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Water-based synthesis of hydrophobic ionic liquids for high-energy electrochemical devices

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ABSTRACT

In this work is described an innovative synthesis route for hydrophobic ionic liquids (ILs) composed of *N*-methyl-*N*-alkylpyrrolidinium (or piperidinium) or imidazolium or tetralkylammonium cations and (perfluoroalkylsulfonyl)imide, $((C_nF_{2n+1}SO_2)(C_mF_{2m+1}SO_2)N^-)$, anions. This synthesis does not require the use of any environmental unfriendly solvent such as acetone, acetonitrile or halogen-containing compounds, which is not welcome in industrial applications. Only water is used as the process solvent throughout the entire process. In addition, the commonly used iodine-containing reagents were replaced by the cheaper, more chemically stable and less toxic bromine-containing compounds. A particular care was devoted to the development of the purification route, which is especially important for ILs to be used in high-energy electrochemical devices such as high voltage supercapacitors and lithium batteries. The effect of the reaction temperature, the time and the stoichiometry in the various steps of the synthesis have been investigated in detail. This novel procedure allowed obtaining ultrapure (>99.9 wt.%), clear, colourless, inodorous ILs with an overall yield above 92 wt.% and moisture content below 1 ppm. NMR measurements were run to confirm the chemical structure whereas elemental analysis and electrochemical tests were performed to check the purity of the synthesized ILs.

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1. Introduction

Room temperature ionic liquids (RTILs) are a very interesting new class of room temperature fluids. The main advantages with respect to organic solvents can be: non-flammability, negligible vapour pressure, high chemical, electrochemical and thermal stability, high ionic conductivity and, in some cases, hydrophobicity. Therefore, RTILs have attracted a large attention for use as "green" solvents for chemical reactions, bi-phasic catalysis, chemical synthesis, separations [1-5]. Also, RTILs have been extensively investigated for applications as advanced hightemperature lubricants and transfer fluids in solar thermal energy systems. More recently, they are under wide investigation as electrolytes (or electrolyte components) in the place of hazardous and volatile organic compounds for the realization of highly safe electrochemical devices including rechargeable lithium batteries, fuel cells, double-layer capacitors, hybrid supercapacitors, photoelectrochemical cells [6-22]. Ionic liquid electrolytes based on the N-methyl-N-alkylpyrrolidinium, PYR_{1A}^+ (A = propyl or

butyl), cation and the bis(trifluoromethanesulfonyl)imide, TFSI⁻, or bis(fluorosulfonyl)imide, FSI⁻, have been showing very good cycling reversibility with respect to lithium [14] and graphite [15–18] anodes, and LiCoO₂ cathodes [19]. Particularly, PYR₁₄FSI-LiTFSI mixtures have been recently employed as electrolytes in Li₄Ti₅O₁₂/LiFePO₄ lithium-ion cells, which have displayed very good cycling performance [20–22]. Also, incorporation of PYR_{1A}TFSI into PEO-based electrolytes was found to enhance the room temperature ionic conductivity above 10^{-4} S cm⁻¹, thus allowing to overcome the conduction drawback of solvent-free polymer electrolytes [23,24]. For instance, PEO-LiTFSI-PYR_{1A}TFSI ternary electrolyte systems were tested at low-medium temperatures (from 20 to 40 °C) in dry, all-solid-state, Li/LiFePO₄ polymer batteries, which delivered large capacity with high reversibility and very good cycling performance [22–25].

However, ionic liquids in the purity level required for electrochemical applications are not widely available commercially. Therefore, the electrochemistry community has devoted large efforts for obtaining highly pure ionic liquid materials. Previous work by MacFarlane et al. focused on the purification of ionic liquids [26,27]. The most stringent requirement in designing the synthesis of the hydrophobic ionic liquids is the solvent restriction. In our laboratory it was previously developed a synthetic route for PYR_{1A}TFSI ionic liquids, which has involved the use of acetone in the purification step of the PYR_{1A}I precursor [28]. It is known,

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Scheme 1. Chemical structure of the PYR₁₄TFSI ionic liquid.

however, that acetone is an undesirable solvent for industrial applications since its high volatility. In addition, tests carried out in our laboratory have indicated that acetone traces remaining in ionic liquids can form unwelcome, yellowish compounds with unpleasant odour when in contact with the materials (i.e., activated carbon and alumina) used for the purification of the final product, even at moderate temperatures (>50 °C).

Successively, we have proposed an improved procedure for the synthesis of hydrophobic room temperature ionic liquids, composed of PYR_{1A}^+ or piperidinium (PIP_{1A}^+) cations and (perfluoroalkylsulfonyl)imide ($C_nF_{2n+1}SO_2$)($C_mF_{2m+1}SO_2$)N⁻), PFSI, anions, which involves ethyl acetate (EtAc) and water as the solvents [29]. EtAc and H₂O are safer and more environmentally friend than acetone and, in particular, than acetonitrile and halogen-containing solvents generally used for IL synthesis processes [11,12,30].

