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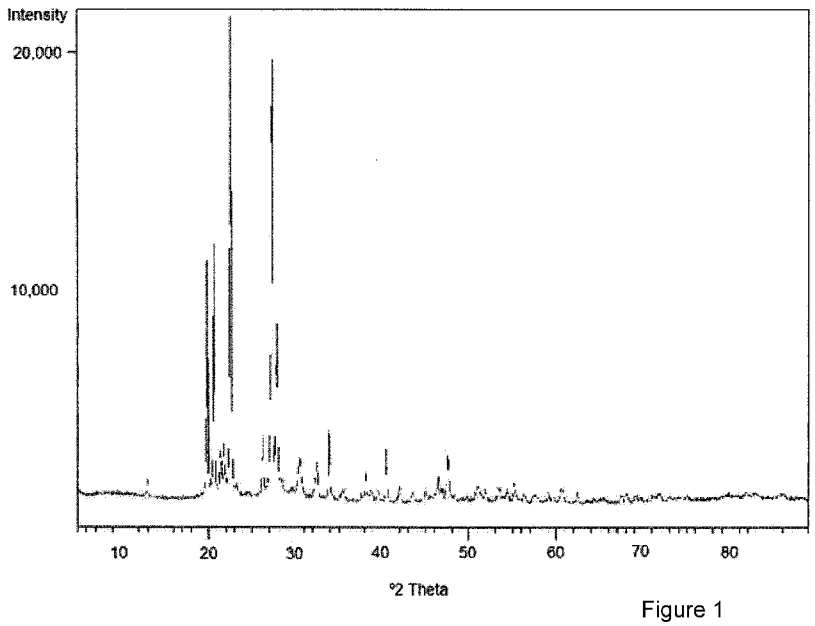

Figure 1

(57) Abstract: The present invention relates to a method for the production of metal difluorophosphates, specifically to the production of $LiPO_2F_2$, in an inorganic solvent. More specifically, it relates to a method for the production of metal difluorophosphates comprising a step of reacting a phosphorus-containing reactant selected from the group consisting of phosphorus pentafluoride (PF_5),phosphoryl fluoride (POF_3), and mixtures thereof, with a metal orthophosphate, bicarbonate or carbonate in an inorganic solvent, preferably in an excess of the phosphorus-containing reactant.

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Production of metal difluorophosphates in an inorganic solvent

This application claims priority to European applications No. 13182079.7, filed August 28, 2013 and No. 14153455.2, filed January 31, 2014, the whole content of these applications being incorporated herein by reference for all purposes.

The present invention relates to a method for the production of metal difluorophosphates, specifically to the production of $LiPO_2F_2$, in an inorganic solvent. More specifically, it relates to a method for the production of metal difluorophosphates comprising a step of reacting a phosphorus-containing reactant selected from the group consisting of phosphorus pentafluoride (PF_5), phosphoryl fluoride (POF_3), and mixtures thereof, with a metal orthophosphate, bicarbonate or carbonate in an inorganic solvent, preferably in an excess of the phosphorus-containing reactant.

Metal difluorophosphates are useful compounds in electrolyte compositions for metal ion batteries. As a specific example, lithium difluorophosphate, $LiPO_2F_2$, is useful as electrolyte salt or additive for an electrolyte composition used in lithium ion batteries.

WO 2012/016924 describes the reaction of solid Li_3PO_4 with gaseous POF_3 and/or PF_5 to yield $LiPO_2F_2$. Furthermore, WO 2012/016924 outlines the possibility of performing the process in presence of an aprotic organic solvent.

Now therefore, the invention makes available an improved process for the production of metal difluorophosphates, specifically for the production of $LiPO_2F_2$ in a technically feasible and economical manner. It is an object of the present invention to provide a process for the production of metal difluorophosphates, specifically for the production of $LiPO_2F_2$, which is advantageous in terms of the overall yield, the purity, the physicochemical properties including but not limited to the crystallinity and/or density of the product, the energy consumption, the safety requirements, the ease of work-up, and/or the side-product profile. Furthermore, it is an object of the present invention to provide $LiPO_2F_2$ in a form which is advantageous in terms of stability, solubility, crystallinity, dissolution rate, and/or ease of handling.

This object and other objects are achieved by the invention as outlined in the patent claims.

Brief description of the drawing

Figure 1 shows the XRD pattern of $LiPO_2F_2$ produced according to the procedure of example 1.

