⑲ **Octrooicentrum**
Nederland

⑪ **2020683**

⑫ B1 **OCTROOI**

㉑ Aanvraagnummer: **2020683**

㉒ Aanvraag ingediend: **29 maart 2018**

(51) Int. Cl.:
C01D 15/00 (2019.01)

㊶ Aanvraag ingeschreven:
16 juli 2018

㊸ Aanvraag gepubliceerd:
16 juli 2018

㊼ Octrooi verleend:
19 maart 2019

㊺ Octrooischrift uitgegeven:
22 mei 2019

(73) Octrooihouder(s):
The South African Nuclear Energy Corporation SOC Limited te Madibeng Municipality, Zuid-Afrika, ZA.

(72) Uitvinder(s):
Mpho Diphago Stanley Lekgoathi te Madibeng Municipality (ZA).
Petrus John Le Roux te Madibeng Municipality (ZA).
Danny Sello Mmotong te Madibeng Municipality (ZA).

(74) Gemachtigde:
ir. P.J. Hylarides c.s. te Den Haag.

(54) PRODUCTION OF LITHIUM HEXAFLUOROPHOSPHATE

(57) A method of producing lithium hexafluorophosphate ($LiPF_6$) includes fluorinating lithium phosphate (LiF) by reacting it with a fluorination agent in a liquid medium that is non-reactive with, i.e. is inert to, the fluorination agent, thereby producing $LiPF_6$.

PRODUCTION OF LITHIUM HEXAFLUOROPHOSPHATE

FIELD OF THE INVENTION

THIS INVENTION relates to the production of lithium hexafluorophosphate. The invention provides a method of producing lithium hexafluorophosphate, and extends to lithium hexafluorophosphate produced in accordance with the method. The invention also extends to a method of producing an electrolyte, and extends to an electrolyte produced in accordance with the method. The invention also provides an electric battery and a method of manufacturing an electric battery. The invention further provides another method of producing an electrolyte.

BACKGROUND TO THE INVENTION

IT IS KNOWN to use lithium hexafluorophosphate ($LiPF_6$) as an electrolyte in lithium ion batteries.

Conventional preparation methods of $LiPF_6$ include wet chemical synthesis methods in aqueous reaction conditions and dry synthesis methods in non-aqueous conditions.

A common method of preparing $LiPF_6$ using a wet chemical preparation method involves synthesizing water stable organic complexes such as pyridinium or tetraacetonitrilolithium hexafluorophosphate, and converting the complexes into solvated $LiPF_6$. The pyridinium cation is preferred to the acetonitrile cation as the latter poorly dissolves the lithium base used in a subsequent reaction to substitute the organic cation. However, tetraacetonitrilolithium hexafluorophosphate complex produced by a reaction of LiF salt and PF_5 gas in the presence of acetonitrile allows low temperature decomposition of the complex in vacuum (20 °C) to produce high purity $LiPF_6$.

Various phosphorus halides and a solution of pyridinium poly (hydrogen fluoride) has been used to synthesize the pyridinium hexafluorophosphate complex, and further reacted the complex with alkali metal hydroxides to obtain their corresponding hexafluorophosphate complexes. Although several alkali-PF_6 salts are stable in sulphuric acid, $LiPF_6$ is very unstable and cannot be isolated due to the presence of water in the intermediate products. Reaction Equations 1.1 and 1.2 show the chemical reactions involved during the formation of the hexafluorophosphate complex:

$$PZX_3 + C_5H_5NH^+ F(HF)_n^- \longrightarrow C_5H_5NH^+PF_6^- + H_2Z + 3HX \qquad \text{(Eq. A)}$$

$$PX_5 + C_5H_5NH^+ F(HF)_n^- \longrightarrow C_5H_5NH^+ PF_6^- + 5HX \qquad \text{(Eq. B)}$$

where

Z is oxygen or sulphur; and
X is chlorine or bromine.

It is also known that hexafluorophosphate complexes of ammonia and alkali metals can be prepared by reacting ammonium or alkali metal fluorides with phosphorus pentachloride, however, the subsequent isolation process is tedious and time consuming as the yields are very low.