In the present work we have further optimized the previous synthesis route. Only water is used throughout the entire process. In addition, alkyl iodine reagents were replaced by cheaper, more chemically stable and less toxic alkyl bromine compounds. A particular care was devoted in the purification route of the chemical reagents and precursors. The effect of the reaction temperature, the time and the stoichiometry in the various steps of the synthesis has been investigated in detail. NMR measurements were run to confirm the chemical structure whereas elemental analysis and electrochemical tests were performed to check the purity of the synthesized ionic liquid material. The results, referred to the synthesis procedure route of the PYR₁₄TFSI ionic liquid (Scheme 1), are reported in the present paper.

2. Experimental

N-methylpyrrolidine (PYR₁, Acros, 98 wt.%) and 1-bromobutane (1-Br-But, Aldrich, 99 wt.%) were previously purified through activated carbon (Aldrich, Darco-G60) and alumina (Aldrich, acidic, Brockmann I) whereas lithium bis(trifluoromethanesulfonyl) imide salt, LiTFSI (3 M, 99.9 wt. %), activated carbon and alumina were used as received. H_2O was deionized by a Millipore ion resin

exchange deionizer. Typically, ionic liquid batches ranging from 100 g to 250 g were prepared.

A one litre, glass, sealed reactor was consecutively used for the synthesis of the precursor (e.g., *N*-butyl-*N*-methylpyrrolidinium bromide, PYR₁₄Br) and the ionic liquid, this avoiding to expose the reagent materials to the external. The operating temperature of the reactor was controlled using an oil bath connected to the reactor. The filtration steps were performed using a Millipore vacuum filter system through hydrophilic, polyamide membranes whose pore size was lower than 0.2 μ m. An oil-free pump (<1 mTorr) was used to generate vacuum.

The separation of the rinsing fluid (water phase) from the ionic liquid was performed by aspiration generated by a water pump. The water residual was removed using a Heidolph LaboRota 4000 rotary evaporator connected with a KNF oil-free pump. The final drying step of the ionic liquid was performed in a dry room (R.H. <0.1%) using a Büchi B-585 glass vacuum oven connected with a Leybold PT-70 turbo-molecular pump (10^{-6} mTorr). The IL material was dried at 20 °C for 2 h, then at 60 °C for additional 2 h and, successively, at 120 °C for at least 18 h. Finally, the ionic liquid was stored in vacuum-sealed glass tubes.

The concentration of lithium cation (Li⁺) and bromide anion (Br⁻) in the ionic liquid sample was checked by a Spectro ARCOS ICP-OES (Spectro Analytical Instruments) instrument with axial plasma view. A standard Fassel type torch (No. 75160526, Spectro Analytical Instruments) was employed. The sample was introduced using a peristaltic pump system with a cross flow nebulizer and a double-pass spray chamber (Scott type). Elements were simultaneously detected at different individual emission lines.

The water content was measured using the standard Karl Fisher method. The titrations were performed by an automatic Karl Fisher coulometer titrator (Mettler Toledo DL32) located inside the dry room. The Karl Fisher titrant was a one-component (Hydranal 34836 Coulomat AG) reagent provided from Aldrich.

The chemical structure of the ionic liquid was checked by NMR measurements using an Avance III spectrometer working at 200.13 MHz on 1H (Bruker, Rheinstetten). The spectra were recorded with a broadband probe BBFO (Bruker, Rheinstetten). Deuterated DMSO, D6 (>99%, Aldrich), was used as the solvent. The peak assignment was made on the basis of the chemical shifts (expressed in parts per million, ppm) and peak integrals with DMSO (1H NMR δ = 2.49 ppm) signal as the reference.

The electrochemical stability window of the raw ionic liquid and its mixtures with a lithium salt was evaluated by linear sweep voltammetries (LSVs) at 5 mV s⁻¹. A sealed, three-electrode, glass micro-cell, described in details previously [31], was used for the LSV tests. The cell was loaded with a small amount of the ionic liquid sample (about 0.5 ml). A glass-sealed, platinum working electrode (active area = 0.78 mm²) and a platinum foil counter electrode (about 0.5 cm^2) were used. The reference electrode was a silver wire immersed in a 0.01 M solution of AgCF₃SO₃ (Aldrich) in PYR₁₄TFSI, separated from the cell compartment with a fine glass frit [31]. High purity argon (3 ppm water and 2 ppm oxygen) was flown over the ionic liquid sample under investigation for 30 min before the start of the test. The gas flow was continued during the experiment. Separate LSV tests were carried out to determine the cathodic and anodic electrochemical stability limits. The measurements were performed scanning the cell potential from the open circuit potential (OCP) towards more negative (cathodic limit) or positive (anodic limit) voltages. Clean electrodes were used for each LSV test, which was performed at least twice on different fresh samples in order to confirm the results obtained. Cyclic voltammetry (CV) experiments were run with the same cell structure under the analogous operative conditions to investigate both the presence of irreversible reactions associated to impurities and the lithium stripping/plating process. The potential values are given vs. the



Fig. 1. Dependence of the $PYR_{14}Br$ (precursor) synthesis yield as a function of the processing time at different temperatures and LiTFSI excess amounts.

Ag/Ag⁺ redox couple. The LSV and CV measurements were performed (in the dry room) at 20 °C using a Schlumberger (Solartron) Electrochemical Interface (model 1287) controlled by a software developed at ENEA.

