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(54) Title: SOLVENT-FREE PROCESS FOR PREPARING A SALT OF BIS(FLUOROSULFONYL)IMIDE

(57) Abstract: The present disclosure relates to a method for preparing salts of bis(fluorosulfonyl)imide and to a method for preparing alkali metal salts of bis(fluorosulfonyl)imide from said bis(fluorosulfonyl)imide salts. More specifically, the invention provides a new method for producing these salts of bis(fluorosulfonyl)imide which is implementable at industrial scale and providing high-purity bis(fluorosulfonyl)imide salts.



WO 2022/258679 A1

Description

SOLVENT-FREE PROCESS FOR PREPARING A SALT OF
BIS(FLUOROSULFONYL)IMIDETechnical field

[0001] The present invention relates to a method for preparing salts of bis(fluorosulfonyl)imide and to a method for preparing alkali metal salts of bis(fluorosulfonyl)imide from said bis(fluorosulfonyl)imide salts. More specifically, the invention provides a new method for producing these salts of bis(fluorosulfonyl)imide which is implementable at industrial scale and providing high-purity bis(fluorosulfonyl)imide salts.

Background

[0002] 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.

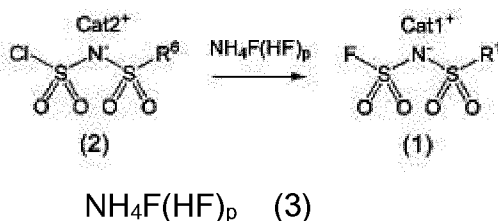
[0003] The production of bis(fluorosulfonyl)imide and salts thereof is described in the literature. Among the various technologies described, the majority uses a fluorination reaction with a fluorinating agent in a solvent.

[0004] Notably, WO 2017/090877 A1 (CLS) describes a method for producing lithium bis(fluorosulfonyl)imide comprising the steps of: (1) reacting bis(chlorosulfonyl)imide with a fluorinating reagent in a solvent, followed by treatment with an alkaline reagent, thereby producing ammonium bis(fluorosulfonyl)imide; and (2) reacting the ammonium bis(fluorosulfonyl)imide with a lithium base. The solvent used in step (1) is selected from the group consisting of alkyl ketones, including acetone, methyl ethyl ketone, and methyl isopropyl ketone; alcohols, including methanol, anhydrous ethanol, 1-propanol, and isopropanol; alkyl nitriles, including acetonitrile, and propionitrile; and ethers, including tetrahydrofuran, and

dialkoxyalkane. The solvent is then removed by distillation and concentration under reduced pressure.

[0005] WO 2012/117961 A1 (Nippon Soda) describes a process for producing a fluorosulfonylimide salt, comprising the reaction between a compound of formula [II] $\text{Cl-CO}_2\text{-NH-SO}_2\text{-R}^1$ wherein R^1 is a fluoroalkyl group, a fluorine atom or a chlorine atom with a fluorinating agent [III], preferably of formula $\text{NH}_4\text{F}(\text{HF})_p$ with p being from 0 to 10. The reaction between compounds [II] and [III] can be conducted in the presence of a solvent or in the absence of a solvent. However, according to examples 1 and 2, ammonium di(fluorosulfonyl)imide is prepared from di(chlorosulfonyl)imide in acetonitrile. The solvent is then removed by distillation under reduced pressure. As a whole, this patent application does not disclose a process for producing a fluorosulfonylimide salt that is performed in the absence of solvent or in the presence of an amount of solvent lower than 5 wt.% based on the total weight of the reaction mixture.

[0006] JP 2016145147 (Nippon Shokubai) relates to a method for providing a fluorosulfonylimide compound represented by the formula (1) by reacting a compound represented by the formula (2) and a compound represented by the composition formula (3) of 1 to 3 equivalence by stoichiometric amount based on 1 mol of the compound in a presence of a solvent of 0 to 4 mass times of the compound.



where R^1 is a C_{1-6} fluoroalkyl group, R^6 is halogen or a C_{1-6} fluoroalkyl group, Cat1^+ and Cat2^+ are monovalent groups and p is an integer of 1 to 10.

[0007] JP 2014201453 (Nippon Shokubai) describes a method for producing an alkali metal salt of fluorosulfonyl imide which comprises a step of synthesizing an alkali metal salt of fluorosulfonyl imide in the presence of a reaction solvent

containing at least one solvent selected from the group consisting of a carbonate-based solvent, an aliphatic ether-based solvent, an ester-based solvent, an amide-based solvent, a nitro-based solvent, a sulfur-based solvent and a nitrile-based solvent and, subsequently concentrating an alkali metal salt solution of fluorosulfonyl imide by distilling off the reaction solvent in the coexistence of the reaction solvent and at least one poor solvent for the alkali metal salt of fluorosulfonyl imide selected from the group consisting of an aromatic hydrocarbon-based solvent, an aliphatic hydrocarbon-based solvent and an aromatic ether-based solvent, the concentration step includes the step of mixing the above poor solvent with the reaction solution containing the reaction solvent and an alkali metal salt of fluorosulfonyl imide.

- [0008] As described in the literature, the production of bis(fluorosulfonyl)imide and salts thereof by fluorination takes place in solvents, for example organic solvents, in order to disperse the reactive entities and allow them to react. However, such solvents need 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 solvent adds to the complexity of the industrial process, as well as its overall cost. In addition, before being implemented in such processes, the solvents typically have to be treated to remove the residual amount water, as only anhydrous solvent, where the residual amount of water is in the ppm amount, are actually to be used.
- [0009] An object of the present invention is to provide a simpler production process of salts of bis(fluorosulfonyl)imide, which does not require the distillation of the reaction solvent.
- [0010] WO 2012/096371 A1 (Sumitomo Electric Ind) relates to a method for producing $\text{KN}(\text{SO}_2\text{F})_2$ by adding $\text{HN}(\text{SO}_2\text{Cl})_2$ (liquid form) drop-wise to KF (powder form) under solvent-free dry conditions, to form an intermediate product, and then allowing the intermediate product and KF to react with each other in an aqueous solvent. More precisely, according to the method described in this document, in a first step, one chlorine element of $\text{HN}(\text{SO}_2\text{Cl})_2$ is substituted with fluorine to lead to an intermediate product which is the alkali metal salt

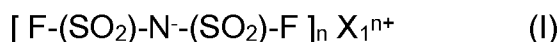
$\text{KN}(\text{SO}_2\text{Cl})(\text{SO}_2\text{F})$; and in a second step, the other chlorine element is substituted with fluorine to lead to the alkali metal salt $\text{KN}(\text{SO}_2\text{F})_2$. In accordance with such a two-stage step, because $\text{HN}(\text{SO}_2\text{Cl})_2$ is converted into an alkali metal salt $\text{KN}(\text{SO}_2\text{Cl})(\text{SO}_2\text{F})$, as a result, it becomes possible to use water in the second step, as water dissolves the alkali metal fluoride.