Another preparation method of $LiPF_6$ using wet chemical synthesis involves reacting hexafluorophosphoric acid with pyridine to form the complex, and then exchanging the pyridinium cation with a lithium cation from a hydroxide or alkoxide to obtain a $LiPF_6$ pyridine complex which can be treated further to produce high purity $LiPF_6$. This is illustrated in Equations 1.3 and 1.4:

$HPF_6 + C_5H_5N \longrightarrow C_5H_5NPF_6$ (Eq. C)

$C_5H_5NHPF_6 + LiOH + CH_3OH \longrightarrow LiPF_6.C_5H_5N$ (Eq. D)

The lithium base used in this method is dissolved in an alcohol media to avoid a subsequent reaction between the synthesized $LiPF_6$ and water. This method is based on the fact that alkali metal ions from corresponding hydroxides are easily exchanged with the pyridinium cation. The pyridinium hexafluorophosphate yield is approximately 70%, and a further 96% $LiPF_6$ crystalline product is obtained from a subsequent reaction of the complex with a lithium base and drying the product in a partial vacuum at 30 °C.

Hexafluorophosphoric acid may also be reacted with lithium hydroxide in water to form $LiPF_6$, however, the formed electrolyte quickly hydrolyzes and precipitate in the form of various other species such as $PO_2F_2^-$, PO_4^{3-}, and HPO_3F^-. Another disadvantage associated with this preparation method includes the use of hexafluorophosphoric acid which is a mixture of several weak acids resulting from gradual decomposition of the HPF_6 itself. Therefore, the amount of PF_6^- ion available to react is not always known. This requires that a preliminary titration be undertaken between the acid and an alkali hydroxide to determine the exact stoichiometry of the PF_6^- ion in the acid before neutralization with pyridine.

Other wet chemical synthesis methods involve the reactions of lithium sources and hexafluorophosphate salts in various solvents. The reaction of LiH with NH_4PF_6 in dimethoxyethane (DME) is one such an example as shown in Equation 1.5:

$$NH_4PF_{6(s)} + LiH_{(s)} \xrightarrow{DME} LiPF_{6(s)} + NH_{3(g)} + H_{2(g)} \qquad \text{(Eq. E)}$$

In this chemical process, an ether with at least two functionalities and enough spacing to complex a lithium ligand, for example, 1,2-dimethoxyethane is used to dissolve the ammonium hexafluorophosphate salt. The complex 2DME.$LiPF_6$, ammonia and hydrogen gas are formed as products. The complex is stable and is further dissolved in an electrolyte solvent for applications in batteries, however, the ether is difficult to remove and will feature in the final electrolyte.

To eliminate the ether interference, the reaction between a lithium source, for example LiH, and NH_4PF_6 can be carried out directly in a solvent to be used in the final electrolyte. At least one of the reactants must be soluble and the other should be insoluble in the solvent used so that excess salts can be easily removed *via* precipitation from the electrolyte. If a two solvent process is carried out, then the initial solvent used must be non-protic, have high solubility for the lithium compound used and possess a low boiling point. A more viscous, high boiling point solvent, such as ethylene carbonate (EC), can then be added as a co-solvent followed by the evaporation of the initial solvent.

Lithium hexafluorophosphate may also be synthesized using LiF and PCl_5 in water, however, low yields are obtained with this preparation method. To improve on the yield, a chloride salt such as LiCl or even LiF is dissolved in anhydrous HF, and then PCl_5 is slowly added to precipitate a lithium hexafluorophosphate salt with a higher yield.

A further method of preparing $LiPF_6$ involves using PCl_3 and HF in an anhydrous organic solvent of the type carbonic ethers and esters. The carbonates such as ethyl carbonate and other related solvents react and form adducts with PF_5 gas. Not only is the reaction of PF_5 and the solvent a challenge when this preparation method is used, but the introduction of HF is not desirable as it will further react and introduce additional complications.

In light of the above, the following shortcomings associated with using wet chemical synthesis methods for the preparation of $LiPF_6$ salt have been identified:

(i) The Li^+ ion is too small to precipitate with a relatively larger PF_6^- ion; hence obtaining $LiPF_6$ crystals directly from the solution is difficult.

(ii) The $LiPF_6$ salt itself is thermally unstable and will decompose during thermal treatment to remove the solvent used.

A widely used method for the synthesis of $LiPF_6$ using non-aqueous conditions involves a reaction between LiF and PF_5 gas to form $LiPF_6$. Various drawbacks are associated with this method, including the difficulty of handling poisonous PF_5 gas and low product purity (90-95%) compared to the required purity of at least 99.9% of $LiPF_6$ used in battery applications. Excess LiF and $LiHF_2$ are also formed as by-products in this preparation method.

This technique has been modified to improve the purity of the $LiPF_6$ product by reacting acetonitrile with the obtained $LiPF_6$ to form tetraacetonitrilolithium hexafluorophosphate, which, upon partial heating in vacuum, regenerates a purer $LiPF_6$ salt.

The $LiPF_6$ salt may also be synthesized by reacting lithium fluoride and bromine trifluoride in excess phosphorous pentoxide. Other methods for $LiPF_6$ synthesis involve in situ generation of PF_5 gas and its subsequent reaction with a lithium source to form the $LiPF_6$ salt. This technique is said to eliminate moisture ingress into the intermediates during the chemical reaction.