3. Results and discussion

The synthesis here proposed was developed considering the use of water as the only solvent. No other compounds were used throughout the synthesis. Work was devoted in determining the minimum excess of reagents and the reaction conditions (temperature and time) necessary to optimize the yield, thus producing the minimum amount of waste. Butyl bromine was used in the place of the more expensive, more oxygen- and light-sensitive, and more toxic butyl iodine [29]. Particular care was taken in the purification route, which was carried out on both the chemical reagents (with the exception of LiTFSI) and the precursor (instead of the final ionic liquid), e.g., before the addition of the most expensive chemical (LiTFSI). This allowed to reduce the final cost of the ionic liquid and avoid the use of any organic solvent for the ionic liquid dilution. Finally, the possibility of chemical recycling was investigated. The procedure route was also optimized for the use of a single reactor.

In the following the results of the investigation performed to optimize the synthesis of PYR₁₄TFSI, starting from PYR₁, 1-Br-But and LiTFSI, are reported. The effect of the processing temperature and time, as well as the weight ratio of reagents and the amount of purifying materials and solvents, was investigated. The results are illustrated in Figs. 1–4. The weight of the reagents as well as the purification materials and deionized water used in the overall synthesis process of a 250-g batch is reported in Table 1. However, the same procedure has been successfully carried out for the synthesis of several other ionic liquids composed of PYR_{1A}⁺ or PIP_{1A}⁺ or imidazolium or tetraalkylammonium cations and PFSI anions.

3.1. Synthetic route of the PYR₁₄TFSI ionic liquid

The synthesis of the hydrophobic PYR₁₄TFSI ionic liquid through the aqueous route was performed through five iterative steps: (i) purification of the chemicals; (ii) synthesis of the PYR₁₄Br precursor; (iii) purification of the PYR₁₄Br precursor; (iv) synthesis of the PYR₁₄TFSI ionic liquid; (v) rinsing of the PYR₁₄TFSI ionic liquid. The overall synthesis process is schematized in Fig. 5 (panels from A through D).



Fig. 2. Yield of the PYR₁₄Br precursor purification step as a function of the water/(AC+Al₂O₃) weight ratio used for the rinsing of the purifying materials. The Al₂O₃/AC and (AC+Al₂O₃)/PYR₁₄Br weight ratios are also indicated.

3.1.1. Purification of chemicals

In order to enhance the purity of the resulting ionic liquid, a purification step was run on the neat reagents before the synthetic route. PYR_1 and 1-Br-But were previously purified through activated carbon (AC) and alumina (Al_2O_3) whereas LiTFSI, provided with a purity higher than 99.9%, was used as received.

Activated carbon (0.30 g and 0.15 g of AC per gram of PYR₁ and 1-Br-But, respectively) and alumina (0.30 g and 0.15 g of Al₂O₃ per gram of PYR₁ and 1-Br-But, respectively) were loaded in a glass reactor containing PYR₁ or 1-Br-But. The resulting slurry was stirred or ball-milled for 12–20 h at room temperature. Then, AC and Al₂O₃ were separated from the liquid fraction (containing the purified reagent) by vacuum filtration (oil-free pump) with PTFE filter (pore size < 0.2 μ m). Finally, the liquid fraction, constituted by clear and slightly coloured PYR₁ or 1-Br-But, was collected for the synthesis of PYR₁₄TFSI. No solvents were added during the purification of the reagents. A fraction lower than 10 wt.% of the two reagents was physically trapped into the purifying materials. This fraction could be recovered by rinsing the separated AC and Al₂O₃ with water (PYR₁) or water and ethanol (1Br-But).

3.1.2. Synthesis of PYR₁₄Br precursor

The precursor, $PYR_{14}Br$, was synthesized from PYR_1 and 1-Br-But through the following reaction performed in deionized water:

$$PYR_1(aqueous) + 1 - Br \rightarrow PYR_{14}Br(aqueous)$$
(1)



Fig. 3. Yield vs. processing time dependence of the Br^{-/}/TFSI⁻ anion exchange step at different LiTFSI excess amounts (vs. the stoichiometric amount). T = 20 °C.



Fig. 4. Summary of the yields and losses detected through the entire PYR₁₄TFSI aqueous synthesis route. The data given for each synthesis step are referred to the expected yield for that step. The overall process yield is reported in the last panel.

Purified PYR₁ was previously dissolved in deionized water (PYR₁/H₂O volume ratio equal to 1/1) and loaded into the glass reactor. Then, the appropriate amount of purified 1-Br-But was added. The latter chemical is immiscible with water and, therefore, a liquid phase separation was observed. The lower phase was mostly composed by the heavier 1-Br-But (1-Br-But density = 1.276 g cm^{-3} ;

 PYR_1 density = 0.819 g cm⁻³) whereas the upper one was mainly a PYR_1 /water mixture. The two phases (typically, clear and slightly coloured) were mixed (by magnetic stirring) at suitable temperature and time (Fig. 1). The progressive disappearance of the lower phase (and the simultaneous increase of the upper one) has given a clear indication of the ongoing formation of the PYR₁₄Br

Table 1

Weight of all chemical used in the overall aqueous synthesis route for a 250 g PYR₁₄TFSI ionic liquid batch.