[0011] According to this document, the first part of reaction takes place under solvent-free dry conditions, by dropping of the reactant in a liquid form onto the second reactant, which is in powder form. This leads to a paste-like intermediate product, which is very difficult to handle industrially. Additionally, because the overall conversion of $\text{HN}(\text{SO}_2\text{Cl})_2$ into $\text{KN}(\text{SO}_2\text{F})_2$ is conducted in two steps with an individualized intermediate, the yield of the reaction is negatively impacted, as well as the level of impurities of the final product.

[0012] An object of the present invention is to provide a method for preparing salts of bis(fluorosulfonyl)imide $\text{X}_1\text{N}(\text{SO}_2\text{F})_2$, with X_1 being K^+ , Na^+ or an onium cation (for example NH_4^+), such method being implementable at industrial scale and providing high-purity bis(fluorosulfonyl)imide salts. In particular, the method of the present invention is carried out in the presence of the molten reaction product, for example molten $\text{KN}(\text{SO}_2\text{F})_2$ or molten $\text{NH}_4\text{N}(\text{SO}_2\text{F})_2$, acting to disperse the reactants, and in the absence of solvent (or in the presence of a very limited quantity of solvent).

Summary

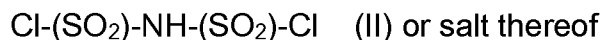
[0013] The present invention relates to a process for preparing a salt of bis(fluorosulfonyl)imide of formula (I):



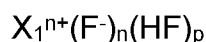
wherein:

- X_1^{n+} is a cation selected from the group consisting of K^+ , Na^+ and an onium cation, and
- n is 1 representing the valence of the cation,

the process comprising the fluorination of a bis(chlorosulfonyl)imide of formula (II):



with a fluorinating agent represented by formula (III):

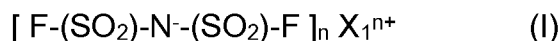


wherein:

- p varies between 0 and 10,

wherein the process is carried out in molten bis(fluorosulfonyl)imide salt of formula (I), in the absence of solvent or in the presence of an amount of solvent lower than 5 wt. % based on the total weight of the reaction mixture.

[0014] The present invention also relates to a salt of bis(fluorosulfonyl)imide of formula (I):



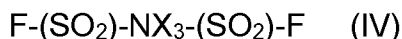
wherein:

- X_1^{n+} is a cation selected from the group consisting of K^+ , Na^+ and an onium cation, and

- n is 1 representing the valence of the cation,

Such salt being obtainable by the process of the present invention, which is characterized in that its amount of solvent is less than 100 ppm, for example less than 50 ppm.

[0015] The present invention also relates to a process for preparing an alkali salt of bis(fluorosulfonyl)imide of formula (V),



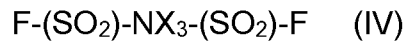
wherein X_3 represents Li or Cs, preferably Li,

comprising the steps of:

(a) preparing a salt of bis(fluorosulfonyl)imide of formula (I) according to any one of the claims 1-8, and

(b) reacting the salt bis(fluorosulfonyl)imide (I) obtained in step (a) with an alkali agent consisting in a lithium salt or a cesium salt.

[0016] The present invention also relates to a salt of bis(fluorosulfonyl)imide of formula (IV):



wherein X_3 represents Li or Cs, preferably Li

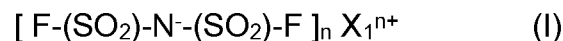
[0017] as well as to the use of such salt in a battery electrolyte solution.

Disclosure of the invention

[0018] In the present application :

- the expressions “between ... and ...” as well as “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.

[0019] A **first object** of the present invention is a process for preparing a salt of bis(fluorosulfonyl)imide of formula (I):



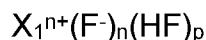
wherein:

- X_1^{n+} is a cation selected from the group consisting of K^+ , Na^+ and an onium cation, preferably NH_4^+ , and
- n is 1 representing the valence of the cation,

the process comprising the fluorination of a bis(chlorosulfonyl)imide of formula (II):

Cl-(SO₂)-NH-(SO₂)-Cl (II) or salt thereof

with a fluorinating agent represented by formula (III):



wherein:

- p varies between 0 and 10,

wherein the process is carried out in molten salt of bis(fluorosulfonyl)imide of formula (I), in the absence of solvent or in the presence of an amount of solvent less than 5 wt.% based on the total weight of the reaction mixture.

[0020] The salt (I) described herein is characterized by a low residual amount of solvent, advantageously a non-detectable amount of solvent which makes the salt (I) well-suited for many applications, notably battery applications.

[0021] The method of the present invention is performed in the melt in the absence of solvents and diluents. More precisely, the method is carried out in molten salt of bis(fluorosulfonyl)imide of formula (I), for example molten KN(SO₂F)₂ or molten NH₄N(SO₂F)₂, acting to disperse the reactants and allowing the reactants (II) and (III) to meet and react. Importantly, the method of the present invention is a solvent-free method. In other words, no solvent/diluent, alternatively a very low amount of solvent/diluent, is added to the reaction mixture during the reaction. This is advantageous because first, the step for removing the solvent adds to the complexity of the industrial process, as well as its overall cost. Secondly, the solvents typically need to be treated before being used in such process, as only anhydrous solvent (characterized by a residual amount of water is in the order of the ppm amount) can actually be used.

[0022] In the context of the present invention, the term "solvent" is intended to mean a compound which presents the following three cumulative properties of 1/ being present from the beginning to the end of the reaction, possibly added during the process, 2/ unchanged during the process, in other words non-reactive towards the involved reactants, and 3/ having to be removed at the end of the process in case the reaction product is to be in its pure form. Examples of solvents falling within the scope of this definition are given below.

For the sake of clarity, the molten salt of bis(fluorosulfonyl)imide of formula (I) used in the process of the present invention does not fall under the definition of "solvent" above-mentioned.

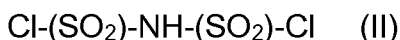
- [0023] According to one embodiment of the present invention, the method described herein is carried out or in the presence of a very low amount of solvent, that-is-to-say an amount of solvent less than 5 wt.%, based on the total weight of the reaction mixture. Preferably, according to this embodiment, the amount of solvent is less than 4 wt.%, less than 3 wt.%, less than 2 wt.%, less than 1 wt.%, less than 0.5 wt.%, less than 0.1 wt.%, less than 0.01 wt.%, or less than 0.001 wt.% of solvent, based on the total weight of the reaction mixture. The total weight of the reaction mixture is obtained by adding the weight of the reactants, as well as the weight of the molten salt of bis(fluorosulfonyl)imide of formula (I).
- [0024] Solvents which are typically used in such processes are well-known and extensively described in the literature. Such solvents may be aprotic, for example polar aprotic solvents, and may be 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, and

- cyano-, nitro-, chloro- or alkyl- substituted alkane or aromatic hydrocarbon, for instance acetonitrile, valeronitrile, adiponitrile, benzonitrile, nitromethane, nitrobenzene.