Solid state thermal reactions provide alternative dry synthesis methods to the gaseous routes for the preparation of $LiPF_6$. A lithium source, for an example, may be reacted with a phosphate such as ammonium phosphate at a high temperature (300 °C) in a solid state to form lithium metaphosphate, which is then further reacted with ammonium fluoride at 150 °C to obtain $LiPF_6$. This is shown in Equations 1.6 and 1.7 below:

$$(NH_4)_2HPO_4 + Li_2O \longrightarrow 2LiPO_3 + 4NH_3 + 3H_2O \qquad \text{(Eq. F)}$$

$$LiPO_3 + 6NH_4F \longrightarrow LiPF_6 + 6NH_3 + 3H_2O \qquad \text{(Eq. G)}$$

Solid state thermal reactions tend to be incomplete if powders are mixed as received and heated at elevated temperatures. This, therefore, presents a challenge to thoroughly grind the reactants together and press them into pellets to facilitate contact between them. Despite the high temperature and pressures needed to facilitate solid state reactions, these types of chemical reactions are still the preferred reaction methods for producing advanced, highly ordered crystal structures such as special ceramics, piezoelectrics and some scintillation crystals, hence the technique may be used to produce highly crystalline $LiPF_6$.

The quest for water free and pure $LiPF_6$ electrolyte salt has also prompted the use of fluorine gas at room temperature to make the salt. In contrast to using anhydrous hydrogen fluoride as a solvent during fluorination of LiF by PF_5 gas, the use of pure fluorine does not produce oxyfluorides of the form $LiPO_xF_y$ as impurities. These oxyfluorides are partially dissolved in HF and therefore remain as impurities in the final product.

It has been shown that $LiPF_6$ can be produced by reacting phosphorus with fluorine gas at a temperature of 23°C to generate PF_5 gas, which, is then reacted in situ with LiF to produce $LiPF_6$. The fluorine gas is first liquefied at -196 °C using liquid nitrogen, and then the temperature is increased stepwise to -80 °C, where the reaction commenced. The reaction is allowed to occur slowly until a temperature of 23 °C where the $LiPF_6$ production rate is high. The temperature is further elevated to 150 °C to obtain a purer product. This technique is time consuming, and the reaction is expected to be completed after 10 hr, which is expensive in terms of production time.

It is an object of the invention to at least alleviate the drawbacks mentioned above, and particularly to minimize and more preferably to avoid completely the formation of HF.

SUMMARY OF THE INVENTION

IN ACCORDANCE WITH A FIRST ASPECT OF THE INVENTION IS PROVIDED a method of producing lithium hexafluorophosphate ($LiPF_6$), the method including fluorinating lithium fluoride (LiF) by reacting it with a fluorination agent in a liquid medium that is non-reactive with, i.e. is inert to, the fluorination agent, thereby producing $LiPF_6$.

The reaction is therefore performed in the liquid medium.

The liquid medium may, in particular, be a perhalogenated organic compound.

In this specification *"perhalogenated"* means, as is conventionally understood in the art of the invention, a fully halogenated version of an organic compound, in that all of the hydrogen atoms of the organic compound have been substituted with halogen atoms, thus providing the perhalogenated organic compound. For example, if the organic compound is decalin ($C_{10}H_{18}$), the perhalogenated organic compound is perfluorodecalin ($C_{10}F_{18}$).

However, the above meaning of *"perhalogenated"* does not exclude

that the perhalogenated organic compound may be a virtually fully halogenated version of the organic compound, in which case the perhalogenated organic compound may still include some hydrogen atoms; and/or

that the perhalogenated organic compound is not a saturated organic compound, e.g. that it is an alkene or an alkyne, and the meaning afforded to "*perhalogenated*" in this specification is therefore broader in scope than the conventional meaning.

In any event, the extent of halogenation of the organic compound, as embodied in the perhalogenated organic compound when it provides the liquid medium, is preferably such that the perhalogenated organic compound is inert to the fluorination agent, i.e. is non-reactive with the fluorination agent, and is preferably a solvent for the fluorination agent.

The LiF may be in solid, e.g. granular, form.

The fluorination agent may, in particular, be phosphorous pentafluoride (PF_5). Thus, fluorinating the LiF may include reacting the LiF withPF_5.

The PF_5 may, in particular, be gaseous PF_5.

More particularly, reacting the LiF with gaseous PF_5 may include

providing the LiF in the liquid medium, e.g. by dispersing it in the liquid medium when the LiF is in solid form; and

dissolving PF_5 in the liquid medium containing the LiF.