Chemicals	Weight/g	Notes
(i) Purification of chemicals		
PYR ₁	56.0	Impurity content: 2 wt.%
1-Br-But	88.8	Impurity content: 1 wt.%
Activated carbon	30.1	$AC/PYR_1 = 0.30 AC/1-Br-But = 0.15$
Alumina	30.1	$Al_2O_3/PYR_1 = 0.30 Al_2O_3/1-Br-But = 0.15$
Purified PYR ₁ (product)	54.9	
Purified 1-Br-But (product)	87.9	
(ii) Synthesis of the PYR ₁₄ Br precursor		
Purified PYR ₁	54.9	0.5 wt.% PYR ₁ excess
Purified 1-Br-But	87.9	$PYR_1/1$ -Br-But weight ratio = 0.62
H ₂ O	67.0	PYR_1/H_2O volume ratio = 1/1
$PYR_{14}Br$ in aqueous solution	142.5	Step yield: about 100 mol.%
		(about 260 g of PYR ₁₄ Br per 100 g of PYR ₁)
		Process vield: about 100 mol.%
(iii) Purification of the PYR ₁₄ Br precursor		
PYR ₁₄ Br (aqueous)	142.5	From the synthesis step
H ₂ O	67.0	Extra dilution to reduce viscosity
Activated carbon	85.5	60 g of carbon per 100 g of PYR ₁₄ Br
Alumina	128.3	90 g of alumina per 100 g of $PYR_{14}Br$
H ₂ O	641.0	Extraction of PYR ₁₄ Br from the filtered solids
$Purified PYR_{14}Br$ in aqueous solution	139.5	Step yield: about 98 mol.%
•		Process yield: about 98 mol.%
		$(254 \text{ g of } PYR_{14}Br \text{ per } 100 \text{ g of } PYR_1).$
		The final solution contains 708 ml of H_2O .
(iv) Synthesis of the PYR ₁₄ TFSI ionic liquid		
Purified PYR ₁₄ Br(in aqueous solution)	139.5	From the purification step
LiTFSI (99.9 wt.%)	185.5	3 wt.% LiTFSI excess
		(133 g of LiTFSI per 100 g of PYR ₁₄ Br)
PYR ₁₄ TFSI	250	Step yield: 94.3 mol.%
		(about 180 g of PYR ₁₄ TFSI per 100 g of PYR ₁₄ Br)
		Process yield: 92.3 mol.%
		$(455g \text{ of } PYR_{14}TFSI \text{ per } 100 \text{ g of } PYR_1)$
(v) Rinsing of the PYR ₁₄ TFSI ionic liquid		
PYR ₁₄ TFSI	250	From the synthesis step
H ₂ O	186(5×)	$H_2O/PYR_{14}TFSI$ volume ratio = 1/1 for each single rinse
Purified PYR ₁₄ TFSI	250	Step yield: about 100 mol.%
		Process yield: 92.3 mol.%
		$(455 \text{ g of } PYR_{14}TFSI \text{ per } 100 \text{ g of } PYR_1)$



Fig. 5. Schematic representation of the synthesis process of the PYR₁₄TFSI, ionic liquid. Panel A: purification of chemicals. Panel B: synthesis of the PYR₁₄Br precursor. Panel C: purification of PYR₁₄Br. Panel D: synthesis and rinsing of PYR₁₄TFSI. Thick arrows indicate solids or slurries, thin arrows indicate liquids.

precursor (soluble in water and, therefore, in the upper phase). The completion of the reaction (1) has been easily detected by complete disappearance of the lower phase, e.g., a transparent, aqueous solution of PYR₁₄Br was obtained as final product. Although reaction (1) could be performed by directly mixing the two reagents in a reactor, water (which is a good solvent for PYR₁ but not for 1-Br-But) was used as diluent to promote the formation of the soluble precursor. It is to note that PYR₁₄Br (as well as butyl bromine) is much less sensitive to light and oxygen than PYR₁₄I [29] and, therefore, it may be easily handled without particular precautions.

The effect of the temperature, time and PYR₁ excess (vs. the stoichiometric amount of 1-Br-But) on the yield of the precursor synthesis process was investigated. Several trail tests were carried out under different operative conditions. After each test, the liquid compound was massively removed through vacuum distillation (by rotary evaporator at 90 °C for 3 h) to obtain a white, crystalline precipitate of PYR₁₄Br. Then, the solid precursor was dried (in the dry room) under vacuum at 90 °C overnight and, successively, weighted. The results are summarized in Fig. 1. The data clearly show that the processing temperature largely affects the kinetic of the PYR₁₄Br synthetic route. At room temperature (20 °C),

