



Are room temperature ionic liquids able to improve the safety of supercapacitors organic electrolytes without degrading the performances?

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ABSTRACT

Acetonitrile (ACN) is widely used as solvent for electrolyte in supercapacitors in the presence of tetraethylammonium tetrafluoroborate ($\text{Et}_4\text{N}^+\text{BF}_4^-$). The main advantage is its low viscosity leading to high conductivities in the presence of salts, but unfortunately it is too volatile and flammable. In order to reduce both the flammability and the volatility of ACN based electrolytes, aprotic room temperature ionic liquids, RTILs, are added either to ACN or to γ -butyrolactone (GBL), another typical solvent for the electrochemical devices. The effects of these molten salts on ACN and GBL are investigated with the aim of improving the supercapacitors security. Flammability tests are performed on these electrolytes to study their security. The results show that mixtures GBL based are more flammable than those ACN based, in spite of a higher boiling point for pure GBL because of the presence of solvates. DSC measurements over ambient temperature strengthen these flammability results. To complete this study, physical and electrochemical characteristics (density, viscosity, conductivity, linear and cyclic voltamperometry) are investigated. The results indicate that no degradation of the electrochemical performances appears with RTIL/ACN mixture by comparison with the standard electrolyte ($\text{ACN} + 1 \text{ M Et}_4\text{N}^+\text{BF}_4^-$).

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1. Introduction

The interests aroused by supercapacitors are their high storage capacity of energy and their power density. Supercapacitors are playing an important role in transportation. Indeed they can be coupled with batteries and fuel cells to provide power peaks during acceleration and to recover energy during the braking of HEVs (hybrid electric vehicles) [1–4].

Room temperature ionic liquids (RTILs) are entirely composed of organic cation and organic or inorganic anion. These liquids hold attention because of their chemical and physical properties such as a good thermal, chemical and electrochemical stability, a negligible vapour pressure (non flammability), a high ionic conductivity and being liquid on a wide liquid range [5,6]. RTILs can be used as electrolytes for these devices, leading to the improvement of the supercapacitor characteristics and to the reduction of the vehicle pollution due to its exhaust fumes [2]. A classical electrolyte is composed of a molecular organic solvent such as acetonitrile (ACN) or γ -butyrolactone (GBL) and a dissociating salt (i.e. the tetraethylammonium tetrafluoroborate ($\text{Et}_4\text{N}^+\text{BF}_4^-$)) [7,8]. ACN is a reference solvent mainly used in different countries inside

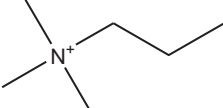
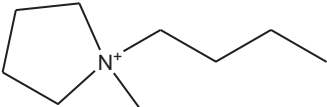
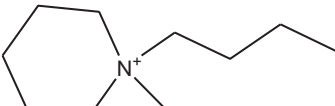
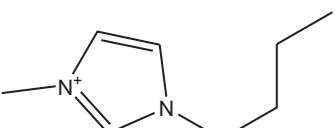
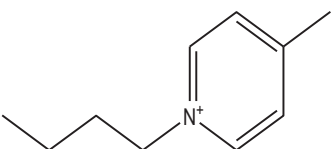
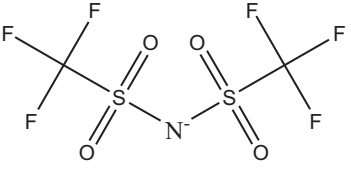
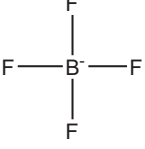

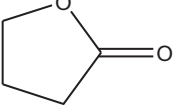
Europe and America. This solvent presents many advantages such as a low viscosity, a good conductivity and a strong permittivity, however it is highly flammable and very toxic [8]. GBL can be a good alternative to ACN for solvent in supercapacitor electrolyte, because of its high boiling point and its nice solubilizing ability, its good electrochemical behaviour, furthermore it is safer [7]. In a preceding work, the mixtures ionic liquid–GBL were studied in our laboratory [9,10] nevertheless GBL is more viscous, heavier, and it is presenting a less separating effect [7] than ACN. Owing to its high vapour pressure, ACN presents a very low flash point (6°C) and emits toxic vapours of hydrogen cyanide (HCN) when it burns. In order to palliate this problem, RTILs can be incorporated in fluid molecular solvents, particularly because of their great thermal stability and their low toxicity [5]. They are able to dissolve a wide range of organic and inorganic compounds, however pure ionic liquids are highly viscous and exhibit relatively low conductivities. Thus, in order to decrease the viscosity of RTILs, organic dipolar aprotic solvents are added [1,9].