It will be appreciated that reacting the LiF with gaseous PF_5 therefore does not necessarily include directly contacting the LiF with gaseous PF_5. Instead, reacting the LiF with gaseous PF_5 would include contacting the liquid medium that contains the LiF with gaseous PF_5.

Typically, the liquid medium would consist of the perhalogenated organic compound, or conceivably mixtures of two or more perhalogenated organic compounds.

As alluded to above, the perhalogenated organic compound is preferably inert to the PF_5. In other words, the perhalogenated organic compound may be non-reactive with the PF_5.

In one embodiment of the invention, the perhalogenated organic compound may be a perhalogenated alkane. For example, the perhalogenated alkane may be a cyclic or non-cyclic perfluorocarbon, preferably of the formula C_xF_y where x is an integer selected from 1 to 10 and y is an integer selected from 4 to 20, such as perfluorodecalin or perfluoroheptane or a non-cyclic perfluorocarbon selected from C_1F_4 and C_6F_{14} to C_9F_{20}.

In another embodiment of the invention, the perhalogenated organic compound may be a perfluoroalkene. For example, the perfluoroalkene may be a perfluoroaromatic compound such as hexafluorobenzene or a perfluoroaromatic compound selected from C_6F_6 to $C_{10}F_8$, or tetrafluoroethylene or a perfluoroalkene selected from C_3F_6 or C_4F_8.

It is envisaged that the perhalogenated organic compound may further be an ether, and particularly a perfluoroalkene ether. A typical generic formula may be R-O-R'.

When the LiF is in solid form and provided that the liquid medium is not a solvent for $LiPF_6$, the produced $LiPF_6$ would also typically be in solid form. Thus, the fluorination would convert the LiF in solid form into $LiPF_6$ in solid form.

Typically, the method may in such a case typically produce a mixture of $LiPF_6$ in solid form and unreacted LiF in solid form, in residual liquid medium. The method may then include recovering $LiPF_6$ in solid form and unreacted LiF in solid form from the residual liquid medium, e.g. by filtration.

When the produced $LiPF_6$ is in solid form, the method may include dissolving produced $LiPF_6$ in solid form in a solvent therefor, thus providing a solution of produced $LiPF_6$, typically after recovering $LiPF_6$ in solid form and unreacted LiF in solid form.

Providing the solution of produced $LiPF_6$ may therefore be particularly applicable when the method produces the mixture of $LiPF_6$ in solid form and unreacted LiF in solid form as hereinbefore described, to recover $LiPF_6$ from the mixture of $LiPF_6$ in solid form and unreacted LiF in solid form. Thus, the method may include treating the mixture of $LiPF_6$ in solid form and unreacted LiF in solid form with a solvent for $LiPF_6$ in solid form. It will be appreciated in this regard that the solvent for $LiPF_6$ in solid form would not be a solvent for LiF in solid form.

The solvent for $LiPF_6$ in solid form may be an electrolyte solvent, suitable for use in an electric battery. For example, the solvent may be selected from ethylene carbonate, propylene carbonate, dimethyl carbonate, dimethyl ether, and mixtures thereof.

Temperature conditions for the reaction would preferably be selected such that the perhalogenated organic compound would be in the liquid phase.

It is noted that the invention does not exclude the possibility that the liquid medium may be a solvent for $LiPF_6$, in the case of which the produced $LiPF_6$ would be in dissolved form in the liquid medium, and not in solid form as hereinbefore described. In such an embodiment, no subsequent dilution of produced $LiPF_6$ would be required and $LiPF_6$ in solution can then merely be separated from unreacted LiF through filtration, thus directly obtaining dissolved $LiPF_6$.

THE INVENTION EXTENDS, AS A SECOND ASPECT THEREOF, to $LiPF_6$ produced in accordance with the method of the invention as hereinbefore described, in solid form or in solution.

IN ACCORDANCE WITH A THIRD ASPECT OF THE INVENTION IS PROVIDED a method of producing an electrolyte, the method including

producing $LiPF_6$ in solid form, in accordance with the method of the first aspect of the invention; and

dissolving the $LiPF_6$ in solid form in a solvent therefor.

The solvent for $LiPF_6$ in solid form may be an electrolyte solvent, suitable for use in an electric battery. For example, the solvent may be selected from ethylene carbonate, propylene carbonate, dimethyl carbonate, dimethyl ether, and mixtures thereof.

THE INVENTION EXTENDS, AS A FOURTH ASPECT THEREOF, to an electrolyte produced in accordance with the method of the third aspect of the invention.

The electrolyte may be an electrolyte for an electric battery.