Accordingly, one embodiment of the present invention is a process for the production of a compound of general formula MPO_2F_2, wherein M is Li, Na or K; comprising a reaction step (I) of a compound of the general formula M_3PO_4, M_2CO_3, $MHCO_3$ or a mixture thereof, wherein each M is defined as above; with a phosphorous-containing reactant selected from the group consisting of POF_3, PF_5 and a mixture thereof; to form the compound of general formula MPO_2F_2, wherein the reaction is performed in the presence of an inorganic solvent. The inventive process is not limited to the metals M as given above. It can also be used to produce metal difluorophosphates of other metals like Mg, Zn, Ca, Sr, Ba, or Fe.

In a preferred embodiment, M is Li. In a more preferred embodiment, the reaction is the reaction of Li_3PO_4 with POF_3 to form $LiPO_2F_2$. Accordingly, $LiPO_2F_2$ is produced by the reaction of phosphoryl fluoride (POF_3) and lithium orthophosphate (Li_3PO_4) following the reaction scheme:

$$2POF_3 + Li_3PO_4 \rightarrow 3\ LiPO_2F_2$$

The term "solvent" is intended to denote a chemical compound which is a liquid under the reaction conditions of reaction step (I) and in which at least part of the starting materials, reactants and/or reaction products is dissolved during the performance of reaction step (I).

The term "inorganic" is intended to denote any compound that lacks both carbon and hydrogen atoms.

Suitable examples of inorganic solvents include carbon monoxide, carbon dioxide, hydrogen fluoride, urea, POF_3, PF_5 and mixtures thereof. Although some of the aforementioned inorganic solvents are solid or gaseous under ambient conditions, they fall under the definition "inorganic solvent" as used in the context of this invention when in the liquid state under the reaction conditions of reaction step (I). In one preferred embodiment, supercritical CO_2 is used as the inorganic solvent. In another preferred embodiment the phosphorous-containing reactant according to this invention is used as the inorganic solvent, more preferably POF_3 is used as the inorganic solvent. Thus, one compound can serve both the roles of the phosphorous-containing reactant as well as the inorganic solvent.

Preferably, the initial molar ratio of POF_3 to Li_3PO_4 is equal to or greater than 1 and equal to or lower than 3. Also preferably, the phosphorous-containing reactant is used in an excess molar ratio. In case of the reaction of Li_3PO_4 with POF_3, the preferred molar ratio of POF_3 to Li_3PO_4 is equal to or greater than 2, more preferably equal to or greater than 5. Alternatively, the ratio is suitably chosen to create a liquid phase of POF_3 under the given reactor volume at room temperature.

Phosphoryl fluoride (POF_3) can be obtained commercially, e.g. from ABCR GmbH & Co. KG, or can be prepared by a known process in the art. For example, POF_3 can be prepared by fluorination of phosphoryl chloride with HF and/or other fluorinating agents, for example, ZnF_2. Alternatively, it may be also prepared by the reaction of H_3PO_4/P_2O_5, HF/H_2O and SO_3/H_2SO_4. Sometimes, the POF_3 obtained may contain PF_5 as impurity, or vice versa, PF_5 may comprise POF_3 as impurity. The advantage of the process of the invention is that even such mixtures can be applied without impact on the yield.

PF_5 may be obtained commercially, e.g. from Praxair, or it may be prepared from PCl_5 and HF or, as described in EP-A-0816287, for example from PCl_3, Cl_2 and HF.

Li_3PO_4 is commercially available, e.g. from Strem Chemicals, Inc, Newburyport, USA, or from Chemetall GmbH, Germany. It is a solid with a melting point far above 1000°C.

Preferably, the reaction between PF_5 and Li_3PO_4, between POF_3 and Li_3PO_4 and between mixtures of POF_3 and PF_5, respectively, and Li_3PO_4 is performed in the absence of water or moisture. It is preferred to perform the reaction in apparatus made from steel or other materials resistant against corrosion, e.g. in reactors made of or clad with Monel metal and/or Fluorpolymer (Teflon®) coated.

Li_3PO_4 is preferably applied in the form of small particles, e.g. in the form of a powder. If desired, it can be dried before introducing it into the reaction.