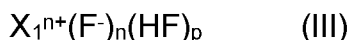
[0025] Typically, the organic solvent used to carry out such processes may be selected from the group consisting of ethyl acetate, isopropyl acetate, butyl acetate, ethylene carbonate, dimethyl carbonate, ethyl methyl carbonate, propylene carbonate, valeronitrile and acetonitrile, as for example in the literature described in the background section.

[0026] According to the process of the present invention, a quantity of the salt of bis(fluorosulfonyl)imide of formula (I), for example $\text{KN}(\text{SO}_2\text{F})_2$ and $\text{NH}_4\text{N}(\text{SO}_2\text{F})_2$, is heated above its melting temperature $T_{m(l)}$, before the addition of the reactants (or reactive entities), in order to be in a molten state (also called liquid state). The reactants, which can be in a powder form or in a liquid form, are then added into the reaction mixture and allowed to react in order to produce the salt of bis(fluorosulfonyl)imide of formula (I), for example $\text{KN}(\text{SO}_2\text{F})_2$ or $\text{NH}_4\text{N}(\text{SO}_2\text{F})_2$. This means that the quantity of such reaction product (i.e. salt of bis(fluorosulfonyl)imide of formula (I)) increases over the reaction time. In other words, the molten reaction product is used to provide a medium to disperse the reactants and allow them to meet and react. No solvent is therefore necessary according to the present invention. This is advantageous, as it significantly simplifies the overall production process since such solvent does not need to be removed after the reaction, in order to obtain a high-purity bis(fluorosulfonyl)imide salt. It presents the additional advantage that no additional step is needed to remove the water for the solvent.

[0027] According to the present invention, the bis(chlorosulfonyl)imide (II) or its salt:



is reacted with a fluorinating agent represented by formula (III):



in which X_1^{n+} and n are as above-mentioned and p varies between 0 and 10, preferably 0.

- [0028] According to the present invention, X_1^{n+} represents K^+ , Na^+ or an onium cation, wherein an onium cation has its usual meaning for the skilled person.
- [0029] Examples of the onium cation include phosphonium cation, oxonium cation, sulfonium cation, fluoronium cation, chloronium cation, bromonium cation, iodonium cation, selenonium cation, telluronium cation, arsonium cation, stibonium cation, bismutonium cation; iminium cation, diazenium cation, nitronium cation, diazonium cation, nitrosonium cation, hydrazonium cation, diazenium dication, diazonium dication, imidazolium cation, pyridinium cation, quaternary ammonium cation, tertiary ammonium cation, secondary ammonium cation, primary ammonium cation, ammonium NH_4^+ cation, piperidinium cation, pyrrolidinium cation, morpholinium cation, pyrazolium cation, guanidinium cation, isouronium cation and isothiuronium cation.
- [0030] Among these, imidazolium cation, pyridinium cation, quaternary ammonium cation, tertiary ammonium cation, secondary ammonium cation, primary ammonium cation, ammonium NH_4^+ cation, piperidinium cation, pyrrolidinium cation, morpholinium cation, pyrazolium cation, guanidinium cation, and isouronium cation are more preferred.
- [0031] Examples of onium cations of these types include:
- imidazolium cations such as a 1,3-dimethylimidazolium cation, 1-ethyl-3-methylimidazolium cation, 1-propyl-3-methylimidazolium cation, 1-butyl-3-methylimidazolium cation, 1-pentyl-3-methylimidazolium cation, 1-hexyl-3-methylimidazolium cation, 1-heptyl-3-methylimidazolium cation, 1-octyl-3-methylimidazolium cation, 1-decyl-3-methylimidazolium cation, 1-tetradecyl-3-methylimidazolium cation, 1-hexadecyl-3-methylimidazolium cation, 1-octadecyl-3-methylimidazolium cation, 1-allyl-3-ethylimidazolium cation, 1-allyl-3-butylimidazolium cation, 1,3-diallylimidazolium cation, 1-ethyl-2,3-dimethylimidazolium cation, 1-butyl-2,3-dimethylimidazolium cation, 1-hexyl-2,3-methylimidazolium cation, and 1-hexadecyl-2,3-methylimidazolium cation;
 - pyridinium cations such as a 1-ethylpyridinium cation, 1-butylpyridinium cation, 1-hexylpyridinium cation, 1-octylpyridinium cation, 1-ethyl-3-methylpyridinium cation, 1-ethyl-3-hydroxymethylpyridinium cation, 1-butyl-3-

methylpyridinium cation, 1-butyl-4-methylpyridinium cation, 1-octyl-4-methylpyridinium cation, 1-butyl-3,4-dimethylpyridinium cation, and 1-butyl-3,5-dimethylpyridinium cation;

- quaternary ammonium cations such as a tetramethylammonium cation, tetraethylammonium cation, tetrapropylammonium cation, tetrabutylammonium cation, tetraheptylammonium cation, tetrahexylammonium cation, tetraoctylammonium cation, triethylmethylammonium cation, propyltrimethylammonium cation, diethyl-2-methoxyethylmethylammonium cation, methyltrioctylammonium cation, cyclohexyltrimethylammonium cation, 2-hydroxyethyltrimethylammonium cation, trimethylphenylammonium cation, benzyltrimethylammonium cation, benzyltributylammonium cation, benzyltriethylammonium cation, dimethyldistearyl ammonium cation, diallyldimethylammonium cation, 2-methoxyethoxymethyltrimethylammonium cation, N-methoxytrimethylammonium cation, N-ethoxytrimethylammonium cation, N-propoxytrimethylammonium cation and tetrakis(pentafluoroethyl)ammonium cation;

- tertiary ammonium cations such as a trimethylammonium cation, triethylammonium cation, tributylammonium cation, diethylmethylammonium cation, dimethylethylammonium cation, dibutylmethylammonium cation, and 4-aza-1-azoniabicyclo[2.2.2]octane cation;

- secondary ammonium cations such as a dimethylammonium cation, diethylammonium cation, and dibutylammonium cation;

- primary ammonium cations such as a methylammonium cation, ethylammonium cation, butylammonium cation, hexylammonium cation, and octylammonium cation;

- ammonium cation NH_4^+ ;

- piperidinium cations such as a 1-propyl-1-methylpiperidinium cation and 1-(2-methoxyethyl)-1-methylpiperidinium cation;

- pyrrolidinium cations such as a 1-propyl-1-methylpyrrolidinium cation, 1-butyl-1-methylpyrrolidinium cation, 1-hexyl-1-methylpyrrolidinium cation, and 1-octyl-1-methylpyrrolidinium cation;
- morpholinium cations such as a 4-propyl-4-methylmorpholinium cation and 4-(2-methoxyethyl)-4-methylmorpholinium cation;
- pyrazolium cations such as a 2-ethyl-1,3,5-trimethylpyrazolium cation, 2-propyl-1,3,5-trimethylpyrazolium cation, 2-butyl-1,3,5-trimethylpyrazolium cation, and 2-hexyl-1,3,5-trimethylpyrazolium cation;
- guanidinium cations such as a guanidinium cation and a 2-ethyl-1,1,3,3-tetramethylguanidinium cation; and
- isouronium cations such as a 2-ethyl-1,1,3,3-tetramethylisouronium cation.