The present work focuses on the use of RTILs in association with molecular solvents especially the ACN and the GBL as electrolytes for safer supercapacitors. Flammability tests of the mixtures are carried out in air. DSC measurements lead to the physico-chemical characterization of the mixtures. We also compare their ionic transport properties to choose the best mixture to be tested in an electrochemical device. Finally, voltamperometry tests are

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Table 1
Names, formula and abbreviations of RTILs and molecular solvents.

Component	Formula	Abbreviation
N-trimethyl-N-propylammonium		TMPA ⁺
N-methyl-N-butyl-pyrrolidinium		P ₁₄ ⁺
N-methyl-N-butyl-piperidinium		PIP ₁₄ ⁺
1-Butyl-3-methyl-imidazolium		BMIm ⁺
1-Butyl-4-methyl-pyridinium		Py ₁₄ ⁺
Bis(trifluoromethylsulfonyl) imide		TFSI ⁻
Tetrafluoroborate		BF ₄ ⁻
Acetonitrile		ACN
γ-Butyrolactone		GBL

performed to determine the electrochemical behaviour of both the standard electrolyte (ACN + 1 M Et₄N⁺BF₄⁻) and mixture under study.

2. Experimental

2.1. Materials

RTILs selected in this study are based on the bis(trifluoromethylsulfonyl) imide (TFSI⁻) and the tetrafluoroborate (BF₄⁻) anions: N-trimethyl-N-propylammonium bis(trifluoromethylsulfonyl) imide (TMPA-TFSI), N-methyl-N-butyl pyrrolidinium bis(trifluoromethylsulfonyl) imide (P₁₄-TFSI), N-methyl-N-butyl piperidinium bis(trifluoromethylsulfonyl) imide (PIP₁₄-TFSI), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF₄) and 1-butyl-4-methylpyridinium tetrafluoroborate (Py₁₄-BF₄).

The TFSI-based ionic liquids were synthesized in our laboratory according to the classical method: quaternization and anionic metathesis [5]. ACN (anhydrous, 99+%), GBL (99+%), BMIm-BF₄ (98+%) and Py₁₄-BF₄ (97+%) were obtained from Sigma-Aldrich. ACN and GBL were used as received whereas BMIm-BF₄ and Py₁₄-BF₄ were dried in a vacuum oven at 120 °C during 72 h before their utilization. Both of the RTILs and the molecular solvents were stocked in a glove box under argon atmosphere to avoid the contamination by the ambient atmosphere.

Table 1 gathers all the chemical formulas of the molecular solvents and the RTILs of interest in this study, in the same way, their main physico-chemical characteristics at ambient temperature are listed and compared to other results presented in the literature in Table 2. Our values are in good agreement with the published results [5,6,9,11–16] validating our experimental methods for determining these characteristics.

Table 2
Main physico-chemical characteristics of RTILs studied at 25 °C, electrochemical window on a Pt rotating disk electrode.

		M (g mol ⁻¹)	d	η (mPas)	σ (mS cm ⁻¹)	M_p (°C)	T_d (°C)	T_g (°C)	Electrochemical window (V)
TMPA-TFSI		382.34	1.43 ^a	72.0 ^a	3.24 ^a	19 ^a	368 ^a	-78 ^a	5.5 ^a
	Lit.	-	1.44 ^b	72.0 ^b	3.27 ^b	22 ^b	-	-	5.8 ^c
P ₁₄ -TFSI		422.41	1.39 ^a	83.5 ^a	2.83 ^a	-15 ^a	398 ^a	-81 ^a	5.5 ^a
	Lit.	-	1.41 ^d	85.0 ^d	2.20 ^d	-18 ^d	377 ^e	-87 ^d	5.5 ^d
PIP ₁₄ -TFSI		436.49	1.38 ^a	155.3 ^a	1.11 ^a	-	371 ^a	-76 ^a	5.2 ^a
	Lit.	-	1.38 ^f	183.0 ^f	1.20 ^f	-25 ^f	400 ^f	-73 ^f	4.5 ^f
BMIm-BF ₄		226.03	-	-	-	-	-	-	4.0 ^a
	Lit.	-	1.20 ^g	75.0 ^g	4.50 ^g	-	-	-83 ^g	4.1 ^h
Py ₁₄ -BF ₄		237.05	-	-	-	-	-	-	4.0 ^a
	Lit.	-	1.18 ^h	129.0 ⁱ	1.43 ⁱ	-65 ^j	233 ^k	-76 ^k	-

M , molecular weight; d , density; η , viscosity; σ , conductivity; M_p , melting point; T_d , decomposition temperature; T_g , glass transition temperature.

