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(54) Title: PROCESS FOR THE AT LEAST PARTIAL REMOVAL OF FLUOROSULFONIC ACID AND/OR DERIVATIVES THEREOF FROM A CRUDE FLUOROSULFONYLIMIDE COMPOUND MIXTURE

(57) Abstract: The invention relates to a process for the at least partial removal of fluorosulfonic acid and/or derivatives thereof from a crude bis(fluorosulfonyl)imide mixture, containing a hydrogen bis(fluorosulfonyl)imide compound, and fluorosulfonic acid and/or derivatives thereof so as to create a purified mixture by reacting said crude mixture in the molten phase with a halide or sulfate salt.

Description

Process for the at least partial removal of fluorosulfonic acid and/or derivatives thereof from a crude fluorosulfonylimide compound mixture

Cross-reference to related patent application(s)

[0001] This patent application claims priority from patent application No. 23305876.7, filed in Europe on 2 June 2023, the whole content of this application being incorporated herein for all purposes.

Technical Field

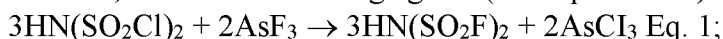
[0002] The invention relates to a process for the at least partial removal of fluorosulfonic acid and/or derivatives thereof from a crude fluorosulfonylimide compound mixture.

Background Art

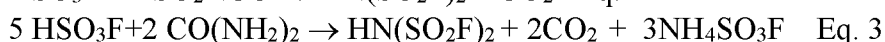
[0003] Bis(fluorosulfonyl)imide and salts thereof, in particular the lithium salt of bis(fluorosulfonyl)imide (LiFSI), are useful compounds in a variety of technical fields. Bis(fluorosulfonyl)imide and their salts are especially useful in battery electrolytes.

[0004] Bis(fluorosulfonyl) imide (HFSI, of formula $\text{HN}(\text{SO}_2\text{F})_2$) is a well-known intermediate in the production of second generation battery salts (e.g. LiFSI or NaFSI); various synthetic routes for preparing HFSI have been proposed:

- HFSI may be manufactured by fluorination of bis(chlorosulfonyl) imide (HCSI), with various fluorinating agents, in particular by nucleophilic fluorination, e.g. using HF, AsF_3 , SbF_3 as fluorinating agents (see Eq. 1 below):



- HFSI may be manufactured by reaction of fluorosulfonic acid (FSA, of formula FSO_3H) with e.g. fluorosulfonyl isocyanate (see Eq. 2 below) or urea (see Eq. 3 below):



[0005] Regardless of the method of making it, manufacture of HFSI comes with the presence of several impurities that might remain in the final product (as such or transformed by the downstream process) and be detrimental to the performance of the FSI salt in battery applications. FSA is a critical impurity for that purpose.

[0006] Indeed, in the reactions of Equations 2 and 3, the HFSI is often contaminated with excess fluorosulfonic acid (FSA). Further, FSA is a recurrent contaminant for HFSI manufactured from other routes not involving the use of FSA itself as raw material, as it is a recurrent side-product, which may be notably formed by decomposition/hydrolysis of HFSI itself or by fluorination of CSA.

[0007] Now, HFSI and FSA have very close boiling points (170°C for HFSI and 165°C for FSA, respectively), thus making purification by fractional distillation both difficult and expensive.

[0008] Methods for the removal of FSA from HFSI have been proposed in the past.

- [0009] Methods for purifying HFSI from F-SO₃H (FSA) by selective salification with an organic solvent dispersion of a metal halide were already known in the art. For example, **J.K. Ruff *et al.*, Inorganic Synthesis, Volume XI (1968), 138-142** discloses contacting crude HFSI containing FSA with a suspension of NaCl in dichloromethane at room temperature, followed by removal of solids by filtration, and distillation for removal of dichloromethane and recovery of purified HFSI under reduced pressure. This document discloses a process that requires a solvent. Similar technique is referred in **Ruzicka *et al.*, Z. Chem., 27. Jg. (1987), Heft 5, 180**; **Vij *et al.*, Coordination Chemistry Review, 158 (1997), 413-432** generally disclose that yield of HFSI in the fluorination of bis(chlorosulfonyl) imide (HCSI) can be improved by better separation of bis(chlorosulfonyl) imide, chlorosulfonic acid and fluorosulfonic acid, citing a stoichiometric addition of KCl. Now, these lab scale methodologies, using organic solvents, like dichloromethane, are not suitable for industrialization, due to the additional complexities caused by the introduction of an additional organic component in the system, subject to further separation, and recycle process steps, and cause by the toxicological profile of the same.
- [0010] More recently, **US11267707** to HONEYWELL has proposed a method of producing purified bis(fluorosulfonyl) imide, said method including providing a liquid mixture including bis(fluorosulfonyl) imide and fluorosulfonic acid and then contacting the liquid mixture with gaseous ammonia. The gaseous ammonia reacts with the fluorosulfonic acid to produce ammonium fluorosulfate. The method further includes separating the liquid mixture from the ammonium fluorosulfate. Separating the liquid mixture from the ammonium fluorosulfate may include any of (i) filtering the solid ammonium fluorosulfate from the liquid mixture; flash distilling the HFSI from the ammonium fluorosulfate, leaving behind the solid ammonium fluorosulfate. The method thereby described does not introduce any additional water or organic solvent into the system, unlike processes known in the art. Yet, this method requires the use of toxic, corrosive and flammable ammonia gas.
- [0011] There is hence a shortfall in the art for an improved, efficient and economically effective method to remove fluorosulfonic acid from HFSI, without the use of toxic, dangerous or harmful solvents/reactants, which could supply high purity HFSI for use as a raw material in the production of lithium bis(fluorosulfonyl) imide.

