

TITLE OF THE INVENTION

**A PROCESS FOR PREPARING HIGH-PURITY ALKALI METAL
HEXAFLUOROPHOSPHATE AND THE ALKALI METAL
HEXAFLUOROPHOSPHATE PREPARED THEREFROM**

5

FIELD OF THE INVENTION

[001] The present disclosure relates to a process for preparing alkali metal hexafluorophosphate. More particularly, the present invention relates to a process for preparing high purity alkali
10 hexafluorophosphate based on Group 1 elements, preferably selected from Sodium Hexafluorophosphate (NaPF_6), Potassium Hexafluorophosphate (KPF_6) and Cesium Hexafluorophosphate (CsPF_6). The alkali hexafluorophosphates are useful as an electrolyte in batteries for stationary storage batteries, low-speed electric vehicles.

15 **BACKGROUND OF THE INVENTION**

[002] Lithium-ion batteries (LIBs) have found application in various sectors over the years, since its commercialization in 1991. Starting from its usage in portable electronics, currently its requirement is majorly shifting towards Electric Vehicles (EV) & Energy Storage Systems (ESS)
20 applications. This leads to the unprecedented demand for the core raw material of LIB, that is "Lithium". Globally the demand of lithium by 2030 would be 2.5 million tons as per Statista report while the demand of the same in 2021 was 0.5 million tons. But the challenge is Lithium is less abundant in earth's crust, which creates a serious threat of its availability in future. So, the need of hours is to find the right alternative to the lithium-ion batteries. Here, the Sodium-ion
25 batteries come into play.

[003] Sodium and potassium fall under the same group of lithium in periodic table and reflect the similar characteristics of the lithium. Accordingly, electrolytes based on sodium and potassium are of interest.

30

[004] Sodium is the sixth most abundant element in the earth's crust and so there is no threat to its availability. Although the sodium-ion batteries (NIBs) have their limitations in adapting it for high-speed EVs as of now, it perfectly suits for the Energy Storage System (ESS) & low-speed vehicles applications. With the continuous R&D activity on sodium-ion batteries (NIBs) in the
35 foreseeable future, it is expected that sodium-ion batteries would find its usage in the high-speed

EVs too in the future. In that way, Sodium-ion batteries will become a potential alternative for the lithium-ion batteries in future.

[005] Similarly, potassium-ion batteries (KIBs) are emerging as a promising energy storage system due to the abundance of potassium. The potassium-ion has certain advantages over similar lithium-ion (e.g., lithium-ion batteries): the cell design is simple, and both the material and the fabrication procedures are cheaper. The key advantage is the abundance and low cost of potassium in comparison with lithium, which makes potassium batteries a promising candidate for large scale batteries such as household energy storage and electric vehicles.

[006] Though NaClO_4 is the most studied electrolyte salt in Sodium-ion batteries (NIBs) and KClO_4 in Potassium-ion batteries (KIBs), the strong oxidizing nature of perchlorate anion prohibits commercial use. Analogous to Lithium hexafluorophosphate (LiPF_6): Sodium hexafluorophosphate (NaPF_6), Potassium hexafluorophosphate (KPF_6) or Cesium hexafluorophosphate (CsPF_6) are electrolyte salts for sodium-ion, potassium-ion or cesium-ion batteries, respectively. Accordingly, they can undertake the mature battery technology that has been commercialized for example by Li-Battery salt with good solubility and ionic conductivity in battery solvents like ethylene carbonate, propylene carbonate, dimethyl carbonate, etc. and mixtures thereof.

[007] For long term cycle life of batteries, it is necessary that the electrolyte salts are extremely pure.

[008] In the conventional preparation of NaPF_6 , the PF_5 gas is passed through a solution of NaF in HF , to form NaPF_6 . Thereafter, HF is removed and the NaPF_6 is crystallized. However, one of the drawbacks of the conventional approach is that large amounts of impurity, in the form of Fluorinated solids sink down with NaPF_6 crystals and get mixed together. Further, it is very difficult to decrease the amount of impurities such as fluorinated solids in NaPF_6 without resorting to complex reactions, procedures and additional purification steps.

[009] Similarly, for the preparation of KPF_6 , the PF_5 gas is passed through a solution of KF in HF , to form KPF_6 . Thereafter, HF is removed and the KPF_6 is crystallized. However, one of the drawbacks of the conventional approach is that large amounts of impurity, in the form of Fluorinated solids sink down with KPF_6 crystals and get mixed together. Further, it is very difficult to decrease the amount of impurities such as Fluorinated solids in KPF_6 without resorting to

complex reactions, procedures and additional purification steps.

[010] Impurities in the form of fluorinated solids causes erosion of the electrodes, which directly affects the capacity and performance of the batteries.

5

[011] Further, the presence of various metallic impurities such as transition metal impurities is detrimental to battery performance. For example, the transition metal ions dissolved in the electrolytes might deposit on the anode surface. This might cause decomposition of NaPF_6 and KPF_6 , sodium and potassium dendrite growth from the surface of the negative electrode and cause internal short circuit.