prolonged reaction times (24 h) were required to increase the yield up to reasonable values (70 wt.%) with a 5 wt.% PYR₁ excess. At higher temperatures ($\geq 60 \circ C$) more than 80 wt.% of the stoichiometric amount of PYR14Br was obtained in relatively short times. At 60 $^\circ\text{C}$ (5 wt.% PYR1 excess) yield values equal to 85 wt.% and approaching 100 wt.% were achieved after 1 and 2 h process, respectively. At 70 °C about 80 wt.% and 100 wt.% of the stoichiometric PYR₁₄Br amount were obtained after 15 and 25 min process, respectively. In addition, a PYR₁ excess ten times lower (0.5 wt.%) was used, this allowing to reduce the cost for chemicals and purification. Higher processing temperatures were not investigated for safety reasons (e.g., to avoid to get close to the boiling temperature of the compounds). Therefore, the operative conditions to synthesize the precursor were fixed at 70 °C (temperature) and 25 min (reaction time) with a PYR₁ excess equal to 0.5 wt.%. (e.g., allowing to drive the synthesis process of the PYR₁₄Br precursor with a 100% yield). It is to note that the reaction of PYR₁ with bromoalkyl compounds exhibits slower kinetics with respect to the iodoalkyl reagents [29] (e.g., the removal of bromide from haloalkyl compounds is slower with respect to iodide [32,33]), thus leading to higher process temperatures. However, this results in enhanced safety of the synthesis route of the precursor, especially when using haloalkyl compounds with long (haloesane and longer) or short (haloethane and shorter) chain since the reaction with PYR_1 is much more exothermic (e.g., the removal of halide from long chain haloalkyl compounds is easier since the higher stability of the carbocation [32,34] whereas the reduced steric hindrance of the carbocation from short chain haloalkyl compounds results in faster addition to the nitrogen of the pyrrolidinium ring) [29,33].

3.1.3. Purification of the PYR₁₄Br precursor

The purification of the precursor was performed through AC and Al₂O₃ which were found able to trap impurities [29]. The suitable amount of purifying materials (Table 1) was loaded into the reactor containing the aqueous PYR14Br solution (previously diluted with deionized water to reduce the viscosity) obtained from the synthesis step of the precursor. The resulting slurry was continuously stirred at room temperature (20 °C) for 3-4 h. Then, AC and Al₂O₃ were separated from the liquid fraction by vacuum filtration (performed using cellulose filter paper). The liquid fraction (constituted by a clear and colourless aqueous solution of PYR₁₄Br) was collected for the synthesis of PYR₁₄TFSI whereas the solid fraction (still loaded in the filtering glassware) was rinsed (Fig. 5) in situ with deionized water to remove PYR₁₄Br trapped through AC and Al₂O₃. The liquid fraction from the rinsing step (constituted by a clear and colourless diluted aqueous solution of PYR14Br) was combined with the previous one (from the filtering step).

The amount of AC and Al_2O_3 used to purify the PYR₁₄Br precursor as well the temperature and the stirring time was selected on the basis of an iterative process in which the amount of the purifying materials was increased until to obtain a complete discoloration of the PYR₁₄Br/H₂O solution. The optimum C/PYR₁₄Br and Al_2O_3 /PYR₁₄Br weight ratios were found to be 0.6 and 0.9, respectively (Table 1). Higher weight ratios are not recommended because the fraction of precursor obtained during the first filtration is reduced and larger amounts of deionized water are required for the further extraction of PYR₁₄Br. Therefore, the purification step was run at room temperature (20 °C), e.g., no relevant temperature effect was observed, with stirring time ranging from 3 to 4 h. The operative conditions selected as above were found to give good results for all precursors synthesized.

The water amount used for the rinsing step of AC and Al_2O_3 needs to be accurately dosed in order to recover most of the precursor without extracting the impurities trapped. Therefore, the solid fraction (AC and Al_2O_3) was progressively treated in situ (rinsed) with fixed amounts of water until the extracted solution turned from uncoloured to slightly yellowish. The liquid fractions, collecting upon rinsing, were vacuum distilled (in rotary evaporator at 90 °C for 3 h) to remove most of H_2O (from the precursor). Then, the (white) PYR₁₄Br precursor was dried under vacuum (by a oil-free pump) at 90 °C overnight and, successively, weighted. The results are displayed in Fig. 2, which reports the yield, in terms of the expected PYR14Br stoichiometric amount, as a function of the water/ $(AC + Al_2O_3)$ weight ratio used for rinsing the purifying materials. Both Al_2O_3/AC and $(AC + Al_2O_3)/PYR_{14}Br$ weight ratios were fixed to 1.5. The first data point, about 70 mol.%, represents the fraction of precursor directly obtained by the vacuum filtration of the AC + Al_2O_3 slurry. The rinsing of the purifying materials allowed to enhance the yield of the purification step up to about 97 mol.% for a water/(AC + Al₂O₃) weight ratio of 3.0. Repeated tests performed on different size batches (the precursor was fully dried and weighed) indicated a reproducible yield of the purification test close to 97 mol.%. No relevant amount of PYR14Br was recovered for further water addition (Fig. 2) whereas a more extensive rinsing led to a slightly yellowish colouration of the liquid fraction, this indicating the partial release of impurities by carbon and alumina. Therefore, the overall amount of deionized water used for the rinsing step was equal to 641 g whereas the final volume of the aqueous solution, containing approximately 140 g of PYR₁₄Br precursor, was about 770 ml.