Summary of invention

- [0012] One object of the present invention is a method for the at least partial removal of fluorosulfonic acid and derivatives thereof from a crude bis(sulfonyl)imide mixture comprising a compound of formula (I)
 $\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1$ (I) wherein R¹ represents F or Cl; preferably R¹ is F; and further comprising fluorosulfonic acid of formula (II):
 $\text{F-SO}_2\text{-OH}$ (II) or a salt thereof
 [crude mixture (C-HFSI)] ;
 said method comprising:
 Step (a) - melting the crude mixture (C-HFSI) at a temperature exceeding the melting point of compound of formula (I), so as to obtain a molten mixture [molten mixture (M-FSI)];

- Step (b) - contacting the molten mixture (M-HFSI) with at least one salt (S) of formula M^pX_p or $M^p_2(SO_4)_p$, whereas M^p is a metal cation of valence p, with $p=1$ or 2 , or is an ammonium cation of valence $p=1$; X is a halide, preferably selected from Cl and Br, wherein the amount of Salt (S) is of 0.9 to 10 molar equivalent for each molar equivalent of compound of formula (II) present in crude mixture (C-HFSI), so as to at least partially convert compound (II) into its corresponding fluorosulfonic acid salt of formula $(F-SO_3)_pM^p$; and
- Step (c) - at least partially removing said fluorosulfonic acid salt, so as to obtain a purified mixture [purified mixture (P-HFSI)];
 wherein Step (b) is carried out in the substantial absence of any diluent; and
 wherein the content of compound (II) or salt thereof in mixture (P-HFSI) is lower than the content of the same in mixture (C-HFSI).
- [0013] The Applicant has surprisingly found that the method detailed above has the following advantages:
1. Providing high purity bis(sulfonyl)imide compounds which simplifies downstream purification steps in the manufacture of bis(sulfonyl)imide salts.
 2. Efficient removal of FSO_3H to ppm level
 3. Absence of process diluents (also referred to as solvents) (sustainability, HSE, final product quality)
 4. Salification reagents are cheap and have low toxicity;
 5. Only acid halides and fluorosulfonate salts are generated as side products which can be easily separated;
 6. Reaction proceeds in mild conditions (RT, Patm).

Disclosure of the invention

- [0014] In the present disclosure:
- the expressions “comprised between ... and ...” as well as “ranging from...to...” or the like should be understood as including the limits;
 - any description, even though described in relation to a specific embodiment, is applicable to and interchangeable with other embodiments of the present invention;
 - where an element or component is said to be included in and/or selected from a list of recited elements or components, it should be understood that in related embodiments explicitly contemplated here, the element or component can also be any one of the individual recited elements or components, or can also be selected from a group consisting of any two or more of the explicitly listed elements or components; any element or component recited in a list of elements or components may be omitted from such list; and
 - any recitation herein of numerical ranges by endpoints includes all numbers subsumed within the recited ranges as well as the endpoints of the range and equivalents.
- [0015] According to the present invention, in step (a), crude mixture (C-HFSI) comprising compound (I) of formula $F-SO_2-NH-SO_2-R^1$ is molten, by raising the temperature beyond the melting point of compound (I); when R^1 is F, that is to say in preferred embodiments of the present invention, compound (I) is bis(fluorosulfonyl) imide (HFSI); its melting point is about $17^\circ C$, which means that in step (a) crude mixture (C-HFSI) comprising compound (I) of formula $F-SO_2-NH-SO_2-R^1$ is molten by heating at a temperature exceeding about $17^\circ C$.

