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Estimating cost and energy demand in producing Lithium hexafluorophosphate (LiPF) for Li-ion battery electrolyte

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Estimating cost and energy demand in producing Lithium hexafluorophosphate (LiPF$_6$) for Li-ion battery electrolyte

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Abstract

In this work, the production of Lithium hexafluorophosphate ($LiPF_6$) for Lithium-ion battery application is studied. Spreadsheet-based process models are developed to simulate three different production processes. These process models are then used to estimate and analyze the factors affecting cost of manufacturing, energy demand, and environmental impact due to greenhouse gas (GHG) emissions. The results indicate that in a facility with a capacity of making 10,000 metric tons per year of $LiPF_6$ the cost of production is around $20 per kg of $LiPF_6$, energy consumption is around 30 GWh per year, and the emission of greenhouse gases in CO_2-equivalent gases is around 80 metric tons per day. The impact of change in process and economic parameters on the cost of production, energy demand, and emissions is studied. In addition, a few insights on reducing the cost of production are presented. Finally, the impact of varying LiPF$_6$ costs on the overall cost of a Li-ion battery ($ kWh^{-1}) is presented.

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1. Introduction

The drive towards large-scale commercialization of electric or hybrid electric automobiles is challenged by high prices of lithium-ion batteries. Consequently, the development of low cost and high energy density lithium-ion batteries is receiving ever greater interest from both academia and industry. The U.S. Department of Energy (U.S. DOE) has sponsored programs in support of the U.S. Advanced Battery Consortium (USABC) goals to develop battery packs for battery electric vehicles (BEV) with a selling price of $100 per kWh[1, 2].

Argonne National Laboratory's BatPaC[3] spreadsheet modeling tool projects the cost of electrolyte to be around 6 – 10% of overall battery pack. Lithium hexafluorophosphate ($LiPF_6$) is a commonly-used electrolyte material in lithium ion batteries. Due to the increasing shift towards making total electric or hybrid electric automobiles, the demand for $LiPF_6$ has increased tremendously in the past few years. Consequently, the price of $LiPF_6$ has increased more than 500% in the last 3 years[4, 5].

The focus of this work is to study the cost, energy demand, and environmental impact of producing lithium hexafluorophosphate ($LiPF_6$) for use in lithium-ion battery electrolytes. This paper reviews a number of processes for making $LiPF_6$, and then defines three plausible manufacturing processes for the large scale production of $LiPF_6$. Process models are developed for these selected processes to estimate the cost and energy demand for the production of $LiPF_6$. The factors affecting the cost of manufacturing and energy demand have been analyzed. Finally, the effect of the cost of $LiPF_6$ on the overall cost of a lithium ion battery cost is presented using Argonne's BatPaC spreadsheet tool for the design of automotive LIBs and estimation of their cost[3].

2. Making Lithium Hexafluorophosphate (LiPF$_6$)

LiPF$_6$ is predominantly produced from the reaction of phosphorus pentafluoride (PF$_5$) and lithium fluoride (LiF) according to the following reaction in the presence of a solvent.

$$LiF + PF_5 \rightleftharpoons LiPF_6 \tag{1}$$

Several researchers[6-13] suggest to produce PF$_5$ from the reaction of phosphorous trichloride (PCl$_3$), chlorine gas (Cl$_2$), and hydrogen fluoride (HF). Production of LiPF$_6$ for Li-ion battery electrolytes is constrained by the required purity (>99.9%) and the type of impurities present in the final product. Trace amounts of impurities such as moisture, metal, and free HF are detrimental for the life, quality, and safety of the Li-ion battery. Thus, the raw materials, processing equipment, and production methodology are selected with great caution to avoid any possible contamination.

