, the conductivities and viscosities of the electrolyte containing this mixture and the lithium salt LiTFSI, are investigated. Finally, the electrochemical performance of lithium iron phosphate (LFP) based electrodes in combination with this innovative electrolyte is ascertained in the temperature range between  $-20\text{ }^{\circ}\text{C}$  and  $80\text{ }^{\circ}\text{C}$ .

## 2. Experimental

Butylpyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr<sub>H4</sub>TFSI) and pyrrolidinium bis(trifluoromethanesulfonyl)imide (Pyr<sub>HH</sub>TFSI) were synthesized as reported in reference [7]. The electrolyte used for all electrochemical tests was a ternary solution containing 0.5 M LiTFSI in Pyr<sub>HH</sub>TFSI: Pyr<sub>H4</sub>TFSI (molar ratio 7:3). The water content of the prepared electrolyte was below 10 ppm, as measured by Karl-Fischer Titration.

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The melting point was evaluated using DSC measurements, which have been carried out as reported in reference [7]. The conductivity and viscosity of the electrolyte were investigated as described in reference [7].

All the electrochemical tests were carried out in three-electrode, Swagelok®-type cells, which were assembled in a dry box (MBraun) with oxygen and water contents lower than 1 ppm. The tests were carried out at  $-20\text{ }^{\circ}\text{C}$ ,  $0\text{ }^{\circ}\text{C}$ ,  $20\text{ }^{\circ}\text{C}$ ,  $40\text{ }^{\circ}\text{C}$ ,  $60\text{ }^{\circ}\text{C}$  and  $80\text{ }^{\circ}\text{C}$  by hosting the cells in a Binder MK 53 climatic chamber. LFP composite electrodes were prepared as reported elsewhere [7]. The composition of the dry electrodes was 85 wt% active material, LFP (JMBM), 10 wt% conductive additive, Super C65® (Imerys), and 5 wt% sodium carboxymethyl cellulose (CMC, Dow-Wolff Cellulosics) as binder. The electrode mass loading was ca.  $3\text{ mg cm}^{-2}$ , while the electrode area was  $1.13\text{ cm}^2$ . In assembling the cells, an LFP-based electrode was used as working electrode while an oversized activated carbon-based electrode (DLC Super 30®, NORIT®) was used as counter electrode and a silver wire was used as pseudo-reference electrode (potential  $\sim 3\text{ V}$  vs.  $\text{Li}/\text{Li}^+$ ). A Whatman GF/D glass microfiber filter (675  $\mu\text{m}$  thickness) drenched with  $150\text{ }\mu\text{L}$  of electrolyte was used as separator. All the electrochemical measurements were carried out using a MACCOR Series 4000 battery tester. Constant current cycling (CC) tests were carried out at the above-mentioned temperatures using current densities of 0.5C and 1C calculated on the basis of the theoretical capacity of LFP (i.e.,  $170\text{ mAh g}^{-1}$ ).

### 3. Results and discussion

$\text{Py}_{\text{rHH}}\text{TFSI}$  and  $\text{Py}_{\text{rH4}}\text{TFSI}$  display melting points of  $37\text{ }^{\circ}\text{C}$  and  $30\text{ }^{\circ}\text{C}$ , respectively [7]. Fig. 1a displays the DSC traces of the binary mixture containing  $\text{Py}_{\text{rHH}}\text{TFSI}$  and  $\text{Py}_{\text{rH4}}\text{TFSI}$  in the molar ratio 7:3, selected based on the previous work [7], upon cooling and heating between  $-100\text{ }^{\circ}\text{C}$  and  $100\text{ }^{\circ}\text{C}$ . As shown in the figure, the PIL mixture does not crystallize, but a glass transition can be observed at  $-81\text{ }^{\circ}\text{C}$  while cooling the sample. During the heating step, the sample melts at  $-79\text{ }^{\circ}\text{C}$ . Considering these results, it is evident that mixing these two PIL is possible to realize a solution which display considerable lower melting point compared to the single components. This behavior, which can be explained by the reduced tendency of ILs to form crystalline phases in presence of other ionic species, has been already observed in some binary mixtures of TFSI-based AIL [12–13]. These results confirm, once more, the similarities existing between PILs and AILs [7]. It is important to notice that the thermal stability of IL-based electrolytes in contact with charged electrodes might be significantly lower compared to that of “free” ILs [1,14]. This important aspect has never been investigated for PIL-based electrolytes and, therefore, need to be carefully evaluated in order to understand the impact on the safety of battery systems of these innovative electrolytes Fig. 3.

In order to use the investigated mixture in batteries, a lithium salt needs to be added to the PIL solution. In particular, the electrolytic solution containing  $0.5\text{ M LiTFSI}$  in  $\text{Py}_{\text{rHH}}\text{TFSI}:\text{Py}_{\text{rH4}}\text{TFSI}$  (7: 3) was made and investigated. Fig. 1b shows the variation of the ionic conductivity of the investigated electrolyte in the temperature range comprise between  $-20\text{ }^{\circ}\text{C}$  and  $80\text{ }^{\circ}\text{C}$ . As shown, at  $40\text{ }^{\circ}\text{C}$  the electrolyte displays an ionic conductivity of  $3.42\text{ mS cm}^{-1}$ . This value is slightly higher than those displayed by the  $0.5\text{ M LiTFSI}$  solution in either  $\text{Py}_{\text{rHH}}\text{TFSI}$  or  $\text{Py}_{\text{rH4}}\text{TFSI}$  at the same temperature, which are equal to  $2.15\text{ mS cm}^{-1}$  and  $2.02\text{ mS cm}^{-1}$ , respectively [4]. An increase of the ionic conductivity of mixtures of different ILs compared to the pure compounds was already reported [15], therefore, this result is not surprising. At  $0\text{ }^{\circ}\text{C}$  and  $-20\text{ }^{\circ}\text{C}$ , the electrolyte displays ionic conductivities of  $0.29\text{ mS cm}^{-1}$  and  $0.03\text{ mS cm}^{-1}$ , respectively, which are comparable to those shown by other TFSI-based AILs at similar temperatures [4,7]. However, it is important to remark that the conductivity of the pure PILs, due to their higher melting points, cannot be evaluated at these temperatures. Fig. 1c shows the viscosity