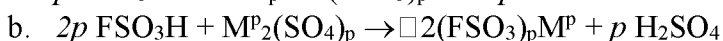
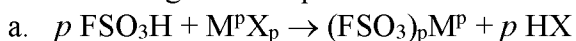
- [0016] The choice of the temperature is not particularly critical, provided that the appropriate molten viscosity is achieved, for delivering the crude mixture (C-HFSI) in molten form to step (b).
- [0001] Generally, temperature in Step (a) is ranging between 17°C and 120°C, preferably between 20°C and 80°C, more preferably between 24°C and 50°C.
- [0017] The content of fluorosulfonic acid and derivatives thereof in crude mixture (C-HFSI) is not particularly limited. The method of the present invention is effective for at least partial removal of the fluorosulfonic acid and derivatives thereof in variable amounts. This said, it is generally understood that crude mixture (C-HFSI) may comprise fluorosulfonic acid and derivatives thereof in an amount of at least 500 ppm, preferably of at least 1000 ppm, more preferably of at least 1500 ppm. Upper boundaries are not particularly limited, although it is practical for the crude mixture (C-HFSI) to comprise fluorosulfonic acid and derivatives thereof in an amount of at most 10 000 ppm, preferably of at most 8000 ppm, more preferably of at most 5000 ppm.
- [0018] Generally, compound (I) of formula $F-SO_2-NH-SO_2-R^1$, and preferably HFSI, is molten under a protective atmosphere, notably under an atmosphere which is substantially exempt from moisture. The amount of moisture in step (a) is generally kept below 5,000 ppm, more preferably below 1,000 ppm, more preferably below 500 ppm, more preferably below 100 ppm even more preferably below 50 ppm, with respect to the compound (I) of formula $F-SO_2-NH-SO_2-R^1$.
- [0019] As said, step (b) is generally carried out in the substantial absence of any diluent. This means that no diluent is added, and if any diluent is present in molten mixture (M-HFSI), its amount is less than 1 wt.% based on the total weight of the crude mixture (C-HFSI).
- [0020] As said, step (b) of the method of the present invention is a substantially diluent-free step. In the present description and in the following claims, the term “diluent” and “solvent” are intended as synonyms. In other words, no solvent/diluent, alternatively a very low amount of diluent, is present in the mixture (M-HFSI) during the reaction of step (b). Carrying out step (b) without adding any further diluent is especially advantageous. Indeed, the use of diluent during such a step implies that the diluent(s) will have to be removed after reaction in order to obtain an as pure as possible product which can be used for battery applications. The step for removing the diluent adds to the complexity of the industrial process, as well as its overall cost. In addition, before being used, the diluents typically have to be treated to remove the residual amount water, as only anhydrous diluents, where the residual amount of water is in the ppm amount, may be tolerated (moisture causing otherwise unwanted hydrolysis reactions of HFSI or its salts). It is therefore a main advantage that step (b) of the present process may be carried out essentially diluent-free. Deleterious reactions, which could occur between HFSI, its impurities or hydrogen chloride by-product formed in step (b) and the diluent possibly used, can be avoided. Additionally, because the step for removing the diluent is not needed for step (b), the present invention overall provides a simpler HFSI purification process, significantly decreasing the complexity of the industrial process, as well as its overall cost.
- [0021] Preferably, the amount of diluent in the molten mixture (M-HFSI) is less than less than 0.5 wt.%, less than 0.1 wt.%, less than 0.01 wt.%, or less than 0.001 wt.%, based on the total weight of the crude mixture (M-HFSI).