One of the earliest methods for preparing lithium hexafluorophosphate (LiPF$_6$) was proposed by Kemmitt et al.[14] and Stacey[15], where lithium fluoride (LiF) was dissolved in anhydrous hydrogen fluoride (HF) and then pass phosphorus pentafluoride (PF$_5$) gas through this solution at 25 °C to produce LiPF$_6$. Hehua et al.[8, 9] propose to pass a mixture of PF$_5$ and HCl through a solution of HF and LiF between -30 to -10 °C to produce LiPF$_6$. Hanezawa[16] proposed to react phosphorus pentachloride (PCl$_5$) with HF to produce PF$_5$ and HCl. PF$_5$ is subsequently separated from the gaseous mixture and added to a 10-20:1 molar solution of HF and LiF at a temperature of -30 to 0 °C. Koyama et al.[17] suggests to react PCl$_5$ with a solution of HF and a lithium halide, LiX (X = Cl, F, I, Br) in a single reactor to produce LiPF$_6$. Mochida[18] suggested a gas phase reaction between HF and PCl$_5$ to produce a gaseous mixture of PF$_5$ and HCl, which is cooled to a temperature of -40 to -80 °C. This mixture is then introduced into a reactor containing a solution of HF and LiF to produce LiPF$_6$. Wuxiao et

al.[19] suggests a continuous manufacturing method for $LiPF_6$, where LiF, PF_5, and HF are mixed and reacted in a tubular reactor at 40-60 °C and 2 MPa. The slurry consisting of unreacted LiF, product $LiPF_6$, and solvent HF is further reacted with PF_5 until LiF is completely converted to $LiPF_6$. $LiPF_6$ is then separated by crystallization and subsequent drying. Na et al.[20] suggests drying of anhydrous HF (AHF) using F_2 gas before reacting it with PCl_5 to produce PF_5 and HCl. The AHF dried with F_2 gas is also reacted with LiCl in a separate reactor to produce LiF. The solution of LiF in AHF is then bubbled with the gaseous mixture of PF_5 and HCl to produce crystals of $LiPF_6$. Several[13, 21-25] researchers propose a similar approach of reacting a slurry of LiF in HF with the gaseous PF_5 to produce $LiPF_6$.

Aramaki et al.[26] and Ito et al.[10] propose to first prepare porous LiF by evaporating HF from a solution of HF and LiF then, react it with PF_5 to produce $LiPF_6$ at > 50 °C. The $LiPF_6$ is then separated from unreacted LiF using 1, 2-dimethoxyethane. Boll et al.[7] propose to prepare LiF by reacting lithium carbonate (Li_2CO_3) with HF in an aqueous medium (preferably water) followed by drying to obtain dry and porous LiF. The authors then suggest to pass a gaseous mixture of PF_5 and HCl through a bed of LiF obtained earlier. The reaction product is dissolved in acetonitrile (CH_3CN) to separate and recover $LiPF_6$. Baojun[6] suggests a similar method, where Li_2CO_3 is reacted with HF in diethyl carbonate at around 100-200 °C for about 10 h to produce LiF. This LiF is reacted with a mixture of PCl_5 and acetonitrile at 30 – 80 °C to produce $LiPF_6$. Similarly, Wiesboeck[27] proposes to pass gaseous PF_5 through the slurry of LiF in excess CH_3CN at about 50-60 °C to produce a complex precipitate of $Li(CH_3CN)_4PF_6$. This precipitate is then dried under vacuum to remove CH_3CN and obtain pure $LiPF_6$. Ito et al.[10, 11] propose to react PF_5 with LiF in diethyl ether or dimethyl carbonate to produce $LiPF_6$. Also, Yuncong et al.[28] suggest to prepare $LiPF_6$ by reacting PF_5 with LiF in CH_3CN or