^a This work.

^b Ref. [11].

^c Ref. [12].

^d Ref. [6].

^e Ref. [13].

^f Ref. [14].

^g Ref. [15].

^h Ref. [5].

ⁱ Ref. [9].

^j Merck.

^k Ref. [16].

2.2. The flammability tests

All samples are prepared by mixing adequate amounts of solvents and RTILs in a glove box under argon atmosphere. Flammability tests in air are performed according to the procedure described in Fig. 1. This kind of preliminary flammability test is currently used by battery manufacturers [17]. For this purpose, a paper (Manilla paper from Dalbe, France) is soaked in the electrolyte at the ambient atmosphere; it is then exposed to the flame in air (20% O₂ and 80% N₂). All the experimental experiments are recorded with a digital camera [18]. Similar tests have been already described in the literature. Nakagawa et al. [19] and Wang et al. [20] undertake flammability tests by using a glass filter soaked with an alkylcarbonate mixture, and an alcohol lamp as lighter. After 10 s, the lighter is removed from under the glass filter. The electrolyte is judged to be non flammable if the electrolyte never ignited during the testing, or if the ignition of electrolyte ceases when the flame is removed. Another approach proposed by Guerfi et al. [21] consists indirectly observing the flame on the surface of each RTIL-alkylcarbonate mixture for a few seconds. Even though the certification standards, such as NF T 51-072, are recommended, they are nevertheless well adapted to polymer materials, which are used in the form of test pieces of defined dimensions. These

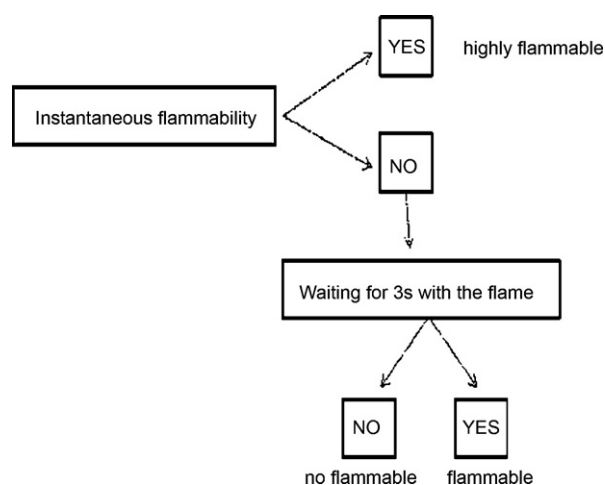


Fig. 1. Method used for the flammability tests in air with soaked Manilla paper.

certification standards cannot be used in this work because of the liquid state of the studied materials.

2.3. Density measurements

Densities are measured with an Anton Paar vibrating tube densimeter. The tube is partially immersed on a thermostated Julabo F25 bath to control the temperature (± 0.1 °C).

2.4. DSC measurements

To avoid any contamination by water or by the ambient atmosphere, all samples are prepared under argon into the glove box, and poured into a 50 μ L hermetically sealed aluminum cell. DSC experiments are performed using 10–20 mg (± 0.1 mg) of sample materials. Curves are recorded on a Perkin-Elmer differential scanning calorimeter DSC6 at fixed scanning rate of 2 C min⁻¹. Standard samples of indium ($M_p = 156.55$ °C) are used for the DSC calibration. A dry nitrogen purge is continuously applied into the oven to avoid any water ambient contamination. For experiments above room temperature (from 25 °C to 400 °C), the oven is cooled by means of cold water. For experiments below room temperature, the DSC6 apparatus is equipped with a nitrogen gas flow system cooled by means of liquid nitrogen. To investigate the stability of phases, the procedure consists in cooling the sample from the room temperature to -80 °C (cooling step).

2.5. Ionic transport measurements

2.5.1. Conductivity measurements

Conductivity measurements are performed using a Radiometer CDM210 conductimeter operating at variable frequency and a conductivity cell Radiometer CDC 749 equipped with platinum electrodes covered by platinum black (cell constant: 1.403 cm⁻¹). Each solution is poured in a 14 mm diameter hemolysis tube and protected against ambient temperature contamination by a laboratory film ("Parafilm®"). This tube is partially immersed in a thermostated Julabo F25 bath to control the temperature (± 0.1 °C).