10

[012] Water is yet another impurity of concern in Sodium-ion batteries and Potassium-ion batteries. The presence of water negatively affects the battery performance. The presence of excess water will also make the electrolyte acidify faster to generate HF gas, which is also one of the main reasons for battery flatulence, which reduces battery life.

15

[013] Water can react with the NaPF_6 and KPF_6 , thereby reducing the capacity of the battery. The presence of water is also implicated in poor cycling performance and loss of active materials. Water can destroy the protective solid electrolyte interface layer and get reduced at the anode to yield H_2 gas. The presence of H_2 gas increases the internal pressure of the batteries and is an explosion hazard.

20

[014] Further, the conventional preparation method further suffer from drawbacks which do not allow the method to be carried out on a large scale such as back pressurization, choking problem and maintaining and controlling pressure for optimized purity.

25

[015] Accordingly, there is a need to develop a process of preparing high purity alkali hexafluorophosphates, preferably selected from NaPF_6 , KPF_6 or CsPF_6 with reduced impurities which addresses one or more of the above-mentioned shortcomings.

30

SUMMARY OF THE INVENTION

[016] In one aspect, the present invention provides process of preparing an ultra-high purity alkali metal hexafluorophosphate (MPF_6), comprising following steps: (a) charging alkali metal fluoride

(MF) in a first reactor 'B' and flushing nitrogen gas through the same, (b) cooling the first reactor 'B' to a predetermined temperature, followed by charging anhydrous hydrogen fluoride (AHF) gas and stirring the mixture comprising alkali metal fluoride (MF) dissolved in AHF in the first reactor 'B', (c) cooling the mixture comprising alkali metal fluoride (MF) dissolved in AHF in the first reactor 'B' to a predetermined temperature, (d) charging phosphorous pentachloride (PCl₅) in a second reactor 'A' and adding AHF in lots, to produce high purity phosphorous pentafluoride (PF₅) and hydrogen chloride (HCl) gas, (e) reacting alkali metal fluoride (MF) dissolved in AHF in the first reactor 'B' with phosphorus pentafluoride (PF₅) and hydrogen chloride (HCl) gas mixture obtained in step (d) to obtain alkali metal hexafluorophosphate mother liquor dissolved in AHF under PF₅ gas blanketing, (f) cooling the first reactor 'B' to a predetermined temperature and maintaining the temperature of alkali metal hexafluorophosphate mother liquor dissolved in AHF for predetermined time, followed by filtration and drying at predetermined temperature to achieve alkali metal hexafluorophosphate (MPF₆).

[017] In another aspect, the present invention provides an ultra-high purity alkali metal hexafluorophosphate with an improved yield of at least 99.50 %, preferably at least 99.8%.

BRIEF DESCRIPTION OF THE DRAWINGS

[018] Reference will be made to embodiments of the invention, examples of which may be illustrated in accompanying figures. These figures are intended to be illustrative, not limiting. Although the invention is generally described in the context of these embodiments, it should be understood that it is not intended to limit the scope of the invention to these particular embodiments.

Figure 1 shows the process flow diagram.

DETAILED DESCRIPTION OF THE INVENTION

[019] It is to be noted that, as used in the specification, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a composition containing "a compound" includes a mixture of two or more compounds. It should also be noted that the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

[020] The expression of various quantities in terms of "%" or "% w/w" means the percentage by weight of the total solution or composition unless otherwise specified.

[021] The present invention is directed towards a process of preparing ultra-high purity alkali metal hexafluorophosphate (MPF₆) useful as an electrolyte in high strength batteries, preferably as an electrolyte in batteries for storage application.

5

[022] In one of the embodiments the process of preparing ultra-high purity alkali metal hexafluorophosphate MPF₆ (preferably M = Na, K or Cs) comprises the following steps:

- a. charging alkali metal fluoride (MF) in a first reactor 'B' and flushing nitrogen gas through the same,
- 10 b. cooling the first reactor 'B' to a predetermined temperature, followed by charging anhydrous hydrogen fluoride (AHF) gas and stirring the mixture comprising alkali metal fluoride (MF) dissolved in AHF in the first reactor 'B',
- c. cooling the mixture comprising alkali metal fluoride (MF) dissolved in AHF in the first reactor 'B' to a predetermined temperature,
- 15 d. charging phosphorous pentachloride (PCl₅) in a second reactor 'A' and adding AHF in lots, to produce high purity phosphorous pentafluoride (PF₅) and hydrogen chloride (HCl) gas,
- e. reacting alkali metal fluoride (MF) dissolved in AHF in the first reactor 'B' with phosphorus pentafluoride (PF₅) and hydrogen chloride (HCl) gas mixture obtained in step
- 20 (d) to obtain alkali metal hexafluorophosphate mother liquor dissolved in AHF under PF₅ gas blanketing,
- f. cooling the first reactor 'B' to a predetermined temperature and maintaining the temperature of alkali metal hexafluorophosphate mother liquor dissolved in AHF for predetermined time, followed by filtration and drying at predetermined temperature to
- 25 achieve alkali metal hexafluorophosphate (MPF₆),
- g. crushing the dried crystals of MPF₆ and optionally sieving to obtain MPF₆ powder.

