

# Mixed ionic liquid as electrolyte for lithium batteries

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## Abstract

Ionic liquids like 1-butyl-3-methylimidazolium tetrafluoroborate (IMIBF<sub>4</sub>) or hexafluorophosphate (IMIPF<sub>6</sub>) and 1-butyl-4-methylpyridinium tetrafluoroborate (PyBF<sub>4</sub>) were mixed with organic solvents such as butyrolactone (BL) and acetonitrile (ACN). A lithium salt (LiBF<sub>4</sub> or LiPF<sub>6</sub>) was added to these mixtures for possible application in the field of energy storage (batteries or supercapacitors). Viscosities, conductivities and electrochemical windows at a Pt electrode of these electrolytes were investigated. All studied electrolytes are stable toward oxidation and exhibit a vitreous phase transition, which has been determined by application of the VTF theory to conductivity measurements. Mixtures containing the BF<sub>4</sub><sup>-</sup> anion exhibit the lowest viscosity and the highest conductivity. Two mixtures have been optimized in terms of conductivity: BL/IMIBF<sub>4</sub> (60/40, v/v) and ACN/IMIBF<sub>4</sub> (70/30, v/v).

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## 1. Introduction

Since the first lithium-ion battery commercialized by Sony in 1990, a tremendous increase of popularity concerns the research of performant electrolytes for low or high temperature applications such as military, space applications or electric vehicle. Up to date, most commercial electrolyte contains ethylencarbonate (EC), dimethylcarbonate (DMC) and diethylcarbonate (DEC) with lithium hexafluorophosphate as lithium salt [1]. EC/DMC/DEC based electrolytes permit numerous charging and discharging cycles without significant loss in capacity but their thermal stability is a safety problem at high temperature (60 °C and more) owing to their volatility (DEC and DMC) and flammability. Ionic liquid may an alternative to classical electrolytes for lithium batteries owing to their low vapor pressure, their non-flammability and wide electrochemical window [2].

Pure ionic liquids are highly viscous and exhibit relatively low conductivities. In order to decrease the viscosity of neat

ionic liquids, organic dipolar aprotic solvent may be added. In this paper, viscosities and conductivities of 1-butyl-3-methylimidazolium (IMI<sup>+</sup>) or 1-butyl-4-methylpyridinium (Py<sup>+</sup>) associated with tetrafluoroborate (BF<sub>4</sub><sup>-</sup>) or hexafluorophosphate (PF<sub>6</sub><sup>-</sup>) anions mixed with acetonitrile (ACN) or  $\gamma$ -butyrolactone (BL) have been investigated in the presence of lithium tetrafluoroborate or lithium hexafluorophosphate.

## 2. Experimental

BL (purity > 99.99%) and ACN (purity > 99.9%) were obtained from Aldrich and used as received. LiBF<sub>4</sub> (99.99%) and LiPF<sub>6</sub> (99.99%) were purchased by Fluka. IMIBF<sub>4</sub>, IMIPF<sub>6</sub> and PyBF<sub>4</sub> (purity > 99.9%) were obtained from Aldrich.

In order to optimize the composition of the electrolytes, ac conductivity measurements were carried out using a Philips PM6303 impedance analyser operating at 1000 Hz and a conductivity cell equipped with platinum electrodes. Viscosities were performed using a Schott viscometer (AUS 310) and an Ubbelohde capillary tube immersed in a thermostated bath

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( $\pm 0.1^\circ\text{C}$ ). Solutions densities were performed using picnometers and used to calculate dynamic viscosities.

Linear sweep voltammetry was performed using an EG & G 273A potentiostat equipped with a three electrodes cell (rotating working electrode (1500 rpm): Pt, reference and counter electrodes: metallic lithium).

### 3. Results and discussions

#### 3.1. Viscosities and conductivities

Fig. 1 displays the evolution of the viscosity versus the temperature for imidazolium and pyridinium salts in the presence or the absence of lithium salts.

Ionic liquids containing the hexafluorophosphate anion are more viscous than ionic liquids containing the tetrafluoroborate anion owing to stronger interactions in solution. As seen in Fig. 2, the increase in viscosity observed when a lithium salt is added, is followed by a decrease in conductivity as the ionic mobilities are strongly affected by the viscosity [3]. In the range of investigated temperatures, electrolytes conductivities decrease in the following order:  $\text{IMIBF}_4 > \text{PyBF}_4 > \text{IMIPF}_6$ . When BL or ACN are added

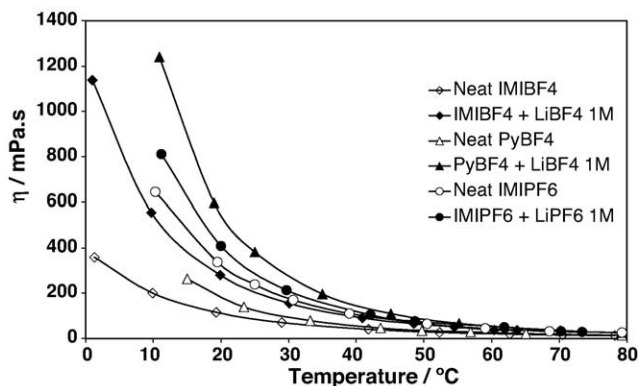


Fig. 1. Viscosity of ionic liquids vs. temperature.