- [0022] Diluents which are typically avoided are for example polar aprotic solvents, and may selected from the group consisting of:
- cyclic and acyclic carbonates, for instance ethylene carbonate, propylene carbonate, butylene carbonate, dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate,
 - cyclic and acyclic esters, for instance gamma-butyrolactone, gamma-valerolactone, methyl formate, methyl acetate, methyl propionate, ethyl acetate, ethyl propionate, isopropyl acetate, propyl propionate, butyl acetate,
 - cyclic and acyclic ethers, for instance diethylether, diisopropylether, methyl-t-butylether, dimethoxymethane, 1,2-dimethoxyethane, tetrahydrofuran, 2-methyltetrahydrofuran, 1,3-dioxane, 4-methyl-1,3-dioxane, 1,4-dioxane,
 - amide compounds, for instance N,N-dimethylformamide, N-methyl oxazolidinone,
 - sulfoxide and sulfone compounds, for instance sulfolane, 3-methylsulfolane, dimethylsulfoxide,
 - cyano-, nitro-, chloro- or alkyl- substituted alkane or aromatic hydrocarbon, for instance acetonitrile, valeronitrile, adiponitrile, benzonitrile, nitromethane, nitrobenzene.
- [0023] According to a preferred embodiment, the Salt (S) used in step (b) is anhydrous. Moisture content in Salt (S) may be preferably below 5,000 ppm, more preferably below 1,000 ppm, more preferably below 500 ppm, more preferably below 100 ppm even more preferably below 50 ppm.
- [0024] Step (b) can be performed in any type of reaction vessel, which allows contacting the molten mixture (M-HFSI) with the Salt (S). Typically, a stirred vessel may be used, which is particularly adapted for ensuring intimate contact between molten HFSI and the salt. Yet, the vessel may be not equipped with stirring means, but may be equipped with other means for ensuring such intimate contact in the molten mixture (M-HFSI), e.g. means for circulating the molten mixture (M-HFSI). The vessel may hence have any suitable three-dimensional shape, including a cylindrical shape or a tubular shape. The part of the vessel which are intended to come in contact with the molten mixture (M-HFSI) may be realized in any corrosion-resistance material; such as the alloys based on molybdenum, chromium, cobalt, iron, copper, manganese, titanium, zirconium, aluminum, carbon and tungsten, sold under the Hastelloy® brands or the alloys of nickel, chromium, iron and manganese to which copper and/or molybdenum are added, sold under the name Inconel® or Monel™, and more particularly the Hastelloy C276 or Inconel 600, 625 or 718 alloys. Stainless steels may also be selected, such as austenitic steels and more particularly the austenitic chromium-nickel stainless steel containing deliberate amount of molybdenum which increases general corrosion resistance and especially improves its pitting resistance to chloride ion solutions, being referred to as SS316, or its SS316L version, which is an extra-low carbon version of SS316 that minimizes harmful carbide precipitation during welding. A steel having a nickel content of at most 22% by weight, preferably of between 6% and 20% and more preferentially of between 8% and 14%, may be used. The 304 and 304L steels have a nickel content that varies between 8% and 12%, and the 316 and 316L steels have a nickel content that varies between 10% and 14%. Use may also be made of vessels consisting of or coated with a polymeric compound resistant to the corrosion of the molten mixture (M-HFSI). Mention may in particular be made of materials such as PTFE (polytetrafluoroethylene) or PFA (perfluoroalkyl resins). Glass equipment may also be used. It will not be outside the scope of the invention to use an equivalent material.

As other materials suitable for being in contact with the molten mixture (M-FSI), mention may also be made of graphite derivatives and ceramic materials.

[0025] In step (b), at least one Salt (S) of formula M^pX_p or $M^p_2(SO_4)_p$, whereas M^p is a metal cation of valence p, with $p=1$ or 2, or is an ammonium cation of valence $p=1$; X is a halide, preferably selected from Cl and F, is used. Combinations of more than one Salt (S) can be used, although a single salt (S) can be conveniently adopted.

[0026] Without being bound by this theory, the Applicant believes that during step (b), the Salt (S) behaves as a weak Bronsted base; because fluorosulfonic acid possesses a higher Bronsted acidity than compound (I) of formula $F-SO_2-NH-SO_2-R^1$, salt (S) is expected to selectively neutralize the FSO_3H contained in the molten mixture (M-HFSI), according to the following reaction paths:



Whereas p is the valence of metal cation M^p .

[0027] As said, salt (S) can be a halide or a sulfate; yet, while sulfates are effective, halides may be preferred, for the reason that their removal from the molten mixture (M-HFSI) can be facilitated by their higher volatility.

[0028] M^p can be an ammonium cation of formula NH_4^+ with $p=1$. Yet, is preferably an alkaline metal cation or an alkaline earth metal cation, for increased thermal stability; it is even more preferable for M^p to be selected among alkaline metal cation, and most preferably M^p is any of Li, Na and K, and even most preferably Na and K.

[0029] Sulfates such as Na_2SO_4 , K_2SO_4 , $NaHSO_4$, $KHSO_4$ can be conveniently used.

[0030] The halide can be any halides, including also I and Br; yet, Cl and F are preferred.

[0031] The Salt (S) of formula M^pX_p is advantageously selected from the group consisting of NH_4Cl , LiCl, LiF, KCl, KF, NaCl, NaF, RbCl, RbF, $CaCl_2$, CaF_2 , $CsCl_2$, CsF_2 ; as said, alkaline metal salts are preferred, so that LiCl, LiF, KCl, KF, NaCl, and NaF are used in those preferred embodiments, and even more preferably KCl, KF, NaCl, and NaF.

[0032] The salt (S) is generally contacted with the molten mixture (M-HFSI) in the solid state; preferably the salt (S) is contacted with the molten mixture (M-HFSI) in Step (b) under the form of a powder

[0033] To this aim, the salt (S) is generally delivered to the reaction vessel of step (b) under the form of a powder. The powdery salt (S) may be delivered to the reaction vessel of step (b) through a powder conveyor, which may use pneumatic conveying means, including both pressure and vacuum pneumatic means; may use screw conveyor means, such as auger conveyors, helix conveyors, worm conveyor means or flexible screw conveyor means; may use belt conveying means; may use vibrating conveying means; or any other means adapted for dispensing powdery salt (S) into vessel b). Alternatively, Salt (S) can be delivered as a slurry, as an example $Na_2SO_4+NaHSO_4$ in anhydrous H_2SO_4 .