[023] Whenever PF₅ gas is purged into the solution of MF/AHF, generally dip pipe gets choked, and the reaction mass gets back pressurized, which results in loss. Accordingly, the process

30 reaction is carried out under PF₅ gas blanketing and allowing back pressurization and choking problem to be completely resolved with the process of the present invention.

[024] Further, according to the disclosed process, the pressure of the reaction mass can be controlled as per the requirement. Over pressurization is controlled by slow, and lot-wise addition

35 of AHF to PCl₅ containing reactor. The generated HCl and PF₅ gas is blanketed in MF/HF reactor.

Hence, pressure can be controlled by releasing excess gases into the scrubber having basic pH and the pressure can be maintained and controlled more effectively in scrubber, so that the flow of acidic fumes becomes unidirectional.

5 [025] In an embodiment, the alkali metal is selected from Na, K and Cs and the alkali metal hexafluorophosphate is selected from NaPF_6 , KPF_6 or CsPF_6 .

[026] In an embodiment, the alkali metal fluoride is obtained from respective metal carbonate and hydrogen fluoride (HF). For example, sodium fluoride (NaF) and Potassium fluoride (KF)
10 used in the process is obtained from sodium carbonate (Na_2CO_3) or potassium carbonate (K_2CO_3) respectively and hydrogen fluoride (HF).

[027] In an embodiment of the present invention, the anhydrous hydrogen fluoride (AHF) gas is a purified anhydrous hydrogen fluoride (AHF) gas comprises cationic (metal) impurities less than
15 or equal to 1 ppm or anionic impurities less than or equal to 1 ppm or moisture less than or equal to 1 ppm or combination thereof.

[028] In yet another embodiment, the purified anhydrous hydrogen fluoride (AHF) gas reacts with PCl_5 solid bed reactor with agitation.
20

[029] In yet another embodiment, the anhydrous hydrogen fluoride (AHF) gas is purified by treatment with fluorine (F_2) gas as an oxidizing agent.

[030] In an embodiment of the process, the PF_5 and HCl gas from the second reactor 'A' was
25 dosed to the first reactor 'B' through vent system without any dip-tube till constant pressure.

[031] In an embodiment of the process, the predetermined temperature in step (b) and (c) is in the range of 0 to 15 °C, preferably in the range of 5 to 10 °C

30 [032] In an embodiment of the process, the AHF is added in multiple lots preferably in the range of 200 to 300 g or 100 to 200 g at 25 to 40°C.

[033] In an embodiment of the process, the predetermined temperature and predetermined time for cooling in step (f) is in the range of -10 to -25°C for 5 to 7 hours.

35

[034] In an embodiment of the process, the predetermined temperature and predetermined time for cooling in step (f) is in the range of -15 to -20°C for 6 hours.

[035] In an embodiment of the process, the predetermined temperature for drying in step (f) is in the range of 35 to 50 °C, preferably between 38 to 40 °C.

[036] In a preferred embodiment, the process involves the use of static crystallizer which takes a single turn in about 48 hours so as to allow the crystals to grow slowly to a large size and minimize surface area for HF adsorption.

10

[037] In another preferred embodiment, the mother liquor is re-used by adding alkali fluoride (preferably selected from NaF or KF or CsF) at -15 to 15 °C, preferably at 10 °C.

[038] In a preferred embodiment, the drying of the crystallized alkali metal hexafluorophosphate is done by hot water circulation in the dryer jacket, followed by passing dry N₂ to dry crystal for about 6-7 hours.

15

[039] In yet another embodiment, the drying of crystallized alkali metal hexafluorophosphate followed by solvent assisted drying preferably with solvents such as ether or dichloromethane.

20

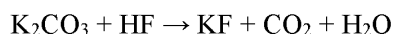
[040] Another aspect of the process is to use a mesh size so as to have lower HF adsorbed crystals of larger size sifted out as the final product. The smaller crystals with higher adsorbed HF are re-circulated through the mother liquor. This reduces the total concentration of HF in the finished product, and the recovery of alkali metal hexafluorophosphate crystals for the next crystallization procedure of the crystal seed and also reduces production costs.

25

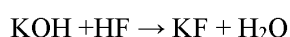
[041] In a preferred embodiment, sieving of dried crystals of alkali metal hexafluorophosphate is done through mesh size of less than or equal to 90.