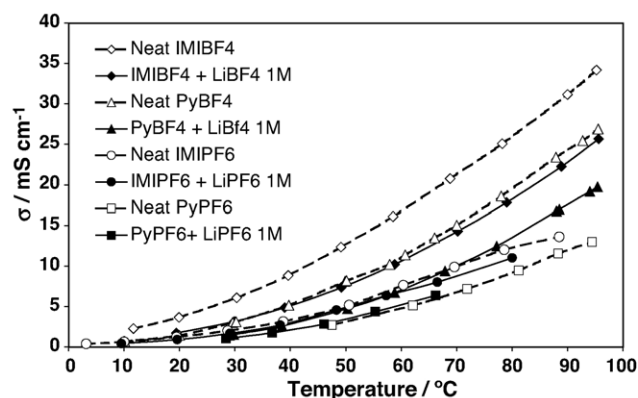


Fig. 2. Variation of conductivity vs. temperature.

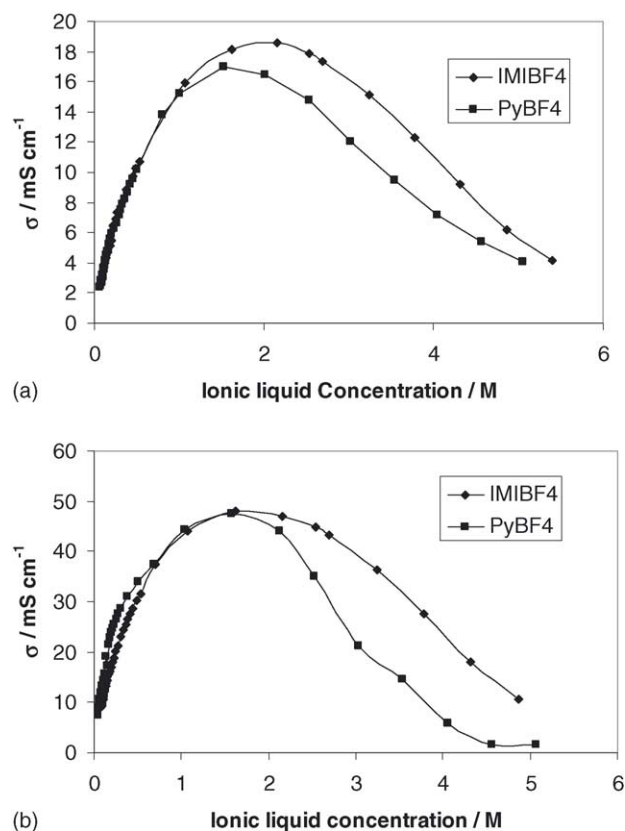


Fig. 3. Variations of conductivity at  $25^\circ\text{C}$  in mixtures containing (a) BL and (b) ACN.

to  $\text{IMIBF}_4$  and  $\text{PyBF}_4$  ionic liquids, the conductivities are enhanced as seen in Fig. 3a and b. The most conducting electrolytes, expressed in volume fraction are: BL/ $\text{IMIBF}_4$  (60/40) and ACN/ $\text{IMIBF}_4$  (70/30).

The same optimal composition is obtained when  $\text{PyBF}_4$  is used as ionic liquid instead of  $\text{IMIBF}_4$  and conductivity values at the maximum are of the same order of magnitude.

Ideal vitreous temperatures ( $T_0$ ) have been deduced from the Vogel–Tammann–Fulcher (VTF) theory [4] applied to conductivity measurements. Results are reported in Table 1.

As no freezing points occur at low temperatures, electrolytes having a vitreous transition temperature remains liquid in a wide range of temperatures and are adequate for use in Li batteries.