[0034] The salt (S) is provided into step (b) under the form of a powder, which advantageously possesses an average particle size of less than 1000 μm .

[0035] When Salt (S) is a metal halide, during step (b), gaseous side-product such as HX may be removed from the molten mixture (M-HFSI); this may be achieved notably by venting the reaction vessel whereas Step (b) takes place. According to this embodiment, a stream of inert gas, such as anhydrous nitrogen or anhydrous air, may be used for facilitating removal of HX from the molten mixture (M-HFSI). As an alternative, removal of HX may be facilitated by operating under reduced pressure, i.e. at a pressure which is inferior

- to ambient pressure (1 bar). This may be achieved by connecting the vessel comprising molten mixture (M-HFSI) to suction means.
- [0036] When the Salt (S) is a halide, the HX recovered from step (b) is generally under the gaseous form; it may be absorbed in water, so as to generate an HX acid solution, or it may be further handled in the gas form, e.g. by distillation or other purification means, so as to obtain a purified HX stream for further valorization.
- [0037] Step (b) is generally carried out at a temperature ranging from melting point of compound (I) of formula $F-SO_2-NH-SO_2-R^1$ [e.g. for HFSI, about 17°C] to a temperature up to 100°C, preferably at a temperature of 20°C to 50°C, even more preferably 20°C to 30°C.
- [0038] As said, the amount of Salt (S) shall be controlled; indeed, the stoichiometry of salt (S) is important since compound (I) of formula $F-SO_2-NH-SO_2-R^1$ may also react with alkaline halide salts or sulfates:
- $p F-SO_2-NH-SO_2-R^1 + M^pX_p \rightarrow [F-SO_2-N-SO_2-R^1]_pM_p + p HX$
 - $2p F-SO_2-NH-SO_2-R^1 + M^p_2(SO_4)_p \rightarrow 2[F-SO_2-N-SO_2-R^1]_pM_p + p H_2SO_4$
- whereas p is the valence of metal cation M^p , with p=1 or 2.
- [0039] Consistently, an excessive amount of Salt(S) is to be avoided, as it may consume the desired product $F-SO_2-NH-SO_2-R^1$, notably HFSI.
- [0040] Nevertheless, an excess of Salt (S) is favorable, as salified forms of fluorosulfonic acids are in equilibrium with the corresponding protonated form (FSO_3H): minimization of protonated form, aka, fluorosulfonic acid, is advantageous, so as to avoid presence of FSO_3H in the distillates.
- [0041] Consistently, the amount of Salt (S) is of 0.9 to 10 molar equivalent for each molar equivalent of compound of formula (II), aka FSO_3H , and salts thereof, present in crude mixture (C-HFSI). Preferably said amount is of 1 to 10, more preferably of 1.5 to 5, even more preferably 1:2 to 1:4 molar equivalent, for each molar equivalent of FSO_3H and salts thereof.
- [0042] The reaction in step (b) may be carried out in a batch, semi-batch or continuous modes; in batch mode, the vessel may be loaded with crude mixture (C-HFSI), and once the same is molten to give the molten mixture (M-HFSI), the Salt (S) may be added to the molten mixture (M-HFSI), and reacted until reaction is completed (e.g. notably when no longer evolution of HX is detected, when Salt (S) is a halide salt). In a semi-batch arrangement, the vessel may be charged with crude mixture (C-HFSI), which, after being submitted to step (a) of melting, is reacted progressively with the Salt (S) which is added continuously, either step-wise or portion-wise, or by continuous conveying, and the molten mixture (M-HFSI) may be reacted until completing the addition of the Salt (S). As a further alternative, molten mixture (M-HFSI) and the salt (S) may be fed simultaneously in a continuous manner to the reaction vessel.
- [0043] Step (c) comprises at least partially removing the fluorosulfonic acid salt formed in Step (b), so as to obtain a purified mixture [purified mixture (P-HFSI)].
- [0044] The Step (c) of removing the fluorosulfonic acid salt can be carried out according to standard techniques.
- [0045] At the end of Step (b) the molten mixture (M-HFSI) is a molten composition comprising molten compound (I) of formula $F-SO_2-NH-SO_2-R^1$ in combination with the fluorosulfonic acid salt of formula $(F-SO_3)_pM^p$, and possibly any unreacted excess of Salt (S) and any side-reacted metal salts of compound (II) of formula $(F-SO_2-NH-SO_2-R^1)_pM^p$.