[0032] Quaternary ammonium cation, tertiary ammonium cation, secondary ammonium cation, primary ammonium cation, and ammonium cation NH_4^+ are more preferred, especially those specifically cited in the above list. Ammonium cation NH_4^+ is the most preferred onium cation.

[0033] One of the reactants (also called sometimes raw materials) involved in the process of the present invention is bis(chlorosulfonyl)imide of formula $(\text{Cl-SO}_2)_2\text{-NH}$ (II), sometimes abbreviated as HCSI. HCSI is commercially available, or produced by a known method, for example:

- by reacting chlorosulfonyl isocyanate ClSO_2NCO with chlorosulfonic acid ClSO_2OH ;
- by reacting cyanogen chloride CNCl with sulfuric anhydride SO_3 , and with chlorosulfonic acid ClSO_2OH ;
- by reacting sulfamic acid $\text{NH}_2\text{SO}_2\text{OH}$ with thionyl chloride SOCl_2 and with chlorosulfonic acid ClSO_2OH .

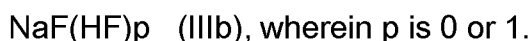
[0034] The other reactant involved in the process of the present invention is the fluorinating agent (III). It may be used in the process of the present invention in any form, for example in the form of a powder or in the form of a liquid. Fluorinating agents are commercially available, or they may be produced by a known method.

[0035] In formula (III), p represents a real number from 0 to 10, preferably from 0 to 4, and more preferably p is an integer from 0 to 4. In some embodiments, p equals 0.

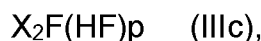
[0036] According to one embodiment, the fluorinating agent (III) is according to formula (IIIa):



[0037] According to another embodiment, the fluorinating agent (III) is according to formula (IIIb):

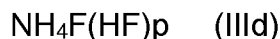


[0038] According to another embodiment, the fluorinating agent (III) is according to formula (IIIc):



in which X_2 is an onium cation as defined above, and p is 0 or 1.

[0039] According to a preferred embodiment, the fluorinating agent (III) is according to formula (IIId):



in which p varies between 0 and 10. According to this preferred embodiment, specific examples of the fluorinating agent (IIId) include NH_4F , $\text{NH}_4\text{F} \cdot \text{HF}$, $\text{NH}_4\text{F} \cdot 2\text{HF}$, $\text{NH}_4\text{F} \cdot 3\text{HF}$, and $\text{NH}_4\text{F} \cdot 4\text{HF}$. The preferred fluorinating agent (IIId) is NH_4F .

[0040] According to another preferred embodiment, the fluorinating agent (III) is anhydrous. Moisture content may be preferably below 5,000 ppm, more preferably below 1,000 ppm, below 500 ppm, below 100 ppm, below 50 ppm or even below 10 ppm, as determined by Karl Fisher water titration, for example performed in a glovebox.

[0041] In some embodiments, the stoichiometry amount (also called molar amount) of fluorinating agent (III) to bis(chlorosulfonyl)imide (II) is from 0.1:1 to 20:1, for example from 1:1 to 10:1, or from 2:1 to 8:1.

[0042] In some embodiments, the stoichiometry amount of fluorinating agent (III) is not less than 1 equivalent per 1 mol of bis(chlorosulfonyl)imide (II), for example between 1 to 10 equivalents per 1 mol of bis(chlorosulfonyl)imide (II).

Preferably, the stoichiometry amount of fluorinating agent (III) is between 2 to 8 equivalents per 1 mol of bis(chlorosulfonyl)imide (II), or between 3 to 6 equivalents per 1 mol of bis(chlorosulfonyl)imide (II). More preferably, the stoichiometry amount of fluorinating agent (III) equals to 4 ± 0.8 equivalents or to 4 ± 0.5 per 1 mol of bis(chlorosulfonyl)imide (II).

[0043] The process of the present invention may be carried out in a batch, semi-batch or continuous mode.

[0044] According to an embodiment, the process is carried out in a continuous or semi-continuous manner, and comprises a step of continuously or semi-continuously withdrawing the salt of bis(fluorosulfonyl)imide (I) from the reaction mixture. It is possible, according to the present invention, to continuously add reactants in the reaction mixture and semi-continuously remove the reaction product.

[0045] In some embodiments, the process of the present invention comprises the steps of:

- (i) heating a quantity Q_0 of the salt of bis(fluorosulfonyl)imide (I) at a temperature $T_a(^{\circ}\text{C})$ equal to or higher than the melting point $T_{m(l)}$ of compound (I) to produce a molten salt of bis(fluorosulfonyl)imide (I), and
- (ii) adding the fluorinating agent (III) and the bis(chlorosulfonyl)imide (II) to the molten salt of bis(fluorosulfonyl)imide (I).

[0046] The temperature $T_a(^{\circ}\text{C})$ may be equal to or higher than the melting point $T_{m(l)}$ of the salt of bis(fluorosulfonyl)imide (I). For example, T_a may be equal to or higher than $T_m(I) + 2^{\circ}\text{C}$ or T_a may be equal to or higher than $T_m(I) + 5^{\circ}\text{C}$.

[0047] It is possible to predisperse one of the reactants, for example the fluorinating agent (III), in the reaction mixture before the introduction of the second reactant, for example the bis(chlorosulfonyl)imide (II).

[0048] According to these embodiments, step (ii) may for example itself comprise the steps of:

- (ii1) adding the fluorinating agent (III) to the molten salt of bis(fluorosulfonyl)imide (I),
- (ii2) optionally removing the residual amount of water or aqueous liquid from the fluorinating agent (III), and

(ii3) adding the bis(chlorosulfonyl)imide (II) to the reaction mixture.

[0049] As explained above, the reactants may be in any form, including in the form of a solid or in the form of a liquid. For example, the fluorinating agent (III) may be added to the molten compound (I) in solid form, e.g. a powder form. The bis(chlorosulfonyl)imide (II) may be in a liquid form and may for example be added dropwise in the reaction mixture.