In Fig. 4 is displayed, the influence of added lithium tetrafluoroborate on the conductivity of  $\text{IMIBF}_4/\text{BL}$  and  $\text{PyBF}_4/\text{BL}$  mixtures. As in Fig. 2, a decrease in conductivity

Table 1  
Ideal vitreous temperature of optimized electrolytes

Optimized electrolytes	$T_0$ ( $^\circ\text{C}$ )
$\text{IMIBF}_4 + \text{ACN}$ [30:70]	–193
$\text{IMIBF}_4 + \text{BL}$ [40:60]	–73
$\text{IMIBF}_4 + \text{BL}$ [40:60] + $[\text{LiBF}_4, 1 \text{ M}]$	–163
$\text{PyBF}_4 + \text{BL}$ [30:70]	–158
$\text{PyBF}_4 + \text{BL}$ [30:70] + $[\text{LiBF}_4, 1 \text{ M}]$	–118

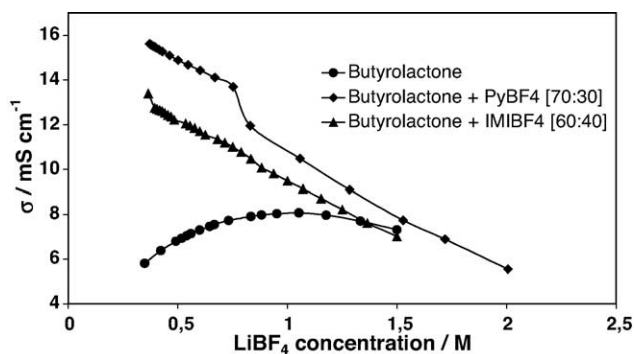


Fig. 4. Evolution of the conductivity vs.  $\text{LiBF}_4$  concentration of optimized electrolytes.

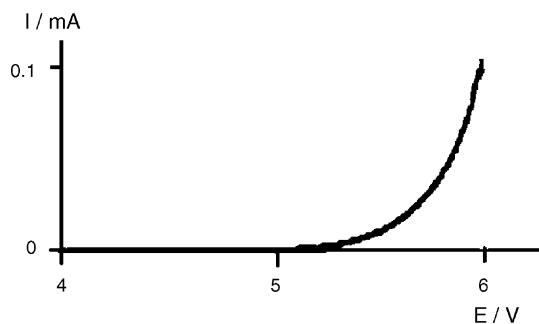


Fig. 5. Linear Sweep Voltammetry of BL/IMIBF<sub>4</sub> (60/40) + LiBF<sub>4</sub> (1 M) at a Pt electrode (1500 rpm).

of the optimized mixed electrolytes is observed when  $\text{LiBF}_4$  is added.

The same behaviour is observed when ACN is used instead of BL. A concentration of 1 M in lithium salt is necessary to avoid concentration polarisation at the electrodes during charging/discharging cycles. IMIBF<sub>4</sub> + BL [40:60] + [LiBF<sub>4</sub>, 1 M] and PyBF<sub>4</sub> + BL [30:70] exhibit higher conductivities than BL + LiBF<sub>4</sub> (1 M) or EC/DMC + LiPF<sub>6</sub> (1 M) electrolytes.

### 3.2. Electrochemical properties

The electrochemical window of IMIBF<sub>4</sub> + BL [40:60] + [LiBF<sub>4</sub>, 1 M] and PyBF<sub>4</sub> + BL [30:70] at a platinum electrode are displayed in Figs. 5 and 6. The optimized electrolytes are stable toward oxidation which occurs, respectively, at 5.2 and 5.5 V versus Li/Li<sup>+</sup> for ACN/IMIBF<sub>4</sub> (70/30) and BL/IMIBF<sub>4</sub> (60/40). These values are neverthe-

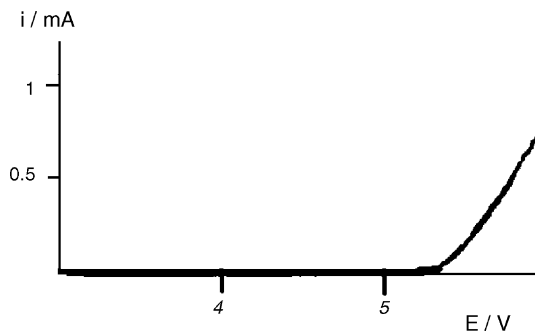


Fig. 6. Linear Sweep Voltammetry of ACN/IMIBF<sub>4</sub> (70/30) + LiBF<sub>4</sub> (1 M) at a Pt electrode (1500 rpm).

less lower than that obtained for BL in presence of LiBF<sub>4</sub>: 5.8 V versus Li/Li<sup>+</sup> [5]. ACN and BL are stable toward oxidation at the platinum electrode but ACN is reactive toward metallic lithium as no stable passivation layer can be formed. Its use as electrolyte in electrochemical applications is limited to electrochemical capacitors or electrochromic windows.

## 4. Conclusion

Imidazolium and pyridinium ionic liquids mixed with organic solvents are relevant electrolytes for electrochemical systems. They exhibit a lower viscosity and a higher conductivity than pure ionic liquids. Their thermal stability, low vapor pressure make them suitable as electrolytes for many electrochemical applications. Their use in lithium batteries requires the addition of a Li salt and a stability toward reduction and, for this purpose, only BL mixed with IMIBF<sub>4</sub> or PyBF<sub>4</sub> are suitable. Future works will be focused on the cycling ability using Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and Li<sub>x</sub>CoO<sub>2</sub> electrodes.

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