2.5.2. Dynamic viscosities measurements

Dynamic viscosity measurements are performed at 25 °C at a scanning rate of 2 °C min⁻¹, with a TA Instruments AR 1000

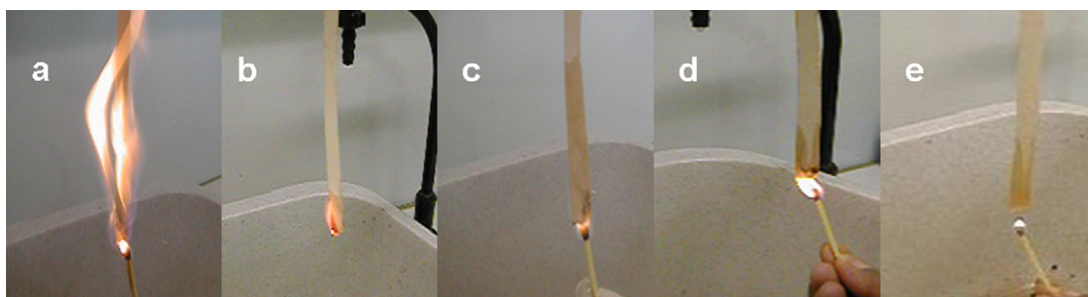


Fig. 2. Flammability tests in air on TMPA–TFSI/ACN mixtures: (a) pure ACN, (b) 12% TMPA–TFSI/88% ACN (in mol), (c) 13% TMPA–TFSI/87% ACN (in mol), (d) 45% TMPA–TFSI/55% ACN (in mol), and (e) pure TMPA–TFSI.

rheometer. A rotating steel cone (angle 00:29:32, diameter 60.00 mm) and a thermostated Peltier plate were used as geometry.

2.6. Electrochemical measurements

The electrochemical windows are obtained from linear sweep voltammetry performed under argon atmosphere on a TACUSSEL VOLTALAB PGZ100 potentiostat. The rotating working disk is a platinum electrode (1000 rpm, 2 mm diameter). A Pt electrode with a surface of 38 mm² is used as a counter electrode. A silver wire immersed in the organic solution is used as a pseudo-reference electrode. The potential of this pseudo-reference electrode is determined using the ferrocene redox system (Fc/Fc⁺). The Fc/Fc⁺ standard redox potential is taken as $E^\circ(\text{Fc}/\text{Fc}^+) = 0.45$ V vs. SHE whatever the solvent used [22].

Cycling tests are performed at 25 °C using a BioLogic Science Instrument MPG2 battery cyler. Cells are on Swagelok® type and composed of two activated carbon electrodes (from Batscap, France), whose active material content is 4.4 mg cm⁻¹. The detailed composition of the electrode is not provided by the manufacturer for confidential reasons. A glass fiber Whatman filled up with the studied electrolyte is used as electrolyte reservoir. The scanning rate is varying from 1 to 50 mV s⁻¹.

3. Results and discussion

3.1. Flammability tests

In the event of a thermal incident affecting a supercapacitor, the first risk is the ignition of the device. Given that the consequences which it can engender, it is essential to evaluate the behaviour of electrolytes in the contact with the flame. For this purpose, in order to investigate their flammability behaviour (depending on both the RTIL and the molecular solvent), tests are performed with strips of Manilla paper soaked with mixtures of molecular organic solvent (ACN or GBL) and RTIL. The mixture composition is given by solvent molar fraction x_S : $x_S = n_S / (n_S + n_{IL})$, where n_S represents the molar quantity of the organic solvent, S (ACN or GBL), and n_{IL} the molar quantity of the RTIL used.

Some significant photos concerning the resulting tests are presented in Figs. 2 and 3. As shown in Fig. 2a, for pure ACN, the inflammation of the soaked strip of paper is quick striding leading to suffocating smokes. Strips soaked by the ACN/TMPA–TFSI mixtures when $87\% < x_{ACN} \leq 90\%$ present quite the same behaviour in the contact with the flame of the lighter (Fig. 2b). Nevertheless, no white smoke is appearing, the electrolyte is gently burning. In the case of ACN/TMPA–TFSI mixtures for $80\% \leq x_{ACN} \leq 87\%$, the soaked strips are very difficult to inflame (Fig. 2c), then after a very brief inflammation, the tiny flame goes out. For mixtures of ACN with TMPA–TFSI, which content is over 20% in mol TMPA–TFSI (Fig. 2d), the soaked strips of paper present a remarkable resistance to the flame, like the pure TMPA–TFSI RTIL does (Fig. 2e), related to its