[0050] Advantageously, the fluorinating agent (III) is added to the molten salt of bis(fluorosulfonyl)imide (I) and then, according to an optional step (ii2), the residual amount of water (or aqueous liquids) that the agent (III) may contain, is removed. This optional step advantageously takes place after the fluorinating agent has been added to the reaction mixture. As explained above, the reaction should be performed with as less as possible residual water, in order to obtain a highly pure salt of bis(fluororosulfonyl)imide (II). However, it is almost impossible to completely remove all residual water from the fluorinating agent (III) (dry limit due to moisture inside the crystals). This is however advantageously possible when the fluorinating agent (III), in particular NH_4F , is dispersed in the molten salt of bis(fluorosulfonyl)imide (I). This optional step greatly contribute to a highly pure product at the end of the reaction.

[0051] Preferably, the optional step (ii2) may be carried out by distillation of the water.

[0052] According to step (ii3), the bis(chlorosulfonyl)imide (II) may be heated to a temperature $T_b(^{\circ}\text{C})$ ranging from 30 to 150°C , prior to be added to the reaction mixture. The temperature $T_b(^{\circ}\text{C})$ may for example range between 35°C and 125°C , or between 40°C and 100°C . According to a specific embodiment, the bis(chlorosulfonyl)imide (II) is heated to the temperature $T_b(^{\circ}\text{C}) = T_a(^{\circ}\text{C}) \pm 10^{\circ}\text{C}$, for example $T_a(^{\circ}\text{C}) \pm 5^{\circ}\text{C}$. According to another embodiment, the bis(chlorosulfonyl)imide (II) is heated to a temperature $T_b(^{\circ}\text{C}) \leq T_a(^{\circ}\text{C}) + 10^{\circ}\text{C}$, or $T_b(^{\circ}\text{C}) \leq T_a(^{\circ}\text{C})$.

[0053] In some embodiments, step (ii) consists in adding the fluorinating agent (III) and the bis(chlorosulfonyl)imide (II), concomitantly to the molten onium salt of bis(fluorosulfonyl)imide (I).

- [0054] The addition of the reactants (II) and (III) in the molten onium salt of bis(fluorosulfonyl)imide (I) may be generally performed sequentially, progressively or continuously. The overall quantities of each reactant may also be added incrementally to the reaction vessel, for example in several time, especially if the process is conducted batch-wise.
- [0055] Batch reactor, extruder and mixing kneader can for example be used in the present invention. Anti-acidic corrosion material (e.g. PTFE) can be coated (in other words, lined) inside the chosen reactor.
- [0056] Reference can be made to industrialized melt mixers or melt blenders.
- [0057] Mixing kneaders used can comprise any of the known suitable mixing kneaders which permit heating above the melting point of the salt (I) and enable discharge of gaseous products. Suitable mixing kneaders generally have one, or preferably at least two, rotating shafts which are parallel to the axis, of which the main shaft can have areas with kneading elements arranged on their periphery. The mixing kneader may have a rotor which is operated at a rotation rate in the range from 5 to 50 revolutions per minute, particularly preferably from 7.5 to 40 revolutions per minute, and in particular from 10 to 30 revolutions per minute. An advantage of the mixing kneaders used in the invention is that the residence time can be substantially longer than in an extruder. Venting is moreover substantially easier and can be carried out to a greater extent, thus permitting easy discharge of the gaseous products. The shear rate of the invention can moreover be established more easily in a mixing kneader. Various feed systems for the reactants can be used in a continuously operated mixing kneader. Liquid metering can be used where molten reactants are involved.
- [0058] Some of the steps or all steps of the method according to the invention are advantageously carried out in equipment capable of withstanding the corrosion of the reaction medium. For this purpose, materials are selected for the part in contact with the reaction medium that are corrosion-resistant, 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 304, 304L, 316 or 316L stainless steels. A steel having a nickel content of at most 22 wt.%, preferably of between 6 wt.% and 20 wt.% and more preferentially of between 8 wt.% and 14 wt.%, is used. The 304 and 304L steels have a nickel content that varies between 8 wt.% and 12 wt.%, and the 316 and 316L steels have a nickel content that varies between 10 wt.% and 14 wt.%. More particularly, 316L steels are chosen. Use may also be made of equipment consisting of or coated with a polymeric compound resistant to the corrosion of the reaction medium. Mention may in particular be made of materials such as PTFE (polytetrafluoroethylene or Teflon) 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 capable of being suitable for being in contact with the reaction medium, mention may also be made of graphite derivatives. Materials for filtration have to be compatible with the medium used. Fluorinated polymers (PTFE, PFA), loaded fluorinated polymers (Viton™), as well as polyesters (PET), polyurethanes, polypropylene, polyethylene, cotton, and other compatible materials can be used.

[0059] The process of the present invention may be carried out at atmospheric pressure or under reduced pressure. Preferably, the process of the present invention is carried out under reduced pressure. Performing the reaction under reduced pressure is preferable as it facilitates the removal of the chlorine atoms from the bis(chlorosulfonyl)imide of formula (II) during the process. There is no particular limitation on the pressure that can be applied to the process. The process may, for example, be carried out at a pressure between 0.5 bar and 3 bars, for example a pressure between 0.7 and 2.5 bars, or between 0.9 and 2 bars.

- [0060] The process of the present invention may advantageously be carried out under inert atmosphere to avoid moisture contamination. The process of the present invention may for example be carried out under azote.
- [0061] The process of the present invention may be carried out at a temperature of less than 150°C, for example less than 125°C, or less than 100°C. The process of the present invention may preferably be carried out at a temperature between the melting temperature ($T_{m(l)}$) of the onium salt of bis(fluorosulfonyl)imide of formula (I), for example $\text{KN}(\text{SO}_2\text{F})_2$ and $\text{NH}_4\text{N}(\text{SO}_2\text{F})_2$ and 150°C.
- [0062] The reaction time of the process of the present invention can be selected freely depending for example on the reactor used, the reaction temperature and the reactant quantities involved. It is preferable that the reaction time is from 1 to 12 hours, particularly from 1.5 to 10 hours or from 2 to 9 hours.
- [0063] The process may comprise a step consisting in heating a quantity Q_0 of the salt of bis(fluorosulfonyl)imide (I) so that the salt (I) is in a molten state or a substantially molten state. In some embodiments, this step consists in heating a quantity Q_0 of the salt of bis(fluorosulfonyl)imide (I) at a temperature $T_a(^{\circ}\text{C})$ equals to or higher than its melting point $T_{m(l)}$, to produce a molten salt of bis(fluorosulfonyl)imide (I). The quantity Q_0 of molten salt of bis(fluorosulfonyl)imide (I), in other words the minimal quantity of molten product used to perform the process, may not be less than 20 wt.% of the total weight of the reaction mixture when all the reactive materials have been added. For example, such quantity Q_0 may be at least 30 wt.%, at least 35 wt.%, at least 40 wt.%, at least 45 wt.%, at least 50 wt.%, at least 55 wt.%, at least 60 wt.%, at least 65 wt.%, at least 70 wt.%. Such quantity Q_0 may be less than 95 wt.%, less than 90 wt.% or less than 85 wt.%. The total weight of the reaction mixture when all the reactive materials have been added, may be calculated by adding the weights of all the reactants involved in the process plus the weight of the molten salt of bis(fluorosulfonyl)imide (I). According to an embodiment, the quantity Q_0 is 50 ± 10 wt.% of the total weight of the reaction mixture when all the reactive materials have been added.