[042] In another embodiment, the alkali metal fluorides (sodium fluoride, Potassium fluoride or Cesium fluoride) used in the process is obtained from the steps of dissolving alkali metal carbonate (preferably selected from sodium carbonate or potassium carbonate or Cesium Carbonate) in water to obtain alkali metal carbonate solution, reacting the alkali metal carbonate solution with ultra-pure hydrogen fluoride to obtain alkali metal fluorides such as sodium fluoride or potassium fluoride or cesium fluoride,

30
35



[043] In another embodiment, the alkali metal fluorides (sodium fluoride, Potassium fluoride or Cesium fluoride) used in the process is obtained from the steps of dissolving treated pure alkali metal hydroxide in ultra-pure water to obtain alkali metal hydroxide solution, or lye solution (caustic lye and caustic potash solution); reacting the alkali metal hydroxide solution / caustic lye/caustic potash with ultra-pure hydrogen fluoride to obtain alkali metal fluoride (sodium fluoride or potassium fluoride or cesium fluoride),



Followed by drying and crushing the obtained desired particle size range alkali metal fluoride (NaF or KF or CsF).

15

[044] In another embodiment, the exhaust from the reactor comprising PF_5 , HCl , oxides of phosphorus and HF is re-guided into the mother liquor for the second stage reabsorption process, which improves the overall efficiency of the process.

20 [045] In another embodiment, the gaseous exhaust from the mother liquor tank comprising HCl and HF is re-guided to a recovery system, which improves the overall efficiency of HF recovery.

[046] Another aspect of the present invention relates to an ultra-high purity alkali metal hexafluorophosphate selected from NaPF_6 , KPF_6 and CsPF_6 with a purity of at least 98.50%, preferably at least 99.8%.

25

[047] In a preferred embodiment of the present invention the ultra-high purity alkali metal hexafluorophosphate (preferably selected from NaPF_6 , KPF_6 or CsPF_6) comprises:

- 30
- insoluble material in an amount less than or equal to 200 ppm, or
 - metallic impurities – each of which is present in an amount less than or equal to 2 ppm, or
 - hydrogen fluoride (HF) in an amount less than or equal to 70 ppm, or
 - sulfate ions (SO_4^{2-}) in an amount less than or equal to 10 ppm, or
 - nitrate ions (NO_3^-) in an amount less than or equal to 5 ppm, or
 - 35 - chloride ions (Cl^-) in an amount less than or equal to 5 ppm, or

- water/moisture in an amount less than or equal to 10 ppm, or combination thereof.

[048] In a preferred embodiment of the present invention the ultra-high purity alkali metal hexafluorophosphate (preferably selected from NaPF_6 , KPF_6 or CsPF_6) comprises metallic
5 impurities as follows:

$\text{Na} \leq 2 \text{ ppm}$

$\text{K} \leq 2 \text{ ppm}$

$\text{Fe} \leq 2 \text{ ppm}$

$\text{Zn} \leq 2 \text{ ppm}$

10 $\text{Ni} \leq 2 \text{ ppm}$

$\text{Mg} \leq 2 \text{ ppm}$

$\text{Ca} \leq 2 \text{ ppm}$

$\text{Pb} \leq 2 \text{ ppm}$

$\text{Cr} \leq 2 \text{ ppm}$

15 [049] According to the process of the present invention, the high purity Phosphorus pentachloride (PCl_5) is obtained from commercial sources. The gaseous high purity anhydrous hydrogen fluoride (AHF) reacts with the solid phosphorus pentachloride (PCl_5) to produce phosphorus pentafluoride (PF_5) and hydrogen chloride (HCl).

20 [050] Impurities in alkali hexafluorophosphates are a direct consequence of the impurities present in the main raw materials, i.e., AHF and NaF or KF. Hence, as discussed below, the AHF and NaF or KF or CsF used in the present invention are purified to minimize moisture, insoluble and metallic impurities. In other words, only high purity battery grade AHF and NaF or KF or CsF are used in the present invention.

25

[051] Usually, PCl_5 is dissolved in AHF to prepare PF_5 . This results in impurities such as AsF_5 , BF_4 etc. However, in the present invention, gaseous AHF reacts with solid PCl_5 in a packed bed reactor. In addition to arsenic and boron-generated gas mixed into PF_5 , most of the impurities brought into PCl_5 react with PF_5 to form fluoride with high boiling point precipitation in the reactor
30 and remain at the bottom in solid form. Thereafter, the resulting PF_5 is passed through a filter to remove any PCl_5 grains that might be adrift in the gas stream, to obtain a high purity PF_5 gas. Accordingly, the process by virtue of being carried out in a packed bed reactor with high purity gaseous AHF eliminates or minimizes impurities and water in the PF_5 gas.

35 [052] PF_5 produced in step (d) enters the first reactor 'B' wherein it reacts with the NaF or KF is

dissolved or suspended in AHF. This results in the formation of NaPF_6 or KPF_6 or CsPF_6 dissolved in AHF, also called as a mother liquor. Preferably, step (d) is carried out at a temperature in the range of -15 to 15°C , more preferably at 10°C .