- [0046] Such mixture may be a homogeneous mixture or may comprise solid particulate suspended in a liquefied/molten compound (I) of formula $F-SO_2-NH-SO_2-R^1$. Solid particulate may generally comprise the fluorosulfonic acid salt of formula $(F-SO_3)_pMP$, and possibly any unreacted excess of Salt (S) and any side-reacted metal salts of compound (II) of formula $(F-SO_2-NH-SO_2-R^1)_pMP$.
- [0047] When a solid particulate is present, a solid/liquid separation step may be applied. Methods for performing such solid/liquid separation are not particularly limited, and any of filtration, decantation, centrifugation, and the like may be used. Purified mixture (P-HFSI) is generally obtained as a liquid phase.
- [0048] Yet, the Step (c) preferably comprises a step of distilling for obtaining the purified mixture (P-HFSI); distillation step can be carried out on the product obtained from Step (b) directly, or can be carried out after completion of any preliminary separation step, such as those described above.
- [0049] A fractional distillation step is preferably carried out in Step (c), wherein the product obtained from Step (b) is submitted to distillation at temperatures of 20 to 170°C, preferably of 25 to 100°C, even more preferably of 25 to 80°C.
- [0050] Fractional distillation may be carried out under atmospheric pressure, or may be carried out under reduced pressure; distillation temperatures will be adapted by one of ordinary skills in the art, depending upon the pressure applied.
- [0051] Fractional distillation may be carried out continuously, or may be carried out batchwise.
- [0052] When fractional distillation is carried out batchwise, upon heating the product obtained from Step (b) in a boiler, a light fraction including e.g. HX (when present) may be first evaporated and separated; by increasing boiler temperature, distillation of purified mixture (P-HFSI) including compound (I) of formula $F-SO_2-NH-SO_2-R^1$ is then achieved. The fluorosulfonic acid salt of formula $(F-SO_3)_pMP$, and possibly any unreacted excess of Salt (S) and any side-reacted metal salts of compound (II) of formula $(F-SO_2-NH-SO_2-R^1)_pMP$ do not vaporize, and are generally eliminated as residues in the boiler.
- [0053] When fractional distillation is carried out continuously, a distillation column is generally used; purified mixture (P-HFSI) comprising compound (I) of formula $F-SO_2-NH-SO_2-R^1$ is generally recovered from the upper part of the column; light fractions, including e.g. HX (when present) may be vented from the top, while the fluorosulfonic acid salt of formula $(F-SO_3)_pMP$, and possibly any unreacted excess of Salt (S) and any side-reacted metal salts of compound (II) of formula $(F-SO_2-NH-SO_2-R^1)_pMP$ will be eliminated as bottom products from the bottom of the column.
- [0054] As said, the content of fluorosulfonic acid and salts thereof in purified mixture (P-HFSI) is lower than in crude mixture (C-HFSI). Preferably, fluorosulfonic acid is present in purified mixture (P-HFSI) in an amount of less than 1000 ppm, preferably less than 100 ppm, even more preferably less than 10 ppm.
- [0055] Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.
- [0056] The invention will now be further described in examples, which are given by way of illustration and which are no intended to limit the specification or the claims in any manner.

[0057] EXAMPLES

[0058] Example 1 according to the invention: purification of HFSI by selective salification using KCl followed by distillation

[0059] Under dry argon atmosphere, a 100 mL PTFE vessel was loaded with 199 g of HFSI, to which 1.16 g FSO₃H were added. The vessel was equipped with a 3-necks PTFE cap and a PTFE magnetic stirring bar. The vessel was continuously fed with a dry argon flow; a venting output was connected to an aqueous KOH scrubber. The initial concentration of FSO₃H in HFSI, as measured by ¹⁹F NMR, was found to be 5520 ppm.

[0060] A solid addition funnel was loaded with potassium chloride (2.73 g) and connected to the PTFE vessel.

[0061] Mixture was heated at a temperature of about 25°C and the stirring speed was set at 400 rpm; addition of KCl was then continued during a 23 min period. At the end of the addition, the stirring was maintained for 2 h at about 25°C.

[0062] The PTFE flask was sealed, moved to a glovebox and its content was discharged in a 100 mL PFA round-bottom flask for vacuum distillation. Two fractions were isolated at a vapor temperature of 33°C (6.7 g and 109.4 g, respectively). No FSO₃H was detected by ¹⁹F-NMR in any of them.

[0063] The distillation residue was equally analyzed by ¹⁹F NMR and found to contain 3.78 wt% fluorosulfonate.