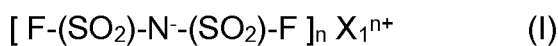
- [0064] It is advantageous for the present invention to select the reaction conditions in such a way that conversion C at the end of the process is at least 95 %, particularly preferably at least 98 %, in particular at least 99 %. For the purposes of the present invention, conversion C is the molar proportion of reactive groups that have been reacted, i.e. bis(chlorosulfonyl)imide (II) and fluorinating agent (III). Surprisingly, it has been found that the conversion of reactants (II) and (III) is very high in the process conditions described herein, despite the absence of any solvent or diluent.
- [0065] In some preferred embodiments, the process is such that the conversion C is at least 95 %, at least 98 %, at least 99 %, at least 99.5 %, at least 99.9 % or at least 99.99%.
- [0066] The process of the present invention may further comprise cooling the reaction mixture to temperature $T_c(^{\circ}\text{C})$ of less than 80°C , for example less than 60°C .
- [0067] The process of the present invention preferably further comprises filtering the reaction mixture. The step of filtration is in order to remove the reaction by-products and/or impurities. The reaction by-products and/or impurities may for example be $X_1\text{Cl}$ and/or $X_1\text{HF}_2$ wherein X_1 is K^+ , Na^+ or an onium cation as described above. If the fluorinating agent is NH_4F for example, the reaction by-products and/or impurities may be NH_4Cl and NH_4HF_2 .
- [0068] Filtration products (funnels, membranes, Nutsche or glass filters, dryers...) are preferably used for the filtration.
- [0069] According to the present invention, a pure or substantially pure salt of bis(fluorosulfonyl)imide of formula (I) is obtained at the end of the reaction in a molten form. While bis(fluorosulfonyl)imide of formula (I) may be maintained at a temperature such that it remains liquid, it may also be post-treated so that to be in a powder form, for example in a crystallized form. The bis(fluorosulfonyl)imide of formula (I), obtained from the process of the present invention may be used in its molten form or in a crystallized form. For example, the molten salt of bis(fluorosulfonyl)imide of formula (I) may be added to an organic solvent at a colder temperature, for example trifluoroethanol, and crystallized before further use. According to yet another embodiment, the salt

(I) may be crystallized in the melt, at least partially, and then extracted or reused/recycled in a new reaction cycle.

[0070] The process of the present invention may also comprise additional steps of measuring and/or monitoring at least one of the following reaction parameters:

- the molar ratio of the bis(chlorosulfonyl)imide (II) to the fluorinating agent (III) in the reaction mixture,
- the number of moles of the reactants in the reaction mixture, notably the number of moles of bis(chlorosulfonyl)imide (II),
- the temperature of the reaction mixture (°C),
- the pressure (atm),
- the melt viscosity of the reaction mixture, or
- the fill level of the reactor, for example of the mixing kneader.

[0071] A **second object** of the present invention is a salt of bis(fluorosulfonyl)imide of formula (I):



wherein:

- X_1^{n+} is a cation selected from the group consisting of K^+ , Na^+ and an onium cation, and
- n is 1 representing the valence of the cation.

[0072] Such salt (I) may advantageously be obtained by the process described above.

[0073] The salt of bis(fluorosulfonyl)imide of formula (I) of the present invention may for example be in a molten state or in a crystallized form.

[0074] According to the present invention, the salt (I) is such that its average crystal length is advantageously at least 400 μm , for example at least 450 μm , at least 500 μm , at least 600 μm or even at least 700 μm . The salt of the prior art is around 300 μm , which means that the salt is not a crystal type.

[0075] Advantageously, due to the fact that no solvent is used in the process of the present invention, such salt is pure or substantially pure with no trace of solvent or with a very low amount of residual solvent. This is advantageous because the solvents that are usually used to prepare the salts (I) need to be removed

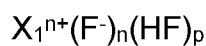
after reaction in order to obtain an as pure as possible product. Indeed, only very pure products can be used for battery applications.

In some preferred embodiments, the amount of solvent in the salt of bis(fluorosulfonyl)imide of formula (I) is less than 100 ppm, for example less than 90 ppm, less than 80 ppm, less than 70 ppm, less than 60 ppm, less than 50 ppm, less than 40 ppm, less than 30 ppm, less than 20 ppm, less than 10 ppm, or even less than 1. This is an advantageous feature of the salt obtained by the process of the present invention. The remaining solvent content may be determined by GC (alternatively headspace GC).

[0076] The salt of bis(fluorosulfonyl)imide of formula (I) described here is obtained by a process comprising the fluorination of a bis(chlorosulfonyl)imide of formula (II):



with a fluorinating agent represented by formula (III):



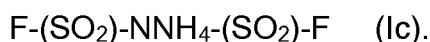
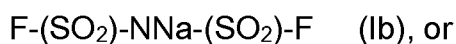
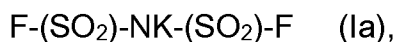
wherein:

p varies between 0 and 10, preferably 0,

wherein the process is carried out in molten salt of bis(fluorosulfonyl)imide of formula (I), in the absence of solvent or in the presence of an amount of solvent less than 5 wt.% based on the total weight of the reaction mixture.

[0077] Such a salt of formula (I) may advantageously be obtained directly from the fluorination of bis(chlorosulfonyl)imide of formula (II), without any additional purification or separation steps.

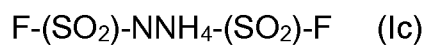
[0078] The salt of bis(fluorosulfonyl)imide of formula (I) is preferably one of the following salts:



[0079] A step of filtration may be used in addition to the above-described process, in order to remove the reaction by-products and/or impurities. The reaction by-

products and/or impurities may for example be $X_1^{n+}Cl^-$ and/or $X_1^{n+}HF_2^-$ wherein X_1 is K^+ , Na^+ or an onium cation as described above.

[0080] A preferred embodiment of the present invention is directed to an ammonium salt of bis(fluorosulfonyl)imide of formula (Ic):



[0081] In this preferred embodiment, the salt may contain at least one of the following impurities:

- NH_4Cl ,
- NH_4F ,
- NH_4HF_2 ,
- NH_4FSO_3 ,
- $NH_4SO_3NH_2$,
- $NH_4[N(SO_3H)(SO_2F)]$ (OFSI), and/or
- $NH_4[N(SO_3H)_2]$ (OSI).