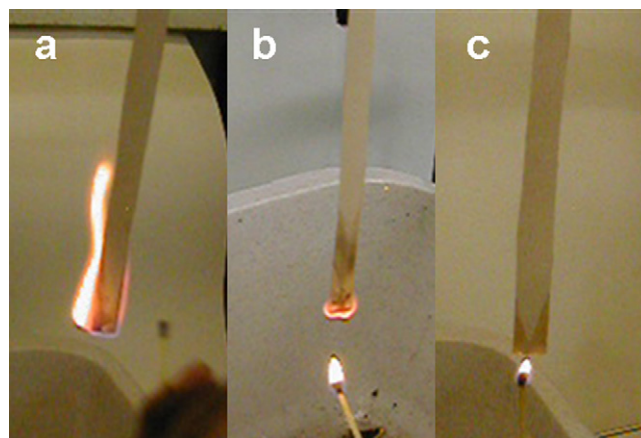


Fig. 3. Flammability tests in air on TMPA–TFSI/GBL mixtures: (a) 20% TMPA–TFSI/80% GBL (in mol), (b) 45% TMPA–TFSI/55% GBL (in mol), and (c) 55% TMPA–TFSI/45% GBL (in mol).

thermal stability at high temperatures [18]. These tests show that under the influence of the heat of the flame of the gas lighter, the most volatile solvent (ACN) partially vaporized ignites briefly when the molar TMPA–TFSI RTIL content is between 10% and 13% in the mixture. As presented in Fig. 3a–c, the same kind of results is obtained with GBL/TMPA–TFSI mixtures. Nevertheless the limit of flammability is dependent on either the organic solvent or the RTIL nature. All the obtained results are gathered in Table 3. According to these results, the minima molar fractions (x_S) of molecular solvent do not follow the same order for ACN and for GBL. This minimum increases according to the orders:

For ACN: $P_{14}\text{-TFSI} = \text{PIP}_{14}\text{-TFSI} < \text{BMIIm-BF}_4 < \text{TMPA-TFSI} = \text{Py}_{14}\text{-BF}_4$.
For GBL: $\text{BMIIm-BF}_4 = \text{TMPA-TFSI} < \text{Py}_{14}\text{-BF}_4 = P_{14}\text{-TFSI} < \text{PIP}_{14}\text{-TFSI}$.

It is noteworthy that these minima are not related to the RTIL density (see Table 2). Nevertheless for a same organic solvent, the limit range of the RTIL molar fraction is not too much extended (15% and 17% for GBL and ACN, respectively, i.e. around 5 mol of solvent for one of RTIL). So the TMPA–TFSI/organic solvent mixture is flammable beyond 42% in weight of ACN and 22% in weight of GBL. It is thus quite difficult to choose the best mixture (solvent/RTIL) only on flammability purposes. Moreover mixtures

Table 3
Minimum molar (x_S) and weight (w_S) fractions of molecular solvent (ACN or GBL) necessary to maintain the combustion in air of RTIL–solvent mixtures.

	BMIIm–BF ₄	Py ₁₄ –BF ₄	TMPA–TFSI	P ₁₄ –TFSI	PIP ₁₄ –TFSI
x_{ACN} (%)>	80	87	87	70	70
w_{ACN} (%)>	42	54	42	18	18
x_{GBL} (%)>	55	60	55	60	70
w_{GBL} (%)>	32	35	22	23	32

Table 4
Results of DSC analysis of mixed electrolyte containing TMPA–TFSI/ACN or GBL.

Mixture	x_S (%)	B_p (°C)
TMPA–TFSI/ACN	60	160
	80	140
	87	124
	100	82
TMPA–TFSI/GBL	50	273
	55	273
	100	204

GBL-based are more flammable than those ACN-based in spite of a higher boiling point for GBL. The main reason for this surprising fact is that ACN can easily form solvates with the RTILs [23], leading to a less flammable electrolyte, whereas GBL does not exhibit the same behaviour. GBL is a larger molecule thus it presents less interactions with the ionic liquid cations which explains this poor solvation. Nakagawa et al. [19] showed that from 60% in weight of organic solvent carbonate based, the mixture with PIP₁₃–TFSI (N-methyl-N-propylpiperidinium bis (trifluoromethylsulfonyl) imide) is flammable. Regarding to Guerfi et al. [21] results, the flammability limit of EMIm–TFSI (1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide)/organic solvent carbonate based is 60% in weight of organic solvent. This limit in carbonate solvent weight goes down to 36% when EMIm–BF₄ is used instead of EMIm–TFSI [20]. This value is quite close to ours for (GBL or ACN)/EMIm–BF₄. Thus the flammability of the RTIL/organic solvent mixtures depends not only on the flash point of the organic solvent [19] but also on the RTIL nature, which will determine the nature and the extend of the RTIL/solvent interactions.