tetrahydrofuran $((CH_2)_4O)$. Mao[29] proposes to react a solution of ammonium hexafluorophosphate (NH_4PF_6) in ethyl carbonate (EC) or di-ethyl carbonate (DEC) with lithium hydride (LiH) to produce $LiPF_6$. Jache and Santad[30] propose to react red phosphorous with LiF in the presence of HF in a closed reactor at 200 °C for making $LiPF_6$. Smith Jr.[31] proposed to react LiF with PF_5 in diethyl ether at 10-30 °C. The solvent is selected such that LiF is insoluble, PF_5 is soluble, and $LiPF_6$ is partially soluble. Bonnet et al.[32] suggest to react a 3-5 % by wt. solution of LiF in HF with a gaseous mixture of PF_5 and HCl in a countercurrent absorption column, maintained at 1 - 20 atm and-10 to 30 °C. Belt et al.[33] suggest to react PCl_5, LiF, and HF at -40 °C to produce $LiPF_6$. Rieland et al.[12] propose to react PCl_3, Cl_2 gas and HF in a reactor using either HF or CH_3CN as a solvent. LiF is added to the same reactor to produce $LiPF_6$, which is separated from the mixture through crystallization. Oe & Sato[34] and Oe et al.[35] suggest a method for preparing $LiPF_6$ by first reacting PCl_3, Cl_2, and lithium chloride (LiCl) in a nonaqueous organic solvent. The reaction products are then reacted with HF to produce $LiPF_6$. Wietelmann & Schade[36] present a method in which LiF is reacted with PCl_5 or $POCl_3$ at -20 – 300 °C to produce $LiPF_6$. Eguchi & Hashimoto[37] describe a combination of steps for purifying $LiPF_6$ produced from different processes involving crystallization in liquid HF and drying. Joubert[38] presents a method, where gaseous mixture of PF_5 and HCl reacts with LiF suspended in liquid SO_2 in the temperature range of -10 to 10 °C. Bowden[39] proposes a method for preparing $LiPF_6$ where ammonium hexafluorophosphate (NH_4PF_6) is reacted with lithium hydride (LiH) in 1, 2-dimethoxyethane. After the reaction, $LiPF_6$ is precipitated and can be separated.

Yanseng et al.[40] suggests to recycle the gaseous mixture of PF_5 and HCl to increase the overall yield of $LiPF_6$. Kikuyama et al. [41] suggest to remove the impurity of lithium

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oxyfluorophosphate ($LiPO_xF_y$) from the crude $LiPF_6$ by reacting it with phosphorous

pentachloride (PCl_5) and HF. Liu et al.[42] and Yunhe et al.[43] propose to produce PF_5 by reacting

CaF_2 and P_2O_5 at $280 – 300\,°C$. The PF_5 is reacted with LiF suspended in CH_3CN in a contacting

column to produce $LiPF_6$, which is then purified from the solvent by crystallization. Ohe[44]

and Ohe et al.[45] present a combination of methods, where LiF and red phosphorus (P) are

heated at $300\,°C$ in presence of F_2 gas and at $25\,°C$ in presence of ClF_3 to produce $LiPF_6$.

Wilmann, Naejus, and co-workers[46, 47] propose to first prepare pyridinium

hexafluorophosphate ($C_5H_5NHPF_6$) from the neutralization of phosphorous hexafluoro acid

(HPF_6) with pyridine (C_5H_5N). Then $C_5H_5NHPF_6$ is converted into a solvate of lithium

hexaflurophosphate and pyridine by reacting the former with lithium hydroxide (LiOH).

Mohamed et al.[48] suggested to prepare the pyridinium hexafluorophosphate by reacting PCl_5

or PBr_5 with pyridinium poly(hydrogen fluoride), which can then be used to prepare $LiPF_6$

from either LiOH or LiCl. Quanchao et al.[49] and Xinji et al.[50] proposed to to purge $LiPF_6$ with

a gaseous mixture consisting of argon and F_2 to remove residual moisture and

oxyfluorophosphates ($LiPO_xF_y$).