The reaction conditions are chosen in a way that at least part of the inorganic solvent is in the liquid state. To this end it is preferred that the reaction is performed under a pressure of equal to or higher than 6 bar, preferably equal to or higher than 8 bar, more preferably equal to of higher than 10 bar. Also preferably, the reaction is performed at a pressure of equal to or below 20 bar, more preferably equal to or below 15 bar. Also preferably, the reaction is

performed at a reaction temperature from 0 to 95 °C, preferably from 15 to 80°C, more preferably from 20 to 65 °C.

The reaction time is selected such that the desired degree of conversion is achieved. Often, a reaction time of 1 second to 5 hours gives good results for the reaction between POF_3, PF_5 and any mixtures thereof with Li_3PO_4. For the reaction between POF_3 and Li_3PO_4, a preferred reaction time of 0.5 to 5 hours gives good results. For the reaction between PF_5 or mixtures of PF_5 and POF_3 and Li_3PO_4, a preferred reaction time of 0.5 to 2 hours, most preferably of around 1 hour gives good results, too. The reaction speed is generally very fast.

In case the inorganic solvent is gaseous under ambient conditions, the inorganic solvent can be removed after reaction step (I) by venting the reaction vessel. The crude product thus obtained may optionally be treated further to remove residual reactant, inorganic solvent or by-products. To this end, the crude product may optionally be purged with a stream of nitrogen, subjected to elevated temperatures and/or subjected to reduced pressure.

In a preferred embodiment, the inorganic solvent can be recycled after the reaction step (I). If POF_3 is used as the inorganic solvent it can be removed from the reaction vessel in gaseous form by lowering the pressure in the reaction vessel, collected in a further suitable vessel and re-used for a subsequent reaction step. The inorganic solvent can optionally be purified before being re-used.

Purification and/or crystallization of $LiPO_2F_2$ in aprotic organic solvents have been described in the prior art. Surprisingly, it has now been found that a compound of general formula MPO_2F_2, preferably $LiPO_2F_2$, can be purified by recrystallisation of the compound from a protic organic solvent, preferably from an alcohol, more preferably from methanol. Thus, another preferred embodiment is a process comprising a further reaction step (II) wherein the crude reaction product from reaction step (I) is dissolved in a solvent mixture comprising a protic solvent, preferably comprising an alcohol, more preferably comprising methanol. Subsequently, the product may be isolated by means of spray drying, evaporation of the solvent, crystallisation, lyophilization or a mixture thereof, preferably by means of crystallisation. If a crystallisation step is performed, this step can be performed using cold crystallisation, anti-solvent crystallisation, seeding or a mixture of these technologies.

The term "protic solvent" is intended to denote a solvent that has a hydrogen atom bound to an oxygen atom (as in a hydroxyl group) or a nitrogen atom (as in an amine group).

The mixture obtained after the reaction step (I) and/or (II) can be too acidic possibly leading to a product of lower quality after isolation. Thus, in another preferred embodiment the mixture obtained after the reaction step (I) and/or (II) is subjected to a neutralization step. Preferably, the neutralization step is performed in the presence of Li_2CO_3. To this end, the neutralization agent, preferably a carbonate or bicarbonate, more preferably lithium carbonate, is added to the mixture after the reaction step (I) and/or (II), preferably added in solid form to a solution or slurry of the crude product from reaction step (I) in a suitable solvent, preferably in methanol. Advantageously, the pH of the mixture after the neutralization step is from 4 to 7, preferably from 5.5 to 6.5, more preferably about 6.

Another embodiment of the present invention concerns a process for the production of a compound of the general formula MPO_2F_2, wherein M is Li, Na or K, comprising a reaction step (I) of a compound of general formula M_3PO_4, M_3PO_4, M_2CO_3, and $MHCO_3$, or a mixture thereof, wherein each M is defined as above, with POF_3, PF_5 or a mixture thereof, to form the compound of general formula MPO_2F_2, wherein the reaction is performed in the presence of an organic solvent, preferably in an organic solvent in which the compound of general formula MPO_2F_2 has a solubility of > 1 g/l at ambient conditions, preferably of > 5 g/l, more preferably of > 10 g/l. The process is not limited to the metals M as given above. It can also be used to produce metal difluorophosphates of other metals like Mg, Zn, Ca, Sr, Ba, or Fe.

In a preferred embodiment, M is Li. In a more preferred embodiment, the reaction is the reaction of Li_3PO_4 with POF_3 to form $LiPO_2F_2$.