IN ACCORDANCE WITH A FIFTH ASPECT OF THE INVENTION IS PROVIDED an electric battery including an electrolyte produced using $LiPF_6$ produced in accordance with the method of the first aspect of the invention.

The electrolyte may be an electrolyte produced in accordance with the method of the third aspect of the invention.

IN ACCORDANCE WITH A SIXTH ASPECT OF THE INVENTION IS PROVIDED a method of manufacturing an electric battery, the method including

producing an electrolyte in accordance with the method of the third aspect of the invention; and

including the electrolyte in an electric battery.

IN ACCORDANCE WITH A SEVENTH ASPECT OF THE INVENTION IS PROVIDED a method of producing an electrolyte, the method including producing $LiPF_6$ dissolved in a liquid medium in accordance with the method of the first aspect of the invention, by performing the method of the first aspect of the invention in a liquid medium that is a solvent for $LiPF_6$.

EXAMPLES

EMBODIMENTS OF THE INVENTION will now be described by way of example only, with reference to the following examples.

Example 1: Reaction between LiF and PF_5 gas in the presence of a cyclic or polycyclic perfluorocarbon solvent

LiF in solid form is dispersed in liquid perfluorodecalin ($C_{10}F_{18}$), and PF_5 in gaseous form is dissolved in the $C_{10}F_{18}$ liquid.

The reaction that takes place is in accordance with reaction equation 1:

$$LiF(s) + PF_5\,(g) \longrightarrow LiPF_6\,(s) \qquad \text{(Eq. 1)}$$

The reaction temperature range is -10°C to 100 °C.

The reaction pressure range is 0 kPa to 1000 kPa.

Up to 99% recovery of $LiPF_6$ is achieved when produced $LiPF_6$ is dissolved in a solvent for $LiPF_6$ in solid form, which solvent comprises ethylene carbonate, propylene carbonate, dimethyl carbonate, dimethyl ether, or any combination thereof.

Example 2: A reaction between LiF and PF_5 gas in the presence of non-cyclic or branched perfluorocarbon solvent

LiF in solid form is dispersed in liquid perfluoroheptane or any non-cyclic perfluorocarbons of range C_1F_4, and C_6F_{14} to C_9F_{20} liquid.

The reaction that takes place is in accordance with reaction equation 1.

The reaction temperature range is -94 °C to 127 °C.

The reaction pressure range is 0 kPa to 1000 kPa.

Up to 99% recovery of $LiPF_6$ is achieved when produced $LiPF_6$ is dissolved in a solvent for $LiPF_6$ in solid form, which solvent comprises ethylene carbonate, propylene carbonate, dimethyl carbonate, dimethyl ether, or any combination thereof.

Example 3: A reaction between LiF and PF_5 gas in the presence of perfluoroaromatic solvent

LiF in solid form is dispersed in liquid hexafluorobenzene or a perfluoroaromatic liquid compound in the range C_6F_6 to $C_{10}F_8$.

The reaction that takes place is in accordance with reaction equation 1.

The reaction temperature range is 5°C to 100 °C.

The reaction pressure range is 0 kPa to 1000 kPa.

Up to 99% recovery of $LiPF_6$ is achieved when produced $LiPF_6$ is dissolved in a solvent for $LiPF_6$ in solid form, which solvent comprises ethylene carbonate, propylene carbonate, dimethyl carbonate, dimethyl ether, or any combination thereof.

Example 4: A reaction between LiF and PF_5 gas in the presence of fluoroalkene solvent.

LiF in solid form is dispersed in liquid tetrafluoroethylene solvent (C_2F_4) or a liquid fluoroalkene compound selected from C_3F_6 or C_4F_8.

The reaction that takes place is in accordance with reaction equation 1.

The reaction temperature range is -94°C to 100 °C.

The reaction pressure range is 0 kPa to 1000 kPa.

Up to 99% recovery of $LiPF_6$ is achieved when produced $LiPF_6$ is dissolved in a solvent for $LiPF_6$ in solid form, which solvent comprises ethylene carbonate, propylene carbonate, dimethyl carbonate, dimethyl ether, or any combination thereof.

DISCUSSION

THE METHOD OF THE FIRST ASPECT OF THE INVENTION uses an inert, non-corrosive, non-poisonous liquid medium for the reaction of LiF and PF_5 instead of corrosive HF which is the preferred liquid medium for this reaction in the art of the invention.

Thus the inventors have eliminated the need to remove the HF from the product through tiresome purification processes such as vacuum distillation.

Furthermore, HF is known to be corrosive and reactive inside a battery, which makes its avoidance for use as a liquid medium all the more desirable.