3.1.4. Synthesis of the PYR₁₄TFSI ionic liquid

PYR₁₄TFSI was synthesized from aqueous PYR₁₄Br and LiTFSI by the following reaction:

$$PYR_{14}Br(aqueous) + LiTFSI(solid) \rightarrow PYR_{14}TFSI(liquid)$$

$$+$$
 LiBr(aqueous) (2)

LiTFSI was added, e.g., in slight excess with respect to the stoichiometric amount (Fig. 3), to the aqueous PYR₁₄Br solution obtained from the purification step, resulting in the dissolution of the former immediately followed by its reaction with PYR14Br (through anion exchange which replaces Br⁻ with TFSI⁻) to form hydrophobic PYR₁₄TFSI and hydrophilic LiBr. The rapid formation of two liquid phases clearly indicated that the anion exchange reaction, driven by the intrinsic hydrophobicity of both the PYR₁₄⁺ cation and the TFSI- anion, proceeded quickly. For instance, both PYR₁₄⁺ and TFSI⁻, in which the charge is well shielded by hydrophobic groups (PYR₁₄⁺) or extensively delocalized (TFSI⁻), do not easily form hydrogen bonds with water molecules and tend to separate from the aqueous phase forming a second (denser) liquid phase. Therefore, the disappearance itself of the (ionic liquid) PYR14TFSI product from the aqueous solution drove the exchange reaction to completion. Then, the two liquid phases were vigorously stirred at room temperature to facilitate the anion exchange reaction. After a selected time (Fig. 3) the stirring was interrupted and the phase separation took place in a few minutes. The upper phase (clear and colourless) was mostly composed of water, lithium bromide (LiBr) and LiTFSI excess whereas the lower one (uncoloured and generally slightly cloudy) was mostly constituted of PYR14TFSI ionic liquid with lithium salts (i.e., LiBr and LiTFSI) and traces of water.

The dependence of the process yield vs. exchange reaction time, for different LiTFSI excess amounts with respect to the stoichiometric amount, is reported in Fig. 3. After 10 min about 91% of the expected stoichiometric amount of PYR₁₄TFSI was obtained with an excess of LiTFSI equal to 1 wt.%. After 30 min, the yield of the anion exchange process levelled to 92 mol.% whereas no practical increase of the yield was observed at longer process times (1 h). An increase of the LiTFSI excess up to 3 wt.% allowed to obtain a yield equal to 94 mol.% even after 1 min reaction whereas no relevant increase was detected at longer process time (1 h). Previous work [29] has demonstrated that further increases of the LiTFSI excess led to a decrease of the anion exchange yield. This behaviour is due to the fact that, even if $PYR_{14}TFSI$ is insoluble in water (at room temperature), its anion (TFSI⁻) bounds very strongly to Li⁺ cations (from LiBr and LiTFSI excess) [35,36]. The strong coordination of lithium ions by water molecules and TFSI⁻ anions is the driving force causing the partial dissolution of $PYR_{14}TFSI$ in the aqueous phase. The higher is the amount of lithium in the aqueous phase the lower is the yield of the anion exchange process. These results suggested the use of a very limited excess of LiTFSI, which, in addition, is the most expensive reagent used in the ionic liquid synthesis process. Therefore, the anion exchange reaction time was limited up to 2–3 min whereas the LiTFSI excess was fixed equal to 3 wt.%.

3.1.5. Rinsing of the PYR₁₄TFSI ionic liquid

The strong coordination of Li⁺ and TFSI⁻ is also the reason for the presence of lithium salts (i.e., unreacted LiTFSI and LiBr) in the ionic liquid phase. Therefore, after removal of the upper aqueous phase, the PYR14 TFSI ionic liquid was rinsed five consecutive times with deionized water to remove water-soluble salts (e.g., LiBr and LiTFSI excess) and impurities. The water/ionic liquid volume ratio was fixed to 1/1 for each rinsing. In previous work [29] we have demonstrated that this rinsing route allows reducing the Li⁺ concentration in the ionic liquid below $3 \mu g dm^{-3}$ (2 ppb). The rinsed PYR14TFSI was vacuum filtered (over polyamide filter having pore size < 0.2 µm) to remove solid residual (mostly AC and Al₂O₃ particles from the purification step) and, then, vacuum distilled (rotary evaporator) at 90 °C for 2-3 h (to remove most of water). Successively, PYR₁₄TFSI was dried (within the dry room) at 20 °C for 1 h, then at 60 °C for 3 h and, finally, at 120 °C for 18 h (the progressive heating avoids fast bubbling of the residual water, this resulting in ionic liquid spying out off the glass container). The ionic liquid was stored in vacuum-sealed glass tubes within the dry room.

In Fig. 4 are summarized the yield and loss values, reported in mol.%, of the entire synthesis process as well as of each step. About 100% of the expected stoichiometric amount was obtained from the PYR₁₄Br precursor synthesis using a very small PYR₁ excess (0.5 wt.%). The purification step allowed to minimize the PYR₁₄Br loss (2.1 mol.%); more than 68 mol.% of precursor was obtained directly through the first filtration whereas about 30 mol.% was recovered through carbon and alumina rinsing. The anion exchange process showed a yield of 94.3 mol.% using a moderate excess (3 wt.%) of LiTFSI. The loss is due to the enhanced ionic force of the aqueous phase due to the presence of LiBr (1:1 mole ratio with respect to the ionic liquid), which favours the ionic liquid dissolution in water [29]. Conversely, no detectable ionic liquid loss was observed upon the (following) rinsing step of PYR14TFSI. To summarize, above 92 mol.% of the expected stoichiometric amount of PYR14TFSI was obtained through the entire aqueous synthetic route, this value resulting higher than the overall yield detected in ethyl acetate solvent (86 mol.%) [29]. More important, the aqueous route (with respect to the organic one) allowed to reduce the loss of the expensive fluorinated anion (TFSI) to about one third (5.7 mol.% vs. 16.3 mol.%).