3.2. Ionic transport properties

To choose the best RTIL to be mixed to ACN, it could be interesting to compare their transport properties. As reported in Table 2, for the pure RTIL under study, the dynamic viscosity increases at 25 °C according to: TMPA–TFSI < BMIm–BF₄ < P₁₄–TFSI < Py₁₄–BF₄ < PIP₁₄–TFSI while their ionic conductivity at 25 °C decreases according to: BMIm–BF₄ > TMPA–TFSI > P₁₄–TFSI > Py₁₄–BF₄ > PIP₁₄–TFSI. Thus it appears that BMIm–BF₄ and TMPA–TFSI are the best RTILs to be considered for electrolyte purposes. As shown in the preceding section, BMIm–BF₄ does not present the best flammability limit, x_{ACN} being quite low compared to the TMPA–TFSI/ACN one. Consequently, the best compromise seems to be a mixture containing 87% in mol of ACN for which the conductivity value at 25 °C is 43.27 mS cm⁻¹. This conductivity is more than thirteen times higher than the pure RTIL conductivity value (Table 2). It can be noticed also that this mixture is 10% less conductive than the best ACN based electrolyte (i.e. ACN + 1 M Et₄N⁺BF₄⁻) [24].

3.3. DSC study

DSC measurements over ambient temperature are realized to strengthen the flammability results. DSC analyses under ambient temperature are performed to determine the liquid state range of temperature.

3.3.1. DSC over ambient temperature

As an example, the thermogram of the mixture 20% TMPA–TFSI/80% ACN (i.e. 4 mol of ACN for one of RTIL) is represented in Fig. 4. We can first observe that the baseline is stable until 140 °C. This temperature characterizes the temperature at which the most volatile solvent is vaporized (neatly the boiling point). In Table 4, the boiling points are reported from the DSC analyses

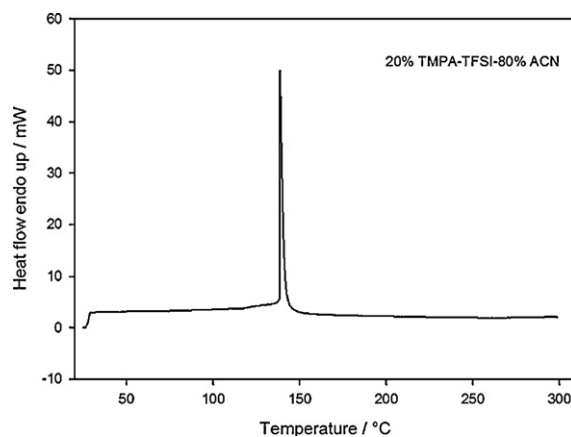


Fig. 4. Thermogram of the TMPA–TFSI/ACN (20/80 in mol) mixture at 2 °C min⁻¹.

performed at 2 °C min⁻¹. As expected for RTIL/organic solvent mixtures [18], their boiling points are increasing with the RTIL content. But this phenomenon is more limited for GBL-based mixtures than for ACN ones. Within the limit range for self-extinguishability ability, B_p increases in the case of ACN (from 124 °C for 87% in mol ACN to 140 °C for 80% in mol ACN), whereas for GBL this B_p does not change (273 °C for both 50% in mol GBL and 55% in mol GBL). Furthermore, when TMPA–TFSI amount is over 20% in mol, the ACN mixture has a higher B_p (160 °C for 40% in mol RTIL), leading to a better prevention of ACN from vaporization. The ACN molecules involved in a solvate are not available for vaporization. The DSC analyses over ambient temperature are in good concordance with the flammability test observations. For vaporization consideration, TMPA–TFSI/ACN (20/80 in mol) can be considered the best compromise among all the studied mixtures as electrolytes for supercapacitor devices.