3. Process Models

As observed from the aforementioned review, primary differences among the various

manufacturing processes presented in the literature are (i) the choice of solvent material,

(ii) precursor materials used for obtaining LiF and PF_5, and (iii) preprocessing and

purification steps. The choice of solvent and starting materials partially governs the need for

preprocessing and product purification steps in a $LiPF_6$ manufacturing process, and affects

the energy demand, cost of production, and greenhouse gas (GHG) emissions. In order to

better understand the selection of materials and their effect on the process economics and

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technical viability, a techno-economic and environmental impact analysis of a few different

$LiPF_6$ production processes is necessary. This paper reports on three different routes for

making $LiPF_6$ using three different solvents (anhydrous HF, liq. SO_2, and CH_3CN). The specific

focus of this paper is to study and analyze the relative differences and similarities of these

manufacturing methods with respect to process requirements, capital and operational

expenses, and environmental impacts.

Some of the key considerations in the selection of starting materials may be summarized as:

- LiF and PF_5 are expensive starting materials for producing $LiPF_6$.

- PF_5 is a highly toxic gas making it difficult and hazardous to store in a plant.

- LiCl and PCl_5 are relatively cheaper to procure. (Table 1 lists the price estimates used in this study).

- PCl_5 is relatively less hazardous and is a crystalline solid at normal conditions.

For the aforementioned reasons, LiCl and PCl_5 are used as the starting materials for all three

processes presented in this work. HF is necessary for the production of $LiPF_6$ by any method

so, it has been used as a solvent by several studies as reported earlier. Thus, anhydrous HF

is used as the solvent in the proposed process 1 (P1). However, HF is an extremely hazardous

chemical. This imposes additional cost burden on the manufacturer to place appropriate

safety and control measures for mitigating any potential accidents involving equipment

failure or HF leakage. Thus, using a different solvent has potential not only to reduce cost but

also to improve the safety of operations.

Alternative solvents suggested in the literature include liquid SO_2, acetonitrile, and other

organic solvents such as diethyl ether, ethyl carbonate, and diethyl carbonate. Liquid SO_2 as

a solvent is easy to separate from the product because of its low boiling point. This reduces

the number of steps in the production process. Thus, the second process (P2) in this study uses liquid SO_2 as the solvent of choice for producing $LiPF_6$. Although SO_2 is not as hazardous as HF, it has a detrimental impact on the environment if released to the atmosphere. The alternative is organic solvents such as acetonitrile, diethyl ether, and ethyl carbonate. Organic solvents are both cheaper and safer than HF and SO_2. In order to compare the cost and energy of producing $LiPF_6$ using organic solvents, acetonitrile is used as a solvent is process 3 (P3).

3.1. Process 1 (P1):

This production process (Figure 1) uses HF as the solvent. The key raw materials are HF (l), LiCl (s), and PCl_5 (s), where l and s represent the physical state of materials, i.e. liquid and solid respectively.
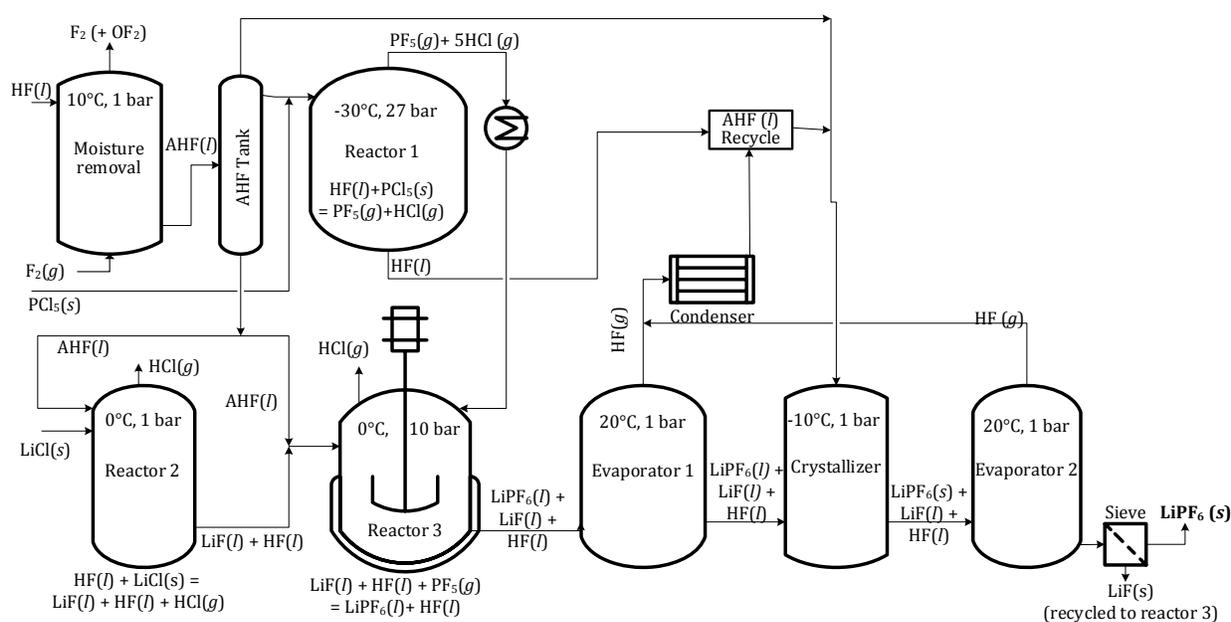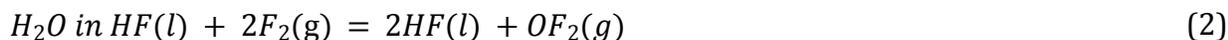