Some advantages associated with the liquid media exploited by the method of the invention are the following:

- it is inert in relation to PF_5 gas;
- it is inert in relation to the product $LiPF_6$;
- it is not poisonous;
- it dissolves the PF_5 gas, making it readily accessible to the lithium fluoride without mass transfer limitations;
- no azeotropic formation of PF_5 gas with the solvent is experienced, which tends to compete with lithium fluoride for PF_5 gas in traditional HF involved processes; and
- the liquid media are non-corrosive.

Thus, the inventors have provided an attractive, utile and sustainable alternative for the production of $LiPF_6$ which is particularly advantageous over prior art processes, some of which have been discussed herein.

CLAUSES

1. A method of producing lithium hexafluorophosphate ($LiPF_6$) in solid form, the method including fluorinating lithium fluoride (LiF) in solid form by reacting it with gaseous phosphorous pentafluoride (PF_5), wherein the reaction is performed in a liquid medium that comprises a perhalogenated organic compound that is inert to the PF_5 and is a solvent for the PF_5, thereby producing $LiPF_6$ in solid form.

2. The method according to clause 1, wherein reacting the LiF with gaseous PF_5 includes

dispersing the LiF in solid form in the liquid medium; and

dissolving gaseous PF_5 in the liquid medium containing the LiF in solid form.

3. The method according to any of clauses 1 to 2, wherein the perhalogenated organic compound is a perfluorocarbon.

4. The method according to clauses 3, wherein the perfluorocarbon is selected from cyclic and non-cyclic perfluoroalkanes, and cyclic and non-cyclic perfluoroalkenes.

5. The method according to any of clauses 1 to 4, wherein the perfluorocarbon is selected from perfluorodecalin, perfluoroheptane, hexafluorobenzene, and tetrafluoroethylene.

6. The method according to any of clauses 1 to 5, which includes dissolving produced $LiPF_6$ in solid form in a solvent for $LiPF_6$.

7. The method according to clause 6, wherein the solvent for $LiPF_6$ is selected from ethylene carbonate, propylene carbonate, dimethyl carbonate, dimethyl ether, and mixtures thereof.

CONCLUSIES

1. Een werkwijze voor de productie van lithiumhexafluorfosfaat ($LiPF_6$) in vaste vorm, waarbij de methode fluoridering van lithiumfluoride (LiF) in vaste vorm omvat door het te laten reageren met gasvormig fosforpentafluoride (PF_5), waarbij de reactie wordt uitgevoerd in een vloeibaar medium dat een geperhalogeneerde organische verbinding omvat die inert is voor de PF_5 en een oplosmiddel is voor de PF_5, waardoor $LiPF_6$ in vaste vorm wordt geproduceerd.

2. Werkwijze volgens conclusie 1, waarbij het laten reageren van de LiF met gasvormig PF_5 omvat

het verspreiden van de LiF in vaste vorm in het vloeibare medium; en

het oplossen van gasvormig PF_5 in het vloeibare medium dat het LiF in vaste vorm bevat.

3. Werkwijze volgens een van de conclusies 1 tot en met 2, met het kenmerk, dat de geperhalogeneerde organische verbinding een perfluorkoolstof is.

4. Werkwijze volgens conclusie 3, waarbij de perfluorkoolstof wordt gekozen uit cyclische en niet-cyclische perfluoralkanen, en cyclische en niet-cyclische perfluoralkenen.

5. Werkwijze volgens één van de conclusies 1 tot en met 4, waarbij de perfluorkoolstof wordt gekozen uit perfluordecaline, perfluorheptaan, hexafluorbenzeen en tetrafluorethyleen.

6. De werkwijze volgens één van de conclusies 1 tot en met 5, omvattende het oplossen van geproduceerd $LiPF_6$ in vaste vorm in een oplosmiddel voor $LiPF_6$.

7. De werkwijze volgens conclusie 6, waarbij het oplosmiddel voor $LiPF_6$ wordt gekozen uit ethyleencarbonaat, propyleencarbonaat, dimethylcarbonaat, dimethylether en mengsels daarvan.

ABSTRACT

A method of producing lithium hexafluorophosphate ($LiPF_6$) includes fluorinating lithium phosphate (LiF) by reacting it with a fluorination agent in a liquid medium that is non-reactive with, i.e. is inert to, the fluorination agent, thereby producing $LiPF_6$.