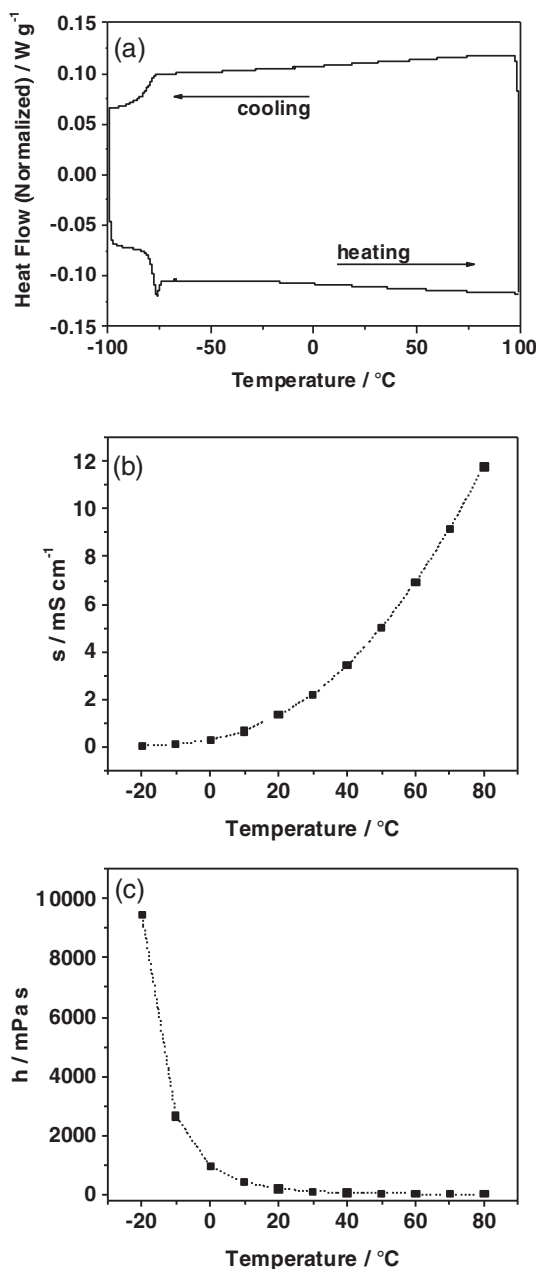


Fig. 1. (a) DSC of the mixture  $\text{Py}_{\text{rHH}}\text{TFSI}:\text{Py}_{\text{rH4}}\text{TFSI}$  (molar ratio 7:3). The measurement was carried out between  $-100\text{ }^{\circ}\text{C}$  and  $100\text{ }^{\circ}\text{C}$  using a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ ; (b) Ionic conductivity and (c) viscosity of the electrolyte  $0.5\text{ M LiTFSI}$  in  $\text{Py}_{\text{rHH}}\text{TFSI}:\text{Py}_{\text{rH4}}\text{TFSI}$  (7: 3) in the temperature range comprise between  $-20\text{ }^{\circ}\text{C}$  and  $80\text{ }^{\circ}\text{C}$ .

variation of the investigated electrolyte between  $-20$  and  $80\text{ }^{\circ}\text{C}$ . At  $40\text{ }^{\circ}\text{C}$  the  $0.5\text{ M LiTFSI}$  in  $\text{Py}_{\text{rHH}}\text{TFSI}:\text{Py}_{\text{rH4}}\text{TFSI}$  (7: 3) displays a viscosity of  $69.61\text{ mPa s}$ . This value is in between that of  $0.5\text{ M LiTFSI}$  in  $\text{Py}_{\text{rHH}}\text{TFSI}$  and  $0.5\text{ M LiTFSI}$  in  $\text{Py}_{\text{rH4}}\text{TFSI}$ , which at  $40\text{ }^{\circ}\text{C}$  display viscosities of  $77.39\text{ mPa s}$  and  $58.40\text{ mPa s}$ , respectively. As expected, at very low temperature the viscosity of the ternary mixture increases: at  $0\text{ }^{\circ}\text{C}$  is equal to  $952.5\text{ mPa}$ , while at  $-20\text{ }^{\circ}\text{C}$  reaches  $9467\text{ mPa}$ . These latter values are certainly quite high. Nevertheless, as for the conductivity, it is important to notice that while the investigated electrolyte is liquids at both (low) temperatures, the single components are not.

As mentioned in the introduction, PIL-based electrolytes are interesting electrolytes for LIBs [3–6]. In order to investigate the impact of the ternary mixture on the electrochemical performance of battery materials, the performance of LFP-based electrodes in such an electro-

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