The overall synthesis route of the PYR₁₄TFSI ionic liquid is schematized in Fig. 5 whereas the weight of all chemicals used is reported in details in Table 1.

3.2. Recycling of chemicals

The ionic liquid losses through the aqueous synthesis route were localized in the precursor purification (2.1 mol.% of PYR₁₄Br trapped on the surface of carbon and alumina) and anion exchange (about $5.7 \text{ mol.\% of PYR_{14}TFSI}$ was lost by dissolution in water) steps. However, these fractions may be recovered by appropriate processing of the carbon and alumina waste (which is fully recycled) and of the aqueous phase waste (from the anion exchange).

The precursor trapped on the surface of the purifying materials was recovered through extensive rinsing (of the carbon and alumina waste) with deionized water. A fixed amount of AC and Al₂O₃ (loaded in a glass reactor) was quickly stirred with H₂O for 1 h at room temperature. The H₂O/(AC and Al₂O₃) weight ratio was fixed equal to 2 for each rinsing step. Then, the solid fraction (AC and Al_2O_3) was separated from the aqueous phase by vacuum filtration (performed using polyamide filter having a pore size lower than 0.2 µm) whereas the liquid fraction (clear and almost uncoloured diluted aqueous solution of PYR14Br) was separately collected. The rinsing steps on the purifying materials were iteratively repeated until no trace of PYR₁₄Br (revealed from the bromide anion) was detected in the aqueous phase. The presence of Br⁻ in the aqueous phase upon each rinsing step was checked with AgNO₃. For instance, 1.0 ml of the aqueous phase was added to 1.0 ml of 0.1 N AgNO₃ in water solution. A pale-yellow, solid precipitate indicated formation of AgBr. After a few rinsing steps, just a turning of the resulting solution from clear to opaque was observed. Therefore, the solution was centrifuged for a few minutes to better evidence the AgBr precipitate. An overall amount equal to 1 litre of H₂O per 100 g of carbon and alumina was required for a complete removal of PYR₁₄Br, e.g., no AgBr precipitate was observed in the aqueous phase upon the last rinsing step, this resulting in an estimated Brconcentration lower than 1 ng dm⁻³. The PYR₁₄Br precursor, recovered from the purifying materials, was separated from the aqueous liquid fractions by vacuum distillation (90 °C). The above-described route, schematized in panel A of Fig. 6, allowed recovering about 100% of the precursor lost in the purification step. Finally, AC and Al₂O₃ from the rinsing steps were vacuum annealed at 200 °C for 3 h to fully remove impurities.

The ionic liquid lost during the anion exchange step was recovered by vacuum distillation $(90 \circ C)$ of the aqueous phase waste (the vapor pressure of LiBr, LiTFSI and PYR₁₄TFSI is not measurable). After water removal, a slurry composed of ionic liquid and a white precipitate of LiBr (mostly undissolved in PYR14 TFSI at room temperature) was obtained, which was, then, vacuum filtered (using Teflon filter having a pore size lower than $0.2 \,\mu\text{m}$) to separate the lithium salt. Successively, the ionic liquid was rinsed (10 min stirring at room temperature) a few times with deionized water to remove the fraction of LiBr (and LiTFSI) dissolved in PYR14 TFSI. The $H_2O/PYR_{14}TFSI$ volume ratio was fixed equal to 1/1 in each rinsing step. As well as reported above for the rinsing of the purifying materials, the presence of Br⁻ in the aqueous phase (removed by vacuum aspiration upon each rinsing step) was checked with 0.1 N AgNO₃ in water. After six consecutive rinsing steps, no practical amount of bromide was detected. This route (panel B of Fig. 6) allowed to recover practically the 100% of the ionic liquid (and LiBr) lost in the anion exchange step.

3.3. Analysis of the PYR₁₄TFSI ionic liquid

The aqueous route described above allowed synthesizing clear and colourless $PYR_{14}TFSI$ ionic liquid with water content lower than 1 ppm. However, we have observed that glass tubes (in which are generally housed ionic liquids) are capable to deliver moisture to ionic liquid material. To demonstrate this issue, we have dried a $PYR_{14}TFSI$ sample, synthesized in external environment and housed in a glass tube, following the protocol described above (within the dry room). After the drying step, the humidity content of the ionic liquid sample was checked, resulting below 1 ppm. Then, the glass tube containing $PYR_{14}TFSI$ was immediately closed, vacuum-sealed in a pouch envelope (previously evacuated for 1 h) and kept in the dry room. The moisture content of the ionic liquid sample was periodically checked. The results (not shown here)



Fig. 6. Schematic representation of the recycling route of PYR₁₄Br lost during the purification step (panel A) and PYR₁₄TFSI lost during the anion exchange step. The recycling of the purifying materials waste and processing water was also investigated. Thick arrows indicate solids or slurries, thin arrows indicate liquids.

showed a progressive increase of the humidity amount with the storage time, achieving 30 ppm and 180 ppm after a storage period of 48 days and 20 months, respectively. This suggests a continuous release of water from the glass tube, which, therefore, has to be carefully dried and stored in a controlled environment before loading with ionic liquid.