The term "organic solvent" is intended to denote any compound comprising at least one carbon atom that is liquid under the reaction conditions. Advantageously, the organic solvent does not react with any of the starting materials or the reaction product. Useful examples of an organic solvent are aprotic organic solvents, for example cyclic and acyclic ethers, esters, ketones, carbonates, nitriles, sulfones and mixtures thereof wherein the solubility of the compound of general formula MPO_2F_2 is > 1 g/l at ambient conditions. Examples of useful organic solvents include acetone, acetonitrile, dimethylformamide, sulfolane.

The term "ambient conditions" is intended to denote conditions referring to the standard ambient temperature and pressure (25°C, 100 kPa).

The term "solubility" is intended to denote the analytical composition of a saturated solution expressed as a proportion of a designated solute in a designated solvent according to IUPAC definition.

In a preferred embodiment, the organic solvent is a diether or a polyether, more preferably a diether, most preferably the diether is 1,2 dimethoxyethane. The term "diether" is intended to denote a compound comprising two moieties of the structural motif "C-O-C", i.e. a compound comprising two oxygen atoms each directly connected to two groups selected from alkyl, alkylene, (hetero)aryl or (hetero)arylene. The term "polyether" is intended to denote a compound comprising at least three moieties of the structural motif "C-O-C", i.e. a compound comprising at least three oxygen atoms each directly connected to two groups selected from alkyl, alkylene, (hetero)aryl or (hetero)arylene. The diether and/or polyether can advantageously be substituted, for example substituted by fluorine. The diether and/or polyether can advantageously be cyclic or acyclic. Useful examples of diethers are 1,2-diethoxyethane. Useful examples of polyethers are glymes of the general formula $CH_3O(CH_2CH_2O)_nCH_3$ with $n > 1$ or crown ethers, for example 12-crown-4, 15-crown-5, 18-crown-6, dibenzo-18-crown-6. Most preferably, the organic solvent is 1,2-dimethoxyethane.

The inventive process yields $LiPO_2F_2$ with superior characteristics, especially in terms of crystallinity and/or purity. Thus, another aspect of the present invention concerns $LiPO_2F_2$ obtainable using the inventive process as described above.

Yet another aspect of the present invention concerns crystalline $LiPO_2F_2$ characterized by an X-ray powder diffraction pattern showing the two strongest peaks at 22.6 ± 0.2 and 27.3 ± 0.2 ° 2-Theta, preferably characterized by an X-ray powder diffraction pattern showing the four strongest peaks at 19.9 ± 0.2, 20.6 ± 0.2, 22.6 ± 0.2, 27.3 ± 0.2 ° 2-Theta.

Still another aspect of the present invention concerns crystalline $LiPO_2F_2$ characterized by an X-ray powder diffraction pattern essentially as shown in Figure 1.

A further aspect concerns crystalline $LiPO_2F_2$ characterized by a bulk density of < 500 g/l, preferably between 100 and 400 g/l, more preferably between 200 and 300 g/l.

Yet another aspect of the present invention concerns an electrolyte composition for lithium-ion batteries, lithium-sulfur batteries and/or lithium-

oxygen batteries comprising the crystalline $LiPO_2F_2$ according to this invention and further comprising a solvent suitable for electrolyte solutions for lithium-ion batteries, lithium-sulfur batteries and/or lithium-oxygen batteries.

Solvents suitable for electrolyte solutions for lithium-ion batteries, lithium-sulfur batteries and/or lithium-oxygen batteries are known in the art. Suitable examples include the group of dialkyl carbonates (which are linear) and alkylene carbonates (which are cyclic), and wherein the term "alkyl" denotes preferably C1 to C4 alkyl, the term "alkylene" denotes preferably C2 to C7 alkylene groups, including a vinylidene group, acetone, acetonitrile, linear dialkyl carbonates, e.g. dimethyl carbonate, diethyl carbonate, methyl ethyl carbonate, cyclic alkylene carbonates, e.g. ethylene carbonate, propylene carbonate, and vinylidene carbonate, and fluorinated derivatives of the compounds mentioned in this paragraph, e.g. 1-fluoroethyl methyl carbonate, 4-fluoroethylene carbonate or 1-fluoroethyl allyl carbonate.