5 [053] The exhaust from the second reactor 'A' comprising PF_5 , HCl , oxides of phosphorus and HF is re-guided into the mother liquor for the second stage re-absorption process, which improves the overall efficiency of the reaction, particularly, by improving the recovery efficiency of PF_5 . After every 1 hr, the excess pressure due to HCl gas was scrubbed into scrubber having basic pH. After complete consumption of the HF and PCl_5 (recognized by non-generation of PF_5 gas
10 pressure) the reactor was cooled to -15 to -20°C .

[054] In an embodiment of the process, crystallization is carried out from the mother liquor preferably in a static crystallization tank, wherein the mother liquor is cooled. The mother liquor is cooled over an extended period.

15

[055] The static crystallizer used in the present invention takes a single turn in 48 hours. The alkali metal hexafluorophosphate crystals are allowed to grow slowly to a large size. Larger size of the crystals of NaPF_6 or KPF_6 or CsPF_6 translates into lesser surface area for HF to get adsorbed onto, resulting in NaPF_6 or KPF_6 or CsPF_6 with minimum HF content. The crystals are separated
20 by passing through mesh sieves. The separated larger crystals of NaPF_6 or KPF_6 or CsPF_6 are crushed and dried to obtain high purity powdered NaPF_6 or KPF_6 at temperatures of $60 - 70^\circ\text{C}$, under vacuum for about 6 hours to drive out maximum HF.

[056] The smaller crystals of NaPF_6 or KPF_6 or CsPF_6 are re-used by adding a certain amount of Sodium fluoride (NaF) or Potassium fluoride (KF) or Cesium fluoride (CsF) respectively into the
25 mother liquor at -15 to 5°C , preferably at -10°C and the process repeated to get larger sized crystals.

[057] If a regular rotating crystallizer is used instead of the static crystallizer, it will give rise to
30 smaller crystals with HF content in the range $150-300$ ppm. If higher temperatures are used for drying, there is decomposition and generation of HF from the NaPF_6 or KPF_6 or CsPF_6 crystals.

[058] Discussed below are some representative embodiments of the present invention.

35 [059] The invention in its broader aspects is not limited to the specific details and representative

processes. An illustrative example is described in this section in connection with the embodiments and processes provided.

[060] Figure 1 illustrates the process flow diagram for preparing NaPF_6 according to an embodiment of the present disclosure. According to the process HF solution (101) is passed through a vaporizer (V1) to convert HF into a gaseous state (102). The HF gaseous state (102) obtained from vaporizer (V1) is reacted with PCl_5 powder (103) in first reactor (R1) to obtain intermediate products PF_5 , HCl (g) and unreacted trace HF (105).

[061] The intermediate products (105) are passed through a filter (F1) and sent to a second reactor (R2) to obtain a product solution (106) comprising NaPF_6 and HF solution which is passed onto a hold-up tank (V2). The product solution (106) from the hold-up tank (V2) is passed onto the crystallizer (V3) wherein the product NaPF_6 (107) is recovered, and mother-liquid (108) is separated. The product (107) is passed through sieves (S1) to obtain the desired size product NaPF_6 and the remaining is recycled to the mother-liquid tank (V4). The mother-liquid (108) comprising NaF and HF solution is sent to a mother liquid tank (V4) wherein HF solution and NaF (104) are further added, and the treated mother-liquid (109) is recycled to the second reactor (R2) to obtain a product solution (106) comprising NaPF_6 and HF solution. The vent gases (111) from the mother-liquid tank (V4) are sent to a recovery system (S2) to reuse and recycle HF gases (101) and the unrecovered vent gases (110) are sent to 3-stage scrubber (S3) for disposal.

[062] Impurities in NaPF_6 are a direct consequence of the impurities present in the main raw materials, i.e., AHF and NaF. Hence, as discussed below, the AHF and NaF used in the present invention are purified to minimize moisture, insoluble and metallic impurities. In other words, only high purity AHF and NaF are used in the present invention.

[063] In commercial HF, metals such as Fe, Ca, Mg react with active PF_5 in synthesis reaction vessel to form FeF_3 , CaF_2 , MgF_2 which increases the impurities in $\text{NaPF}_6/\text{KPF}_6$ crystal. Accordingly, the AHF used in the present invention is purified prior to using it in the process of the present invention.

[064] Commercial AHF is purified by treatment with fluorine (F_2) as an oxidizing agent to fluorinate AHF impurities to remove most metals including Arsenic and boron compounds as gaseous impurities. If AHF is not purified by reacting with F_2 , gaseous impurities such as metallic fluorides, AsF_5 and BF_4 might contaminate the mother liquor. Use of purified AHF in the present

invention, further minimizes impurities in the NaPF₆/KPF₆ crystals of the present invention.