NMR measurements were performed to verify the correct structure of the synthesized ionic liquid. The results, reported in Fig. 7, indicate that the PYR₁₄TFSI material was correctly prepared. Elemental analysis has revealed an extremely low content of lithium cation and bromide anion, e.g., below 1 ppb (Li⁺) and 0.8 ppm (Br⁻), respectively

The purity of the ionic liquid has been investigated also by means of electrochemical measurements. Fig. 8, panel A, reports the result



Fig. 7. NMR spectrum of a PYR₁₄TFSI ionic liquid sample synthesized through the aqueous route. NMR chemical shifts are also reported.

of linear sweep voltammetries (LSVs) performed on PYR14TFSI obtained from aqueous route (solid line) to investigate the anodic and the cathodic electrochemical stability at 20 °C. The anodic current flow observed at voltages above 2.0 V (vs. Ag/Ag⁺) corresponds to the TFSI- anion oxidation whereas the cathodic one recorded at -3.8 (vs. Ag/Ag⁺) is related to the PYR₁₄⁺ cation reduction. No other features were observed during the anodic and cathodic scans, thus excluding the presence of impurities which are oxidized or reduced within the anodic and cathodic electrochemical stability limits of the ionic liquid, showing an ESW exceeding 5 V. On the other hand, an analogous ionic liquid sample from organic solvent route [29] (dotted line) exhibits some current flow during the cathodic scan above -1.7 V (vs. Ag/Ag⁺), i.e., well above the extensive decomposition (reduction) of the PYR14TFSI material. The nature of the processes taking place is not well known but it is to be related with the reduction of impurities. Therefore, the aqueous route allows obtaining ionic liquids with higher purity.

The addition of LiTFSI (previously dried under vacuum at 120 °C for 24 h, PYR_{14}^+/Li^+ mole ratio = 9/1) resulted in the appearance of current features (panel B of Fig. 8) in the voltage (cathodic) region ranging from -1.5 V to -3.3 V (vs. Ag/Ag⁺). In previous work [15] we have demonstrated that these features are due to LiTFSI salt impurities which act as catalyst for the reduction of the TFSIanion. Cathodic features, detected prior the lithium plating onto platinum working electrodes, were observed in lithium salt liquid electrolytes also by Compton et al. [37]. These impurities, however, are eliminated during the PYR14TFSI synthesis route (e.g., PYR₁₄TFSI rinsing step) since no similar profiles were evidenced in the cathodic stability window of the pure ionic liquid. It is important to note, however, that lithium metal is plated on the platinum working electrode, as indicated by the cathodic peak shown at -3.8 V (vs. Ag/Ag⁺), prior the ionic liquid decomposition (reduction). At more cathodic potentials the current associated to the



Fig. 8. Linear sweep voltammetries (LSVs) of pure PYR₁₄TFSI (panel A) synthesized through the aqueous route (solid line) and VOC route (dotted line, from Ref. [29]). In panel B are compared the LSVs of pure PYR₁₄TFSI (aqueous route, solid line) and its mixture with LiTFSI (PYR₁₄⁺/Li⁺ = 9, dotted line). Magnifications of the LSVs are offered in the inserts. Platinum was used as the working and the counter electrode, respectively. The reference electrode was a silver wire immersed in a 0.01 M solution of AgCF₃SO₃ in PYR₁₄TFSI. Scan rate: 5 mV s⁻¹. T = 20 °C. The potential is given vs. the Ag/Ag⁺ redox couple.

lithium plating process assumed the limiting current value until the extensive reduction of the PYR_{14}^+ cations took place at -4.5 V(vs. Ag/Ag⁺). If the cathodic limit was set above such a value, the lithium plating process was found to be reversible as shown by the cyclic voltammetry presented in Fig. 9. Such a good lithium plating-stripping reversibility makes the LiTFSI-PYR₁₄TFSI mixture an appealing electrolyte for high safety lithium batteries.



Fig. 9. Lithium/plating process of a PYR₁₄TFSI-LiTFSI (PYR₁₄⁺/Li⁺ = 9/1) mixture on a platinum working electrode at 20 °C. Platinum was also used as the counter electrode. The reference electrode was a silver wire immersed in a 0.01 M solution of AgCF₃SO₃ in PYR₁₄TFSI. Scan rate: 5 mV s⁻¹. T=20 °C. The potential is given vs. the Ag/Ag⁺ redox couple.

4. Conclusions

An innovative and improved route has been developed to synthesize hydrophobic, ionic liquids composed of Nmethyl-N-alkylpyrrolidinium (or piperidinium) or imidazolium or tetralkylammonium cations and (perfluoroalkylsulfonyl)imide, $((C_nF_{2n+1}SO_2)(C_mF_{2m+1}SO_2)N^-)$, anions. The preparation procedure requires water as the only solvent and is suitable of lab-scale and industrial applications. Particular care was devoted to the purification steps and the recycling of chemicals was investigated. The process allowed to obtain clear, colourless, inodorous, high purity ionic liquid (>99.9 mol.%) with a water content below 1 ppm and an overall yield above 92 mol.%. Electrochemical measurements performed on three-electrode cells containing PYR14TFSI and its mixtures with LiTFSI as the electrolyte have confirmed the high purity of the ionic liquid by showing the possibility to reversibly reduce lithium ions to lithium metal. This ionic liquid is viable for the realization of next generation batteries based on lithium metal anodes and elemental cathodes such as sulphur or air.

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