3.3.2. DSC under ambient temperature

Supercapacitors can be used under ambient temperature. Thus the electrolyte must be liquid at least down to –20 °C. The DSC analysis is then performed to check the liquid state of the chosen mixture. DSC analysis under ambient temperature is realized on the molar mixture 20% TMPA–TFSI/80% ACN in a cooled environment between 20 °C and –80 °C. According to Fig. 5, the mixture is liquid in a wide temperature range until a cold crystallization occurring at –53 °C. This value is lower than the melting point of the pure ACN (i.e. M_p = –46 °C), suggesting the presence of an eutectic point in the

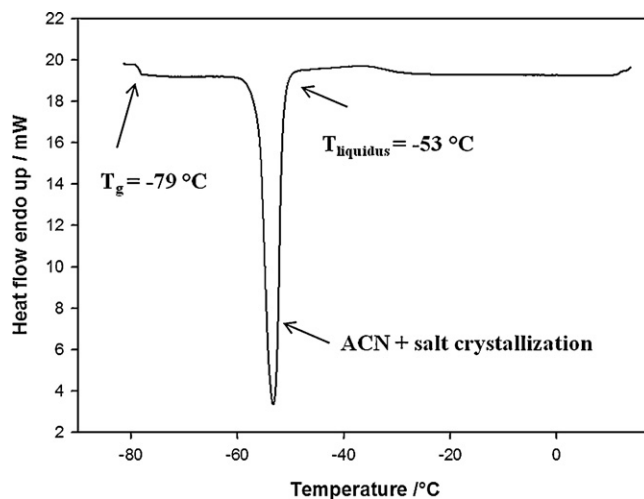


Fig. 5. Thermogram of the TMPA–TFSI/ACN (20/80 in mol) mixture under ambient temperature at 2 °C min⁻¹.

Table 5
Refractive index, n_D^{20} , of the pure ACN and the pure TMPA–TFSI and their 20/80 (in mol) mixture at 20 °C.

	ACN	TMPA–TFSI	20/80 in mol ACN/TMPA–TFSI mixture	
			From solid phase (at –53 °C)	From liquid phase (at –53 °C)
n_D^{20}	1.3438	1.4048	1.3895	1.3831

binary diagram of the TMPA–TFSI/ACN mixture. Under these operating conditions the vitreous transition temperature T_g is –79 °C which is close to the T_g of pure TMPA–TFSI (Table 2). In order to check the nature of the chemical component which crystallizes at –53 °C, a cold crystallization is performed on the 20/80 (in mol) TMPA–TFSI/ACN mixture poured in a pear-shape, two neck under argon atmosphere. It is cooled by the mean of cryostat (TC 100E–NR Huber, Fisher Scientific) and maintained at –53 °C during 2 h. The resulting liquid phase and solid phase are then separated, each of them is analysed at 20 °C by the refractometry method (Abbe's refractometer, Labonline) The results, reported in Table 5, indicate that the solid phase is rather a ACN + TMPA–TFSI solid compound than pure ACN or pure RTIL, this might be a solvate. Under the same experimental conditions (isotherm of 2 h), two gradually cooling experiments are performed on new TMPA–TFSI/ACN molar mixtures (i.e. 20/80 and 5/95). Both show that at –75 °C there is no more liquid phase, indicative of the presence of an eutectic point.

4. Electrochemical studies

In order to be selected as electrolyte, some electrochemical studies must be performed on TMPA–TFSI/ACN (20/80 in mol) and compared to the standard electrolyte ACN + 1 M Et₄N⁺BF₄[–].

4.1. Linear voltammetry

To determine the potential window of the electrolyte, a sweep linear voltamperometry under argon atmosphere is carried out on the 20% TMPA–TFSI/80% ACN molar mixture. The curve obtained is represented in Fig. 6. The potential window obtained with this mixture is 5.5 V, which is very close to the standard one (i.e. 5.9 V [25]). This value is very interesting for application in supercapacitors since it will permit to work on a large domain without risking to oxidize or to reduce the selected electrolyte. This potential window does not differ from the pure TMPA–TFSI one. This RTIL presents with P₁₄–TFSI the best resistance to electrochemical processes among the studied RTILs (see Table 2). Moreover, for power

Table 6
Capacitance values at variable scan rates.

v (mV s ^{–1})	1	10	20	50
i (mA)	0.19	1.89	3.86	9.84
C (Fg ^{–1}) ^a	86.4	85.9	87.7	89.5

^a From Eq. (1).