SAMENWERKINGSVERDRAG (PCT)

RAPPORT BETREFFENDE NIEUWHEIDSONDERZOEK VAN INTERNATIONAAL TYPE

IDENTIFICATIE VAN DE NATIONALE AANVRAGE	KENMERK VAN DE AANVRAGER OF VAN DE GEMACHTIGDE **H/2WV68/2**
Nederlands aanvraag nr. **2020683**	Indieningsdatum **29-03-2018**
	Ingeroepen voorrangsdatum
Aanvrager (Naam) **The South African Nuclear Energy Corporation SOC Limited**	
Datum van het verzoek voor een onderzoek van internationaal type **21-07-2018**	Door de Instantie voor Internationaal Onderzoek aan het verzoek voor een onderzoek van internationaal type toegekend nr. **SN71595**

I. CLASSIFICATIE VAN HET ONDERWERP (bij toepassing van verschillende classificaties, alle classificatiesymbolen opgeven)

Volgens de internationale classificatie (IPC)

C01D15/00

II. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte minimumdocumentatie

Classificatiesysteem	Classificatiesymbolen
IPC	**C01D**

Onderzochte andere documentatie dan de minimum documentatie, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

III. ☐ **GEEN ONDERZOEK MOGELIJK VOOR BEPAALDE CONCLUSIES** (opmerkingen op aanvullingsblad)

IV. ☐ **GEBREK AAN EENHEID VAN UITVINDING** (opmerkingen op aanvullingsblad)

Form PCT/ISA 201 A (11/2000)

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Nummer van het verzoek om een onderzoek naar de stand van de techniek
NL 2020683

A. CLASSIFICATIE VAN HET ONDERWERP
INV. C01D15/00
ADD.

Volgens de Internationale Classificatie van octrooien (IPC) of zowel volgens de nationale classificatie als volgens de IPC

B. ONDERZOCHTE GEBIEDEN VAN DE TECHNIEK

Onderzochte miminum documentatie (classificatie gevolgd door classificatiesymbolen)
C01D

Onderzochte andere documentatie dan de mimimum documentatie, voor dergelijke documenten, voor zover dergelijke documenten in de onderzochte gebieden zijn opgenomen

Tijdens het onderzoek geraadpleegde elektronische gegevensbestanden (naam van de gegevensbestanden en, waar uitvoerbaar, gebruikte trefwoorden)

EPO-Internal, WPI Data, CHEM ABS Data

C. VAN BELANG GEACHTE DOCUMENTEN

Categorie *	Geciteerde documenten, eventueel met aanduiding van speciaal van belang zijnde passages	Van belang voor conclusie nr.
Y	US 2016/090310 A1 (LINDER THOMAS [DE] ET AL) 31 maart 2016 (2016-03-31) * alineas [0013] - [0163] * * voorbeelden 1-6 * -----	1-7
Y	US 2014/205916 A1 (GARCIA-JUAN PLACIDO [DE] ET AL) 24 juli 2014 (2014-07-24) * alineas [0002] - [0064] * -----	1-7

☐ Verdere documenten worden vermeld in het vervolg van vak C.

☒ Leden van dezelfde octrooifamilie zijn vermeld in een bijlage

* Speciale categorieën van aangehaalde documenten

"A" niet tot de categorie X of Y behorende literatuur die de stand van de techniek beschrijft

"D" in de octrooiaanvrage vermeld

"E" eerdere octrooi(aanvrage), gepubliceerd op of na de indieningsdatum, waarin dezelfde uitvinding wordt beschreven

"L" om andere redenen vermelde literatuur

"O" niet-schriftelijke stand van de techniek

"P" tussen de voorrangsdatum en de indieningsdatum gepubliceerde literatuur

"T" na de indieningsdatum of de voorrangsdatum gepubliceerde literatuur die niet bezwarend is voor de octrooiaanvrage, maar wordt vermeld ter verheldering van de theorie of het principe dat ten grondslag ligt aan de uitvinding

"X" de conclusie wordt als niet nieuw of niet inventief beschouwd ten opzichte van deze literatuur

"Y" de conclusie wordt als niet inventief beschouwd ten opzichte van de combinatie van deze literatuur met andere geciteerde literatuur van dezelfde categorie, waarbij de combinatie voor de vakman voor de hand liggend wordt geacht

"&" lid van dezelfde octrooifamilie of overeenkomstige octrooipublicatie

Datum waarop het onderzoek naar de stand van de techniek van internationaal type werd voltooid

11 december 2018

Verzenddatum van het rapport van het onderzoek naar de stand van de techniek van internationaal type