The concentration of the metal difluorophosphates of the invention in the electrolyte solution is preferably 1 ± 0.2 molar. Often, the electrolyte solution may comprise $LiPF_6$ and $LiPO_2F_2$. In the case, the combined concentration of the two compounds in the electrolyte solution is preferably 1 ± 0.2 molar.

Should the disclosure of any of the patents, patent applications, and publications that are incorporated herein by reference be in conflict with the present description to the extent that it might render a term unclear, the present description shall take precedence.

Examples

Example 1 : Production of $LiPO_2F_2$

The reactor is charged with Li_3PO_4 (5.8 kg, 50 mol) and cooled to 16°C. POF_3 (35.5 kg, 350 mol) is fed to a pressure of 14 bar(g) in the reactor while agitating the Li_3PO_4. During addition of the POF_3 the temperature rises continuously to 60°C. After 16 h, the excess POF_3 is pumped off and can be recycled for the next batch. The reactor (double jacket) is then heated to 140°C to evaporate residual gas while under vacuum with an additional purge of 300 l/h nitrogen for 24 h. Subsequently, the reactor is cooled to room temperature and 38 kg MeOH is added. The solution is being processed by filtration through a 5 µm Teflon® sieve.

The filtrate can be further treated by either

(A) Being transferred to a evaporation unit to produce crude $LiPO_2F_2$ in form of crystals. The crystals can be transferred to a glove box and milled to a fine

powder, which again is vacuum dried (100 °C and 100 mbar using a flow of nitrogen of 100 l/h) to remove residual solvent from the crystallization step. The accumulated yield is 85 %.

or

(B) Being spray dried under controlled and ex-proof condition, which results also in a 85 % yield of $LiPO_2F_2$.

Analytical data

PXRD (powder X-ray diffraction): Samples were analysed on a Bruker AXS D8 Advance powder X-ray diffractometer. The wavelength of the radiation was 1.5406Å. Measurement conditions were as follows.

radiation	Cu K_α
source	38 kV / 40 mA
detector	Vantec-1
detector slit	10.39 mm
detector antiscattering slit	6.17 mm
divergence slit	v6.00
antiscattering slit	0.5°
2θ range	$2° \leq 2\theta \leq 55°$
step size	0.017°
step time	0.2 s

Position [° 2 Theta]	Intensity [counts]	Position [° 2 Theta]	Intensity [counts]
13,03	538,88	46,08	310,03
19,91	7900,17	46,52	1011,01
20,64	9222,67	46,89	509,58
21,37	1732,4	47,55	1897,22
21,78	2100,5	48,29	272,25
22,55	17484,82	50,88	588,15
23,32	631,65	51,81	479,78
26,27	2304,76	53,45	560,08
27,31	16984,9	54,33	464,72
27,86	6620,6	55,12	674,57
28,45	729,11	56,35	306,58
29,59	439,26	57,41	269,72
30,56	1769,7	57,72	302,43
32,25	885,48	59,08	343,91
32,51	1351,54	59,66	203,39
33,90	2813,27	60,61	544,44
35,42	426,98	62,45	340,32
37,64	245,17	67,40	246,56
38,13	1005,28	68,07	288,53
38,67	394,43	69,21	269,34
39,53	381,03	69,72	167,86
40,46	1695,09	71,07	206,26
42,01	549,94	71,84	280,12
43,51	344,46	73,04	151,94
44,94	446,99		

Table 1 : XRD data for the compound according to example 1(B)

^{19}F-NMR (470.94 MHz; D_6-acetone): -84.25 ppm (doublet, J= 926 Hz)

The bulk density at ambient conditions of the $LiPO_2F_2$ according to example 1 was determined to be 280 g/l. In a comparable example, the bulk density of the $LiPO_2F_2$ prepared according to example 3 of WO 2012/016924 was determined to be 560 g/l.

Example 2 : Production of $LiPO_2F_2$

58 g Li_3PO4 was dried at 200°C for 18 h and subsequently placed in a Teflon® reactor equipped with a paddle mixer and a Teflon® condenser.