[065] Preparation of high purity AHF: Pure Fluorine gas is purged into commercial AHF at a pressure of 3 kg / cm² for 3 min at temperature of 25°C in a reaction vessel. After the impurities are precipitated as fluorides, the pure AHF is transferred to distillation column from the reaction vessel. The impurity levels of commercial vs purified AHF are provided below:

Impurity level: Commercial AHF vs. Purified AHF

Impurity	Commercial AHF	Purified AHF
Moisture	≤ 250 ppm	≤ 1 ppm
Fe	≤ 3 ppm	≤ 0.1 ppm
Ca	≤ 3 ppm	≤ 0.1 ppm
K	≤ 3 ppm	≤ 0.1 ppm
Na	≤ 3 ppm	≤ 0.1 ppm
Ni	≤ 3 ppm	≤ 0.1 ppm
Pb	≤ 3 ppm	≤ 0.1 ppm
Zn	≤ 3 ppm	≤ 0.1 ppm
Cr	≤ 3 ppm	≤ 0.1 ppm
Cu	≤ 3 ppm	≤ 0.1 ppm
Mg	≤ 3 ppm	≤ 0.1 ppm
Al	≤ 3 ppm	≤ 0.1 ppm
As	≤ 3 ppm	≤ 0.1 ppm
B	≤ 3 ppm	≤ 0.1 ppm
H ₂ SiF ₆	≤ 250 ppm	≤ 10 ppm
H ₂ SO ₄	≤ 150 ppm	≤ 3 ppm

10

[066] Insoluble impurities such as silicates, fluorosilicates and sulphates of metals, such as Fe, Ca, K, Na, Ni, Pb, Zn, Cr, Mg, Cu, and Al are present in NaF. Some metals do not dissolve in AHF and remain as solid particles. Some react with AHF to form fluoride material, for example, FeF₃, NaF, CaF₂, MgF₂. The fluoride material, in these cases, precipitates as a solid at the bottom of the crystallizer and stays with NaPF₆ crystals. This is the main cause of impurities in NaPF₆. These insoluble impurities end up in the NaPF₆ thereby increasing the combined levels of Ca, Mg, Na, K, etc above 100 ppm. Accordingly, in order to produce high purity NaPF₆, the NaF used in the process must be free of said metallic impurities.

15

[067] Preparation of high purity NaF: Commercial Na_2CO_3 is mixed with pure deionized water to prepare a solution. The insoluble impurities are filtered off by passing the Na_2CO_3 solution through two series of cartridge filters. The soluble impurities are then removed by passing the
5 Na_2CO_3 solution through cation and anion exchange resin columns.

[068] The purified Na_2CO_3 solution is then reacted with 50% HF to neutralization yielding NaF. The NaF so formed, is filtered and dried by evaporating water at 130 °C.

10 [069] The purified NaF has metallic impurities below 2 ppm each, and the anionic impurities such as chlorides and sulphates below 5 ppm each.

[070] Alternatively, purified sodium hydroxide (NaOH) or caustic lye may be used instead of sodium carbonate (Na_2CO_3).
15

[001] Preparation of NaPF_6 – The high purity AHF produced as above, is added to solid PCl_5 and the mixture of $\text{PF}_5 + \text{HCl} + \text{HF}$ generated from this reaction is fed into a solution of NaF + AHF to produce NaPF_6 in AHF solvent. NaPF_6 is crystallized from this solution, filtered and dried to get the pure product.
20

[002] The impurity levels of ultra-high purity NaPF_6 according to the present process are provided below:

Impurity level of Ultra-high purity NaPF_6 :

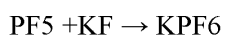
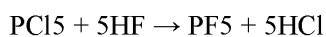
25 $\text{Fe} \leq 2 \text{ ppm}$
 $\text{Ca} \leq 2 \text{ ppm}$
 $\text{K} \leq 2 \text{ ppm}$
 $\text{Na} \leq 2 \text{ ppm}$
 $\text{Ni} \leq 2 \text{ ppm}$
30 $\text{Pb} \leq 2 \text{ ppm}$
 $\text{Zn} \leq 2 \text{ ppm}$
 $\text{Cr} \leq 2 \text{ ppm}$
 $\text{Cu} \leq 2 \text{ ppm}$
 $\text{Mg} \leq 2 \text{ ppm}$
35

[003] The NaPF₆ obtained by the process described hereinabove comprises insoluble material in an amount less than or equal to 200 ppm, and/or comprises metallic impurities – each of which is present in an amount less than or equal to 1 ppm, and/or comprises HF in an amount less than or equal to 70 ppm, and/or comprises SO₄²⁻ in an amount less than or equal to 10 ppm, and/or
5 comprises NO₃⁻ in an amount less than or equal to 5 ppm, and/or comprises Cl⁻ in an amount less than or equal to 5 ppm and/or comprises water in an amount less than or equal to 10 ppm or combination thereof.

[004] The purity of NaPF₆ obtained by the process of the present invention is at least 99.5%,
10 preferably at least 99.8%.