Naam en adres van de instantie

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

De bevoegde ambtenaar

Marino, Emanuela

ONDERZOEKSRAPPORT BETREFFENDE HET RESULTAAT VAN HET ONDERZOEK NAAR DE STAND VAN DE TECHNIEK VAN HET INTERNATIONALE TYPE

Informatie over leden van dezelfde octrooifamilie

Nummer van het verzoek om een onderzoek naar de stand van de techniek

NL 2020683

In het rapport genoemd octrooigeschrift	Datum van publicatie	Overeenkomend(e) geschrift(en)	Datum van publicatie
US 2016090310 A1	31-03-2016	CN 105143106 A	09-12-2015
		EP 2789583 A1	15-10-2014
		EP 2984038 A2	17-02-2016
		US 2016090310 A1	31-03-2016
		WO 2014167055 A2	16-10-2014
US 2014205916 A1	24-07-2014	CN 103874657 A	18-06-2014
		EP 2744753 A1	25-06-2014
		JP 2014528890 A	30-10-2014
		KR 20140054228 A	08-05-2014
		US 2014205916 A1	24-07-2014
		WO 2013023902 A1	21-02-2013

WRITTEN OPINION

File No. SN71595	Filing date *(day/month/year)* 29.03.2018	Priority date *(day/month/year)*	Application No. NL2020683

International Patent Classification (IPC)
INV. C01D15/00

Applicant
The South African Nuclear Energy Corporation SOC Limited

This opinion contains indications relating to the following items:

☒ Box No. I Basis of the opinion
☐ Box No. II Priority
☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐ Box No. IV Lack of unity of invention
☒ Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐ Box No. VI Certain documents cited
☐ Box No. VII Certain defects in the application
☐ Box No. VIII Certain observations on the application

Examiner
Marino, Emanuela

Application number
NL2020683

WRITTEN OPINION

Box No. I Basis of this opinion

1. This opinion has been established on the basis of the latest set of claims filed before the start of the search.

2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the application and necessary to the claimed invention, this opinion has been established on the basis of:

   a. type of material:

   ☐ a sequence listing

   ☐ table(s) related to the sequence listing

   b. format of material:

   ☐ on paper

   ☐ in electronic form

   c. time of filing/furnishing:

   ☐ contained in the application as filed.

   ☐ filed together with the application in electronic form.

   ☐ furnished subsequently for the purposes of search.

3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.

4. Additional comments:

Box No. V Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty	Yes:	Claims	1-7
	No:	Claims	
Inventive step	Yes:	Claims	
	No:	Claims	1-7
Industrial applicability	Yes:	Claims	1-7
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1 US 2016/090310 A1 (LINDER THOMAS [DE] ET AL) 31 maart 2016 (2016-03-31)

D2 US 2014/205916 A1 (GARCIA-JUAN PLACIDO [DE] ET AL) 24 juli 2014 (2014-07-24)

1 Inventive step

The present application does not meet the criteria of patentability, because the subject-matter of claims 1-7 does not involve an inventive step.

1.1 D1 is regarded as being the prior art closest to the subject-matter of claim 1, and discloses a method of producing lithium hexafluorophosphate ($LiPF_6$) in solid form, the method including fluorinating lithium fluoride (LiF) in solid form by reacting it with gaseous phosphorous pentafluoride (PF_5), wherein the reaction is performed in a liquid medium that comprises a nitrile (par. [0013] - [0163]; ex. 1-6).

1.2 The subject-matter of claim 1 therefore differs from this known method in that the reaction is performed in a liquid medium that comprises a perhalogenated organic compound and is therefore new.

1.3 The problem to be solved by the present invention may therefore be regarded as an alternative method for producing lithium hexafluorophosphate.

1.4 D2 discloses a method of producing lithium hexafluorophosphate in solid form starting from LiF and POF_3 by using a fluorinated solvent such as tetrafluoroethylene carbonate (par. [0037]).

1.5 The feature of chosing a fluorinated solvent in which the reaction can be performed is merely one of several straightforward possibilities from which the skilled person would select, in accordance with circumstances, without the exercise of inventive skill, in order to solve the problem posed.

1.6 The solution proposed in claim 1 of the present application can therefore not be considered as involving an inventive step.

1.7 Dependent claims 2-7 do not appear to contain any additional features which, in combination with the features of any claim to which they refer, meet the requirements of inventive step, the reasons being as follows:

1.8 D1 also discloses that afterwards the produced $LiPF_6$ is dissolved in a solvent for $LiPF_6$ such as ethylene carbonate. LiF and PF_5 are reacted by dispersing the LiF in solid form in the liquid medium followed by dissolving the gaseous PF_5 in the liquid medium containing the LiF in solid form (par. [0013] - [0163]; ex. 1-6). The additional technical features of claims 2,6,7 are therefore already known from D1.

1.9 D2 discloses a method of producing lithium hexafluorophosphate in solid form starting from LiF and POF_3 by using a fluorinated solvent such as tetrafluoroethylene carbonate (par. [0037]). The additional technical features of claims 3-5 are therefore already known from D2.