Dimethoxyethane (500 ml) was added and the mixture was stirred at 200 rpm. The reaction vessel was subjected to a nitrogen atmosphere and subsequently, POF_3 (103.4 g) was introduced into the mixture via an immersion tube at room temperature over a period of 4.5 h. After the introduction of POF_3 was completed, reaction mixture and vessel were flushed with nitrogen gas for 30 min. 25 g lithium carbonate was added and stirring continued for another 10 min. The mixture was filtered through a 10 µm Teflon® filter with suction (300 mbar on the filtrate side). The filtrate showed pH 6. Volatiles were removed by means of a spray dryer (Buechi B-295- Inert Loop) under the following conditions: inlet temperature 202°C, outlet temperature 115°C, feed rate 7 g/min.

The crude product is dried at 100°C and 100 mbar using a flow of nitrogen of 100 l/h for 18 h to yield 146 g (90 %) of the product.

Example 3 : Electrolyte solution for lithium ion batteries, lithium sulfur batteries and/or lithium-oxygen batteries

117 g $LiPF_6$, 23 g $LiPO_2F_2$ (obtained analogously to example 1), 50 g 4-fluoroethylene carbonate and propylene carbonate are mixed in amount such that a total volume of 1 liter is obtained. The resulting solution contains 0.77 mol $LiPF_6$ and 0.23 mol $LiPO_2F_2$.

CLAIMS

1. A process for the production of a compound of general formula MPO_2F_2, wherein M is Li, Na or K; comprising a reaction step (I) of a compound of the general formula M_3PO_4, M_2CO_3, $MHCO_3$ or a mixture thereof, wherein each M is defined as above; with a phosphorous-containing reactant selected from the group consisting of POF_3, PF_5 and a mixture thereof; to form the compound of general formula MPO_2F_2, wherein the reaction is performed in the presence of an inorganic solvent.

2. The process according to claim 1 wherein M is Li.

3. The process according to claim 1 or 2 comprising the reaction step (I) is the reaction of Li_3PO_4 with POF_3 to form $LiPO_2F_2$.

4. The process according to any one of claims 1 to 3 wherein the reaction is performed under a pressure of equal to or higher than 6 bar, preferably equal to or higher than 8 bar, more preferably equal to of higher than 10 bar.

5. The process according to any one of claims 1 to 4 wherein the reaction is performed at a reaction temperature from 0 to 100°C, preferably from 10 to 70°C.

6. The process according to any one of claims 1 to 5 wherein the phosphorous-containing reactant is used as the inorganic solvent, preferably POF_3 is used as the inorganic solvent.

7. The process according to any one of claims 1 to 6 wherein the phosphorous-containing reactant is used in an excess molar ratio.

8. The process according to any one of claims 1 to 6 wherein the reaction is performed in excess POF_3.

9. The process according to claim 8 wherein the excess POF_3 is recycled.

10. The process according to any one of claims 1 to 9 comprising a further reaction step (II) wherein the crude reaction product from reaction step (I) is dissolved in a solvent mixture comprising an alcohol, preferably comprising methanol.

11. $LiPO_2F_2$ obtainable using the process according to any one of claims 1 to 10.