[0064] Example 2 according to the invention: purification of HFSI by selective salification using KF followed by distillation

[0065] Under dry argon atmosphere, a 100 mL glass addition funnel was loaded with 117 g HFSI, to which 0.58 g FSO₃H were added. The funnel was connected to a 100 mL double-jacketed glass reactor, equipped with a glass stirring mobile and a bottom valve. The glass reactor was continuously fed with a dry argon flow; a venting output was connected to an aqueous KOH scrubber. The content of the funnel was introduced in the vessel, and maintained at a temperature of 25°C. The initial concentration of FSO₃H in HFSI, as measured by ¹⁹F NMR, was found to be 5040 ppm.

[0066] A glass solid addition funnel previously loaded with potassium fluoride (1.13 g) was then connected to the glass reactor.

[0067] Mixture was maintained at a temperature in the range 25-30°C and the stirring speed was set at 500 rpm; addition of KF was then continued during a 8.5 min period. At the end of the addition, the stirring was maintained for 1.5 h at about 25°C, before recovering the reaction crude mixture in a 100 mL Schott glass bottle.

[0068] Then, into a glove box, 88.8 g of this reaction crude mixture were discharged in a 100 mL PFA round-bottom flask for vacuum distillation. Three first fractions were isolated at a vapor temperature between 25-28°C (4 g, 8 g and 19 g, respectively); the presence of FSO₃H was detected by ¹⁹F-NMR in none of them. The distillation residue was also analyzed by ¹⁹F-NMR and was found to contain 3.0 wt% fluorosulfonate.

CLAIMS

Claim 1. A method for the at least partial removal of fluorosulfonic acid and derivatives thereof from a crude bis(sulfonyl)imide mixture comprising a compound of formula (I) $\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1$ (I) wherein R^1 represents F or Cl; preferably R^1 is F; and further comprising fluorosulfonic acid of formula (II):

$\text{F-SO}_2\text{-OH}$ (II) or a salt thereof

[crude mixture (C-HFSI)] ;

said method comprising:

Step (a) - melting the crude mixture (C-HFSI) at a temperature exceeding the melting point of compound of formula (I), so as to obtain a molten mixture [molten mixture (M-HFSI)];

Step (b) - contacting the molten mixture (M-HFSI) with at least one Salt (S) of formula M^pX_p or $\text{M}^p_2(\text{SO}_4)_p$, whereas M^p is a metal cation of valence p, with $p=1$ or 2, or is an ammonium cation of valence $p=1$; X is a halide, preferably selected from Cl and Br, wherein the amount of Salt (S) is of 0.9 to 10 molar equivalent for each molar equivalent of compound of formula (II) present in crude mixture (C-HFSI), so as to at least partially convert compound (II) into its corresponding fluorosulfonic acid salt of formula $(\text{F-SO}_3)_p\text{M}^p$; and

Step (c) - at least partially removing said fluorosulfonic acid salt, so as to obtain a purified mixture [purified mixture (P-HFSI)];

wherein Step (b) is carried out in the substantial absence of any diluent; and

wherein the content of compound (II) or salt thereof in mixture (P-HFSI) is lower than the content of the same in mixture (C-HFSI).

Claim 2. The method of Claim 1, wherein the temperature in Step (a) is ranging between 17°C and 120°C , preferably between 20°C and 80°C , more preferably between 24°C and 50°C .

Claim 3. The method of claim 1 or 2, wherein the content of fluorosulfonic acid and derivatives thereof in crude mixture (C-HFSI) is of at least 500 ppm, preferably of at least 1000 ppm, more preferably of at least 1500 ppm, and/or of at most 10 000 ppm, preferably of at most 8000 ppm, more preferably of at most 5000 ppm.

Claim 4. The method of anyone of the preceding claims, wherein the amount of diluent is of less than 1 wt.% based on the total weight of the crude mixture (C-HFI).

Claim 5. The method of anyone of the preceding claims, wherein the Salt (S) of formula M^pX_p is selected from the group consisting of NH_4Cl , LiCl , LiF , KCl , KF , NaCl , NaF , RbCl , RbF , CaCl_2 , CaF_2 , CsCl_2 , CsF_2 ; and it is preferably selected from the list consisting of LiCl , LiF , KCl , KF , NaCl , and NaF ; and it is even more preferably selected from the group consisting of KCl , KF , NaCl , and NaF .

Claim 6. The method of anyone of the preceding claims, wherein the Salt (S) is contacted with the molten mixture (M-HFSI) in Step (b) in the solid state, preferably the salt (S) is contacted with the molten mixture (M-HFSI) in Step (b) under the form of a powder, which preferably possesses an average particle size of less than 1000 μm .

Claim 7. The method of Claim 6, wherein the powdery salt (S) is preferably delivered to the reaction vessel of step (b) through a powder conveyor, which uses anyone of (i) pneumatic conveying means, including both pressure and vacuum pneumatic means; (ii) screw conveyor means, such as auger conveyors, helix conveyors, worm conveyor means or

flexible screw conveyor means; (iii) belt conveying means; (iv) vibrating conveying means.