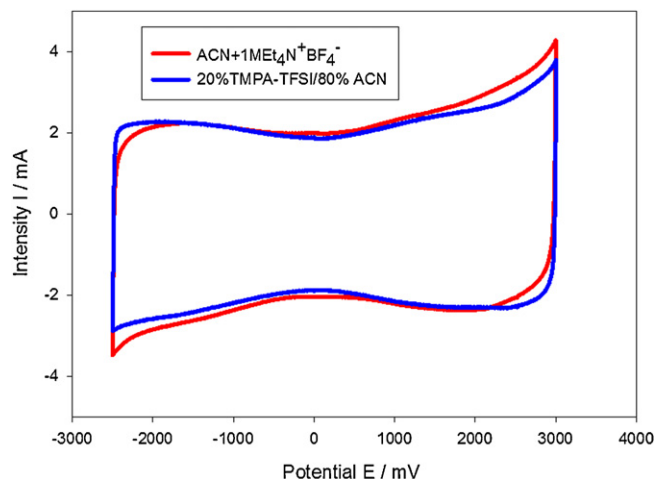


Fig. 7. Cyclic voltamperometry: comparison of the standard electrolyte with the TFSI/ACN (20/80 in mol) mixture at 10 mV s^{–1}.

density consideration, it is useful to have a large electrochemical window. This fact strengthens the choice of TMPA–TFSI instead of BMIm–BF₄, which electrochemical window is 4.0 V.

4.2. Application to supercapacitor

The TMPA–TFSI/ACN mixture (20/80 in mol) is tested by cyclic voltamperometry at variable scan rates, the resulting electrochemical values are reported in Table 6. As shown in Table 6, the current, i , is quite proportional to the scanning rate, v , thus it is possible to use the formula (see Eq. (1)) dedicated to double layer capacitance to calculate the capacitance, C , of the activated carbon:

$$C = \frac{2 \times i}{v \times m} \quad (1)$$

where m is the sample activated carbon material weight.

The capacitance obtained values are varying from 85.9 to 89.5 Fg^{–1}, the mean capacitance value being 87.4 (±1.2) Fg^{–1}. In order to check the validity of the proposed electrolyte, its CV performances are compared to those obtained with the standard electrolytes at a scanning rate of 10 mV s^{–1}. Results reported in Fig. 7 lead to a capacitance value of 90.9 Fg^{–1} for the standard electrolyte close to 85.9 Fg^{–1} obtained in the case of the selected mixture. All these electrochemical results are encouraging to consider the introduction of an ionic liquid in a supercapacitor electrolyte.

5. Conclusion

The mixture of ionic liquid–molecular solvent (ACN or GBL) is examined as possible electrolyte for supercapacitors in

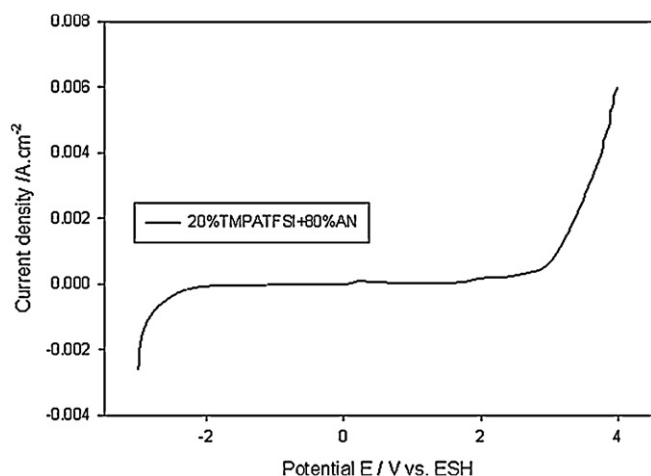


Fig. 6. Linear voltamperometry of the TMPA–TFSI/ACN (20/80 in mol) mixture at ambient temperature; WE: Pt rotating electrode at 1000 rpm at 10 mV s^{–1}, RE: silver wire, CE: Pt.

replacement of the standard ACN-based electrolyte. The ionic liquid–GBL mixtures tend to be flammable as the flammability molar limits in these mixtures are lower than those ACN-based. TMPA–TFSI RTIL is selected not only for its transport properties but also for its ability to protect the organic solvent from flammability. This tendency is strengthened by DSC analyses over ambient temperature, which show that ACN is better protected by TMPA–TFSI from vaporization than GBL. DSC analysis performed under ambient temperature indicates a large domain of temperature in which the mixture ACN-based is in liquid state. Furthermore the electrochemical window of the TMPA–TFSI/ACN (20/80 in mol) mixture is large enough to be introduced in a power density device (5.5 V). The capacitance value obtained with this mixture from cyclic voltamperometry is close to the standard electrolyte one (85.9 F g^{-1} vs. 90.9 F g^{-1}). Thus RTILs are good candidates, especially TMPA–TFSI, for replacing the ammonium salt, $\text{Et}_4\text{N}^+\text{BF}_4^-$, in the standard electrolyte for the safety of the supercapacitor device.

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