[0082] The impurities, such as NH_4Cl and NH_4HF_2 , may for example be present in the salt (Ic) in a residual amount of less than 1,000 ppm, less than 500 ppm, less than 200 ppm or less than 100 ppm, preferably less than 90 ppm. Such impurities may be present in the salt (Ic) in an amount of more than 1 ppm, for example more than 5 ppm or more than 10 ppm.

[0083] The impurities, such as OFSI and OSI, may for example be present in the salt (Ic) in a residual amount of less than 1,000 ppm, less than 500 ppm, less than 400 ppm or less than 300 ppm, preferably less than 250 ppm or even less than 200 ppm. Such impurities may be present in the salt (Ic) in an amount of more than 1 ppm, for example more than 5 ppm or more than 10 ppm.

[0084] The salts (I) of the present invention also preferably exhibit at least one of the following contents of chemical entities:

- a chloride (Cl^-) content of below 10,000 ppm, preferably below 5,000 ppm, more preferably below 1,000 ppm, more preferably below 500 ppm, more preferably below 100 ppm, more preferably below 50 ppm, more preferably below 20 ppm; and/or

- a fluoride (F^-) content of below 10,000 ppm, preferably below 5,000 ppm, more preferably below 1,000 ppm, more preferably below 500 ppm, more preferably below 100 ppm, more preferably below 50 ppm, more preferably below 20 ppm; and/or.
- a sulfate (SO_4^{2-}) content of below 30,000 ppm, preferably below 10,000 ppm, more preferably below 5,000 ppm; and/or
- an iron (Fe) content of below 1,000 ppm, preferably below 800 ppm, more preferably below 500 ppm; and/or
- a chromium (Cr) content of below 1,000 ppm, preferably below 800 ppm, more preferably below 500 ppm; and/or
- a nickel (Ni) content of below 1,000 ppm, preferably below 800 ppm, more preferably below 500 ppm; and/or
- a zinc (Zn) content of below 1,000 ppm, preferably below 100 ppm, more preferably below 10 ppm, and/or
- a copper (Cu) content of below 1,000 ppm, preferably below 100 ppm, more preferably below 10 ppm; and/or
- a bismuth (Bi) content of below 1,000 ppm, preferably below 100 ppm, more preferably below 10 ppm; and/or
- a sodium (Na^+) content of below 10,000 ppm, preferably below 5 000 ppm, more preferably below 500 ppm; and/or
- a potassium (K^+) content of below 10,000 ppm, preferably below 5 000 ppm, more preferably below 500 ppm.

[0085] Fluoride and chloride contents may for example be measured by titration by argentometry using ion selective electrodes (or ISE). Sulfate content may alternatively be measured by ionic chromatography or by turbidimetry.

[0086] Elemental impurity content may for example be measured by ICP-AES (inductively coupled plasma); more specifically, Na content can be measured by AAS (atomic absorption spectroscopy).

[0087] A **third object** of the present invention is a process for preparing an alkali salt of bis(fluorosulfonyl)imide of formula (IV):



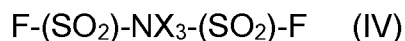
wherein X_3 represents Li or Cs, preferably Li.

[0089] This process comprises the steps of:

- (a) preparing a salt of bis(fluorosulfonyl)imide of formula (I) as described above, and
- (b) reacting the salt of bis(fluorosulfonyl)imide (I) with an alkali agent consisting in a lithium salt or cesium salt.

[0090] According to the present invention, as described above, a pure or substantially pure salt of bis(fluorosulfonyl)imide of formula (I) is obtained. This means that, according to an embodiment, step (b) may be performed directly with the salt (I), for example in a molten form, as obtained according to step (a), for example without any further purification. Alternatively, the molten salt of bis(fluorosulfonyl)imide of formula (I) may be added to an organic solvent, for example trifluoroethanol, which may be cooler. In that case, it is expected that the salt (I) crystallize before performing step (b). According to yet another embodiment, the salt (I) may be crystallized in the melt, at least partially and then extracted or reused/recycled in a new reaction cycle.

[0091] A **fourth object** of the present invention is a salt of bis(fluorosulfonyl)imide of formula (IV):



wherein X_3 represents Li or Cs, preferably Li.

[0092] Such salts (IV) may preferably be obtained by the process described above.

[0093] The salts (IV) of the present invention also preferably exhibit at least one of the following contents of chemical entities:

- a chloride (Cl^-) content of below 10,000 ppm, preferably below 5,000 ppm, more preferably below 1,000 ppm, more preferably below 500 ppm, more preferably below 100 ppm, more preferably below 50 ppm, more preferably below 20 ppm; and/or
- a fluoride (F^-) content of below 10,000 ppm, preferably below 5,000 ppm, more preferably below 1,000 ppm, more preferably below 500 ppm, more preferably below 100 ppm, more preferably below 50 ppm, more preferably below 20 ppm; and/or.

- a sulfate (SO_4^{2-}) content of below 30,000 ppm, preferably below 10,000 ppm, more preferably below 5,000 ppm; and/or
- an iron (Fe) content of below 1,000 ppm, preferably below 800 ppm, more preferably below 500 ppm; and/or
- a chromium (Cr) content of below 1,000 ppm, preferably below 800 ppm, more preferably below 500 ppm; and/or
- a nickel (Ni) content of below 1,000 ppm, preferably below 800 ppm, more preferably below 500 ppm; and/or
- a zinc (Zn) content of below 1,000 ppm, preferably below 100 ppm, more preferably below 10 ppm, and/or
- a copper (Cu) content of below 1,000 ppm, preferably below 100 ppm, more preferably below 10 ppm; and/or
- a bismuth (Bi) content of below 1,000 ppm, preferably below 100 ppm, more preferably below 10 ppm; and/or
- a sodium (Na^+) content of below 10,000 ppm, preferably below 5 000 ppm, more preferably below 500 ppm; and/or
- a potassium (K^+) content of below 10,000 ppm, preferably below 5 000 ppm, more preferably below 500 ppm.

[0094] A **fifth object** of the present invention is directed to the use of the salt of bis(fluorosulfonyl)imide of formula (IV) in a battery electrolyte solution.

[0095] 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.

[0096] EXAMPLES

[0097] The invention will be now described in more detail with reference to the following examples, whose purpose is merely illustrative and not intended to limit the scope of the disclosure.

[0098] Example 1 - Bis(fluorosulfonyl)imide ammonium salt formation

[0099] Under nitrogen, 63.5 g of NH_4F (1.71 mol, 4.4 eq vs HCSI) was mixed with 250 g of NH_4FSI (1.26 mol) and stirred for 1 hour at 90°C. Liquid HCSI was then added continuously to the reaction mixture at a rate of 40 g/h and up to 83.3 g (0.39 mol) using a feeding funnel with a heat belt. The stirring was continued for 12 hours. The temperature of the reaction was continuously monitored and kept below 100°C. The reaction mixture was then cooled to 60 °C in 1 hour. 320 g of TFE was then added to the mixture. The solid was isolated by filtration. The filtrated solution was then cooled to 10 °C in 2 hours. Crystals were isolated by filtration at 25°C, then washed with 160 g of fresh TFE. The solid was dried under vacuum at room temperature for 12 hours.