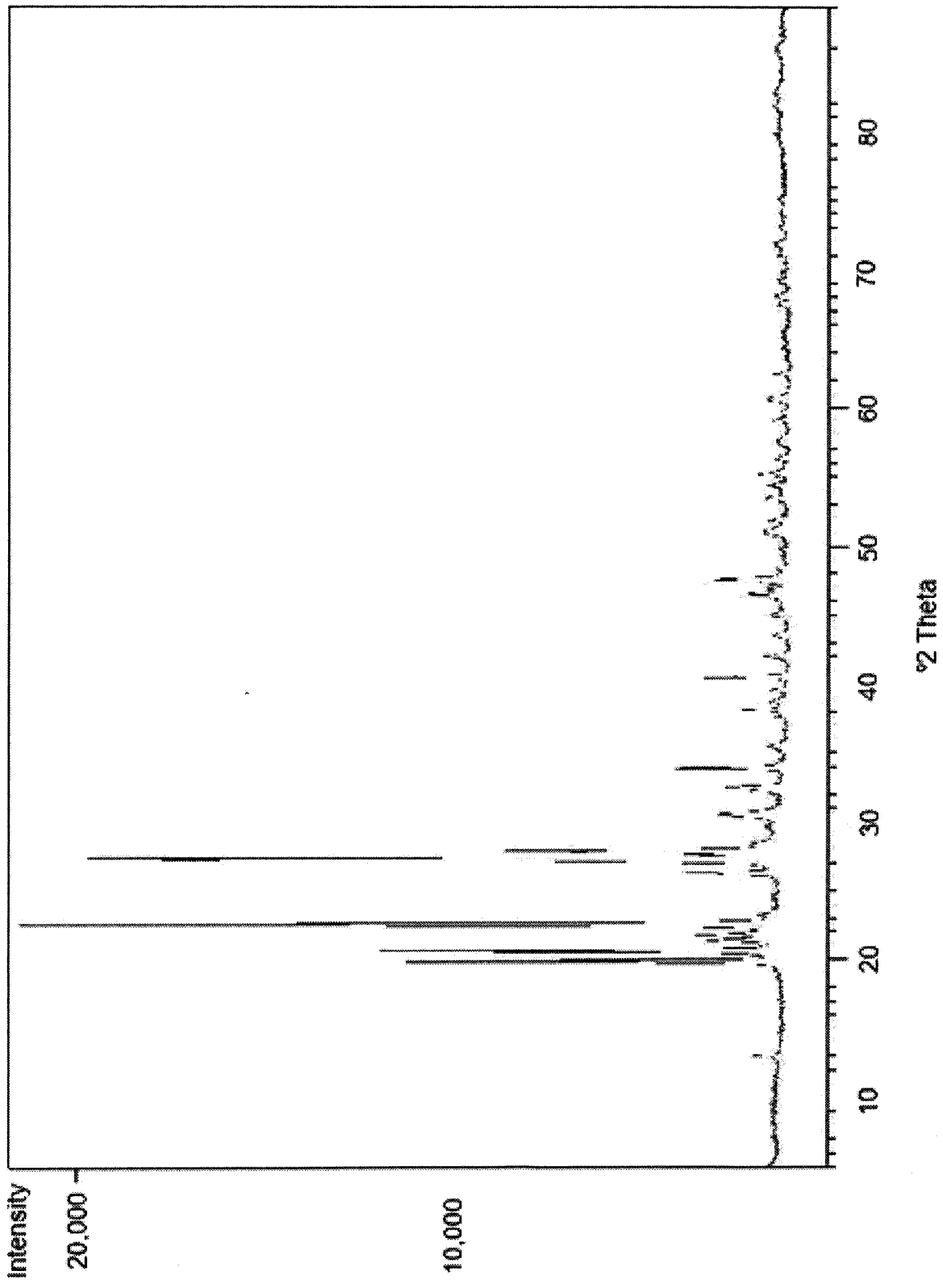
12. Crystalline $LiPO_2F_2$ characterized by an X-ray powder diffraction pattern showing the two strongest peaks at 22.6 ± 0.2 and 27.3 ± 0.2 ° 2-Theta.

13. The crystalline $LiPO_2F_2$ according to claim 12 characterized by an X-ray powder diffraction pattern showing the four strongest peaks at 19.9 ± 0.2, 20.6 ± 0.2, 22.6 ± 0.2, 27.3 ± 0.2 ° 2-Theta.

14. Crystalline $LiPO_2F_2$ characterized by an X-ray powder diffraction pattern essentially as shown in Figure 1.

15. An electrolyte composition for lithium-ion batteries, lithium-sulfur batteries and/or lithium-oxygen batteries comprising the crystalline $LiPO_2F_2$ according to any one of the claims 11 to 14 and further comprising a solvent suitable for electrolyte composition for lithium-ion batteries, lithium-sulfur batteries and/or lithium-oxygen batteries.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/067622

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01B25/455 H01M10/052 H01M10/0567 C01D15/00
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 H01M C01D

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, CHEM ABS Data, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2012/016924 A1 (SOLVAY [BE]; SCHULZ ALF [DE]; GARCIA-JUAN PLACIDO [DE]) 9 February 2012 (2012-02-09) cited in the application	1-5,7,8, 10-15
A	page 1, lines 11-13; claim 7 page 2, lines 4-19 page 3, lines 7-26 page 3, line 35 - page 4, line 2 page 5, line 28 - page 6, line 6 page 15, lines 17-21 page 4, line 23 - page 5, line 6 page 8, lines 20-26	6,9

X	WO 2013/023902 A1 (SOLVAY [BE]; GARCIA-JUAN PLACIDO [DE]; SCHULZ ALF [DE]) 21 February 2013 (2013-02-21)	11-15
A	page 2, lines 1-32; figure 1; example 3	1-10

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
24 October 2014	05/11/2014

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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