[005] In the absence of the AHF purification process, preparation of high purity NaF and the crystallization and drying steps, the metallic impurities get carried over and become a part of the final product i.e., NaPF₆. The NaPF₆ impurity profile then has a total metallic impurity of 30 – 80
15 ppm instead of less than or equal to 1 ppm.

[006] Along similar lines, Potassium hexafluorophosphate (KPF₆) may be prepared by using Potassium fluoride (KF) and Phosphorus pentafluoride (PF₅). Eventually, potassium fluoride (KF) is prepared using potassium carbonate (K₂CO₃) or potassium hydroxide (KOH).
20



[007] Similarly, Cesium hexafluorophosphate (CsPF₆) may be prepared by using Cesium fluoride (CsF) and Phosphorus pentafluoride (PF₅). Eventually, Caesium fluoride (CsF) is prepared using Cesium carbonate (Cs₂CO₃) or Cesium hydroxide (CsOH).
25

[008] Also, high purity alkali metal hexafluorophosphates of other Group 1 elements (Rb and Fr) can be prepared following the above scheme.
30

EXAMPLES

[009] The following examples are illustrative of the invention but not limitative of the scope thereof:

35 [010] **Example-1:** Synthesis of sodium hexafluorophosphate using 1:1.2 molar ratio of sodium

fluoride to phosphorous pentachloride.

Two Hastelloy autoclave (A and B), with non-metallic wet parts for reacting NaF and PCl_5 in the molar ratio 1:1.2 were used. To the reactor B was charged high purity sodium fluoride (100g).

5 Flushed the assembly with nitrogen. Cooled the assembly to 5-10°C. Charged battery grade AHF (800g) from cylinder in controlled condition. Allow the mixture to stir.

Reactor A was charged PCl_5 (594g). Slowly dosed AHF in lots of 100 to 200 g at 25 to 40°C (in totality 380g) in 24 to 30 hrs. timeframe. In between the pressure generated due to formation of PF_5 and HCl gas in reactor A was dosed to Reactor B through vent system without any Dip-tube
10 till constant pressure. The PF_5 gas reacted with NaF in AHF to give NaPF_6 under PF_5 gas blanketing. After every 1 hr, the excess pressure due to HCl gas was released to scrubber having basic pH.

After complete consumption of the HF and PCl_5 (identified by non-generation of PF_5 gas pressure) the reactor was cooled to -15 to -20°C, maintaining the mass for 16 hrs at -15°C and
15 filtering the solid under pressure. The solid was dried and unloaded. The weight of the isolated sodium hexafluorophosphate is 120g. The isolated solid was checked for its assay by ion chromatography based on sodium content and found to be 99.85%.

[011] **Example-2:** Synthesis of sodium hexafluorophosphate using 1:1.4 molar ratio of sodium
20 fluoride to Phosphorous pentachloride.

Two Hastelloy autoclave (A and B), with non-metallic wet parts for reacting NaF and PCl_5 in the molar ratio 1:1.4 were used. To the reactor B was charged high purity sodium fluoride (100g). Flush the assembly with nitrogen. Cooled the assembly to 5-10°C. Charged battery grade AHF
25 (400g) from cylinder in controlled condition. Allow the mixture to stir.

Reactor A was charged PCl_5 (694g). Slowly dosed AHF in lots of 100 to 200 g at 25 to 40°C (in totality 443g) in 24 to 30 hrs. timeframe. In between the pressure generated due to formation of PF_5 and HCl gas in reactor A was dosed to Reactor B through vent system without any Dip-tube
30 till constant pressure. The PF_5 gas reacted with NaF in AHF to give NaPF_6 under PF_5 gas blanketing. After every 1 hr, the excess pressure due to HCl gas was released to scrubber having basic pH.

After complete consumption of the HF and PCl_5 (identified by non-generation of PF_5 gas pressure) the reactor was cooled to -15 to -20°C, maintaining the mass for 16 hrs at -15°C and filtering the solid under pressure. The solid was dried and unloaded. Weight of the isolated sodium

hexafluorophosphate is 321g. The isolated solid was checked for its assay by ion chromatography based on sodium content and found to be 99.8%.

5 [012] **Example-3:** Synthesis of potassium hexafluorophosphate using 1:1.4 molar ratio of potassium fluoride to phosphorous pentachloride

Two Hastelloy autoclaves (A and B), were used for reacting KF and PCl_5 in the molar ratio 1:1.4 were used. To the reactor B was charged high purity potassium fluoride (58 g). Flush the assembly with nitrogen. Cooled the assembly to 5-10°C. Charged purified AHF (200g) from cylinder in
10 controlled condition. Allow the mixture to stir.

Reactor A was charged with PCl_5 (312g) and slowly dosed AHF in lots of 20 - 50 at 25 to 40°C (in totality 220g) in 24 to 30 hrs. timeframe. In between the pressure generated due to formation of PF_5 and HCl gas in reactor A was dosed to Reactor B through vent system without any Dip-tube till constant pressure. The PF_5 gas reacted with KF in AHF to give KPF_6 under PF_5 gas
15 blanketing. After every 1 hr, the excess pressure due to HCl gas was released to scrubber having basic pH.