Claim 8. The method of Claims 1 to 5, wherein the Salt (S) is delivered in Step (b) as a slurry; and preferably, Salt (S) is Na_2SO_4 and NaHSO_4 and is delivered as a slurry in anhydrous H_2SO_4 .

Claim 9. The method of anyone of the preceding Claims, wherein Step (b) is carried out at a temperature ranging from melting point of compound (I) of formula $\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1$ [when compound (I) is HFSI, at a temperature ranging from 17°C] to a temperature up to 100°C , preferably at a temperature of 20°C to 50°C , even more preferably 20°C to 30°C .

Claim 10. The method according to anyone of the preceding Claims, wherein the amount of Salt (S) is of 0.9 to 10 molar equivalent for each molar equivalent of compound of formula (II), and salts thereof, present in crude mixture (C-HFSI); and wherein preferably said amount is of 1 to 10, more preferably of 1.5 to 5, even more preferably 1:2 to 1:4 molar equivalent, for each molar equivalent of compound of formula (II) and salts thereof.

Claim 11. The method according to anyone of the preceding Claims, wherein at the end of Step (b), the molten mixture (M-HFSI) is a molten composition comprising molten compound (I) of formula $\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1$ in combination with the fluorosulfonic acid salt of formula $(\text{F-SO}_3)_p\text{M}^p$, and possibly any unreacted excess of Salt (S) and any side-reacted metal salts of compound (II) of formula $(\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1)_p\text{M}^p$.

Claim 12. The method of Claim 11, wherein at the end of Step (b) the molten mixture (M-HFSI) is a homogeneous mixture or comprises solid particulate suspended in a liquefied/molten compound (I) of formula $\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1$, and wherein, when a solid particulate is present, a solid/liquid separation step may be applied in Step (c).

Claim 13. The method of anyone of the preceding claims, wherein the Step (c) comprises a step of distilling for obtaining the purified mixture (P-HFSI).

Claim 14. The method according to Claim 13, wherein the Step (c) comprises a fractional distillation step, wherein the product obtained from Step (b) is submitted to distillation at temperatures of 20 to 170°C , preferably of 25 to 100°C , even more preferably of 25 to 80°C ; and/o

- when fractional distillation is carried out batchwise, upon heating the product obtained from Step (b) in a boiler, a light fraction is first evaporated and separated; by increasing boiler temperature, distillation of purified mixture (P-HFSI) including compound (I) of formula $\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1$ is then achieved, and the fluorosulfonic acid salt of formula $(\text{F-SO}_3)_p\text{M}^p$, and possibly any unreacted excess of Salt (S) and any side-reacted metal salts of compound (II) of formula $(\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1)_p\text{M}^p$ do not vaporize, and are eliminated as residues in the boiler;
- when fractional distillation is carried out continuously, a distillation column is used; and purified mixture (P-HFSI) comprising compound (I) of formula $\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1$ is recovered from the upper part of the column; and light fractions are vented from the top, while the fluorosulfonic acid salt of formula $(\text{F-SO}_3)_p\text{M}^p$, and possibly any unreacted excess of Salt (S) and any side-reacted metal salts of compound (II) of formula $(\text{F-SO}_2\text{-NH-SO}_2\text{-R}^1)_p\text{M}^p$ are eliminated as bottom products from the bottom of the column.

Claim 15. The method according to anyone of the preceding claims, wherein the content of fluorosulfonic acid and salts thereof in purified mixture (P-HFSI) is lower than in crude mixture (C-HFSI), and wherein fluorosulfonic acid is present in purified mixture (P-HFSI)

in an amount of less than 1000 ppm, preferably less than 100 ppm, even more preferably less than 10 ppm.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/064992

A. CLASSIFICATION OF SUBJECT MATTER INV. C01B21/086 C07C303/34 H01M10/0568 C01B21/093 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C01B C07C H01M Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOHN K RUFF ET AL: "Imidodisulfuryl Fluoride, Cesium Imidodisulfuryl Fluoride, and Fluoroimidodisulfuryl Fluoride: [Imidobis(Sulfuryl Fluoride), Cesium Imidobis(Sulfuryl Fluoride), and Fluoroirnidobis(Sulfuryl Fluoride)]", 1 January 1998 (1998-01-01), INORGANIC SYNTHESIS, WILEY, XX, PAGE(S) 138 - 143, XP008135074, ISBN: 978-0-470-13170-1 [retrieved on 2007-01-05] page 139 -----	1 - 15
A	WO 2020/214560 A1 (HONEYWELL INT INC [US]) 22 October 2020 (2020-10-22) claims 1-10 ----- - / - -	1 - 15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 12 September 2024		Date of mailing of the international search report 26/09/2024
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Gerwann, Jochen

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/064992

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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