[00100] The product was then analysed.

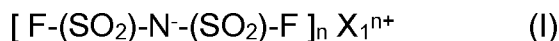
[00101] The conversion was 87.6 %, as measured by ^{19}F NMR (FSI-).

[00102] Example 2 - Bis(fluorosulfonyl)imide lithium salt formation

[00103] Under nitrogen atmosphere, a solution of 6.9 g NH_4FSI (0.35 mmol), as obtained from Example 1, was prepared in 60 g of Ethyl Methyl Carbonate (EMC). 14.6 g of solid $\text{LiOH}\cdot\text{H}_2\text{O}$ (0.35 mmol) was added to the vessel at room temperature in 10 minutes. After 1 hour of stirring, the conversion of NH_4^+ ions (as measured by a NaOH titration) was greater than 90 %. The medium was concentrated a first time under reduced pressure ($P=20\text{mbar}$, $T=0^\circ\text{C}$). 120 mL of EMC was added and the concentration was performed a second time under the same conditions. The concentrated solution was dried under vacuum pressure at 30°C for 24 hours. 5 g of a viscous transparent liquid was obtained. ^{19}F NMR analysis indicated a purity above 99 wt.%. No other fluorinated species was detected.

Claims

Claim 1. A process for preparing a salt of bis(fluorosulfonyl)imide of formula (I):



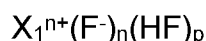
wherein:

- X_1^{n+} is a cation selected from the group consisting of K^+ , Na^+ and an onium cation, and
- n is 1 representing the valence of the cation,

the process comprising the fluorination of a bis(chlorosulfonyl)imide of formula (II):



with a fluorinating agent represented by formula (III):



wherein:

- p varies between 0 and 10,

wherein the process is carried out in molten salt of bis(fluorosulfonyl)imide of formula (I), in the absence of solvent or in the presence of an amount of solvent less than 5 wt.% based on the total weight of the reaction mixture.

Claim 2. The process of claim 1, which is carried out under reduced pressure.

Claim 3. The process of any one of claims 1-2, wherein the stoichiometry amount of fluorinating agent (III) is between 1 to 10 equivalents per 1 mol of bis(chlorosulfonyl)imide (II).

Claim 4. The process of any one of claims 1-3, comprising the steps of:

- (i) heating a quantity Q_0 of the salt of bis(fluorosulfonyl)imide (I) at a temperature $T_a(^{\circ}C)$ higher than its melting point $T_{m(l)}$, to produce a molten salt of bis(fluorosulfonyl)imide (I), and
- (ii) adding the fluorinating agent (III) and the bis(chlorosulfonyl)imide (II) to the molten salt of bis(fluorosulfonyl)imide (I).

Claim 5. The process of claim 4, wherein step (ii) comprises:

- (ii1) adding the fluorinating agent (III) to the molten salt of bis(fluorosulfonyl)imide (I),

(ii2) optionally removing the residual amount of water or aqueous liquid from the fluorinating agent (III), and

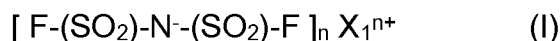
(ii3) adding the bis(chlorosulfonyl)imide (II) to the reaction mixture.

Claim 6. The process of claim 5, wherein the process comprises a step (ii2) carried out by distillation of the water.

Claim 7. The process of any one of claims 4-6, wherein the quantity Q_0 is not less than 20 wt. % of the total weight of the reaction mixture when all the reactive materials have been added.

Claim 8. The process of any one of claims 1-7, which is carried out at a temperature of less than 100°C.

Claim 9. Salt of bis(fluorosulfonyl)imide of formula (I):

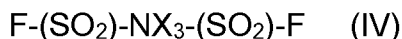


wherein:

- X_1^{n+} is a cation selected from the group consisting of K^+ , Na^+ and an onium cation, and
- n is 1 representing the valence of the cation, obtainable by the process of any one of claims 1-8, wherein the amount of solvent is less than 100 ppm.

Claim 10. The salt of claim 9, wherein the amount of solvent is less than 50 ppm.

Claim 11. A process for preparing an alkali salt of bis(fluorosulfonyl)imide of formula (V),



wherein X_3 represents Li or Cs, preferably Li,

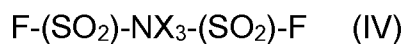
comprising the steps of:

- (a) preparing a salt of bis(fluorosulfonyl)imide of formula (I) according to any one of the claims 1-8, and
- (b) reacting the salt of bis(fluorosulfonyl)imide (I) obtained in step (a) with an alkali agent consisting in a lithium salt or a cesium salt.

Claim 12. The process of claim 11, wherein step (b) is carried out in an organic reaction medium comprising at least one organic solvent, said organic solvent being selected from the aprotic organic solvents, preferably from the group consisting of ethyl acetate,

isopropyl acetate, butyl acetate, ethylene carbonate, dimethyl carbonate, ethyl methyl carbonate, propylene carbonate, valeronitrile and acetonitrile.

Claim 13. Salt of bis(fluorosulfonyl)imide of formula (IV):



wherein X_3 represents Li or Cs, preferably Li,

obtainable by the process of any one of claims 11-12.

Claim 14. Use of the salt of bis(fluorosulfonyl)imide of formula (IV) of claim 13 in a battery electrolyte solution.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/065529

A. CLASSIFICATION OF SUBJECT MATTER INV. C01B21/086 C01B21/093 H01G11/58 H01M10/0525 H01G11/62 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 H01G 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, WPI Data, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
T	International Union Of Pure And Applied Chemistry: "IUPAC Gold Book - onium compounds", , 24 February 2014 (2014-02-24), XP055380674, Retrieved from the Internet: URL: http://goldbook.iupac.org/html/O/O04291.html [retrieved on 2017-06-12] the whole document -----	
X	EP 2 660 196 A1 (NIPPON SODA CO [JP]) 6 November 2013 (2013-11-06)	9-14
A	claims 1-3; examples 1-5 ----- -/--	1-8
☒ 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		Date of mailing of the international search report
23 September 2022		04/10/2022
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 Sevillano Rodriguez

INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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A	claims 1-10; examples 1-4 -----	1-8
X	EP 3 466 871 A1 (MORITA CHEMICAL IND CO LTD [JP]; NIPPON CATALYTIC CHEM IND [JP]) 10 April 2019 (2019-04-10)	13, 14
A	paragraph [0090] - paragraph [0107]; claims 1-10; table 2 -----	1-12

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