After complete consumption of the HF and PCl_5 (identified by non-generation of PF_5 gas pressure) the reactor was cooled to -15 to -20°C, maintaining the reaction mass for 16 hrs at -15°C and filtering the solid under pressure. The solid was dried and unloaded. Weight of the isolated
20 potassium hexafluorophosphate is 158g.

[013] The foregoing description of the invention has been set merely to illustrate the invention and is not intended to be limiting. Since the modifications of the disclosed embodiments incorporating the spirit and substance of the invention may occur to the person skilled in the art,
25 the invention should be construed to include everything within the scope of the disclosure.

We Claim:

1. A process of preparing an ultra-high purity alkali metal hexafluorophosphate (MPF6), comprising following steps:
 - a. charging alkali metal fluoride (MF) in a first reactor 'B' and flushing nitrogen gas through
5 the same,
 - b. cooling the first reactor 'B' to a predetermined temperature, followed by charging anhydrous hydrogen fluoride (AHF) gas and stirring the mixture comprising alkali metal fluoride (MF) dissolved in AHF in the first reactor 'B',
 - c. cooling the mixture comprising alkali metal fluoride (MF) dissolved in AHF in the first
10 reactor 'B' to a predetermined temperature,
 - d. charging phosphorous pentachloride (PCl5) in a second reactor 'A' and adding AHF in multiple lots, to produce high purity phosphorous pentafluoride (PF5) and hydrogen chloride (HCl) gas,
 - e. reacting alkali metal fluoride (MF) dissolved in AHF in the first reactor 'B' with
15 phosphorus pentafluoride (PF5) and hydrogen chloride (HCl) gas mixture obtained in step (d) to obtain alkali metal hexafluorophosphate mother liquor dissolved in AHF under PF5 gas blanketing,
 - f. cooling the first reactor 'B' to a predetermined temperature and maintaining the temperature of alkali metal hexafluorophosphate mother liquor dissolved in AHF for
20 predetermined time, followed by filtration and drying at predetermined temperature to achieve alkali metal hexafluorophosphate (MPF6),
 - g. crushing the dried crystals of MPF6 and optionally sieving to obtain MPF6 powder,

wherein alkali metal 'M' is selected from Na, K and Cs and alkali metal hexafluorophosphate is selected from NaPF6, KPF6 or CsPF6
- 25 2. The method as claimed in claim 1, wherein the PF5 and HCl gas from the second reactor 'A' was dosed to the first reactor 'B' through vent system without any dip-tube till constant pressure.
3. The method as claimed in claim 1, wherein the anhydrous hydrogen fluoride (AHF) gas is purified prior to using it in the process; and wherein the alkali metal fluoride used in the process
30 is obtained from alkali metal bicarbonate and hydrogen fluoride.
4. The process as claimed in claim 1, wherein the predetermined temperature in step (b) and (c) is in the range of 0 to 15 °C, preferably in the range of 5 to 10 °C.
5. The method as claimed in claim 1, wherein the adding AHF is added in multiple lots preferably in the range of 200 to 300 g or 100 to 200 g at 25 to 40°C.

6. The method as claimed in claim 1, wherein the predetermined temperature and predetermined time for cooling in step (f) is in the range of -10 to -25°C for 5 to 7 hours.
7. The method as claimed in claim 1, wherein the predetermined temperature and predetermined time for cooling in step (f) is in the range of -15 to -20°C for 6 hours.
- 5 8. The method as claimed in claim 1, wherein the predetermined temperature for drying in step (f) is in the range of 35 to 50 °C, preferably between 38 to 40 °C.
9. The method as claimed in claim 1, wherein the alkali metal fluoride (MF) used in the process is obtained from the steps of:
 - (1) treating alkali metal carbonate with carbon dioxide to obtain alkali metal bicarbonate,
10 $M_2CO_3 + H_2O + CO_2 \rightarrow 2MHCO_3$;
 - (2) reacting the alkali metal bicarbonate with ultra-pure hydrogen fluoride to obtain alkali metal fluoride (MF),
 $MHCO_3 + HF \rightarrow MF + CO_2 + H_2O$; and
 - (3) drying and crushing the alkali metal fluoride (MF).
- 15 10. An ultra-high purity alkali metal hexafluorophosphate selected from NaPF₆, KPF₆ and CsPF₆ with a purity of at least 98.50%, preferably at least 99.8%.
11. The ultra-high purity sodium hexafluorophosphate (NaPF₆) as claimed in claim 10, comprising metallic impurities as follows:

Fe	≤ 2 ppm
Ca	≤ 2 ppm
K	≤ 2 ppm
Na	≤ 2 ppm
Ni	≤ 2 ppm
Pb	≤ 2 ppm
Zn	≤ 2 ppm
Cr	≤ 2 ppm
Cu	≤ 2ppm
Mg	≤ 2 ppm