Figure 1 Process flow diagram for process 1 (P1)

The purchased HF typically contains around 100-150 ppm of moisture. This moisture is reduced by bubbling fluorine gas (F_2) through it at 10 °C and 1 bar.

$$H_2O \ in \ HF(l) \ + \ 2F_2(g) \ = \ 2HF(l) \ + \ OF_2(g) \tag{2}$$

OF_2 has a very low boiling point (ca. −145 °C) and is easily volatilized and removed from the liquid HF. The dried HF obtained after the moisture removal step is then distributed across the process as anhydrous HF (AHF). AHF is added to Reactors 1, 2, and 3 as shown in Figure 1 to produce PF_5, LiF, and eventually $LiPF_6$, respectively.

In Reactor 1, a slurry is made by adding liquid AHF to the PCl_5 powder. The reactor is maintained at −30 °C, 27 bar, with a residence time of 1 hour. PCl_5 readily reacts with HF in these conditions as follows.

$$PCl_5(s) + 5HF(l) = PF_5(g) + 5HCl(g) \qquad \Delta H = -313 \ kJ \ mol^{-1} \tag{3}$$

Complete conversion of the PCl_5 is ensured by using 5% excess AHF. As the reaction (3) is exothermic and with the feeds at -10 and 25 °C, 924 kW of heat is removed from the reactor with a liquid cooled refrigeration system to maintain the desired temperature of −30 °C.. The gaseous products, PF_5 and HCl with molar ratio of 1:5, exit the top. It is decompressed to 10 bar and then heated to 0 °C with process water in a heat exchanger, before entering Reactor 3. The excess liquid AHF at the bottom is sent to the HF recycling unit.

In Reactor 2, a slurry is formed by mixing excess liquid AHF with LiCl at 0 °C and 1 bar, with a residence time of 1 hour, to facilitate the following reaction.

$$LiCl(s) + HF(l) \xrightleftharpoons{in \ liq \ AHF} LiF(in \ liq \ AHF) + HCl(g) \qquad \Delta H = -1.19 \ kJ \ mol^{-1} \tag{4}$$

The excess AHF is to ensure that the product LiF remains soluble. The LiF in AHF solution is removed from the bottom of the reactor. The gaseous HCl product is collected at the top of the reactor and is packaged to be sold as a byproduct.

Gaseous mixture PF_5 and HCl from Reactor 1 is bubbled through the solution of LiF in AHF in Reactor 3 at 0 °C, and 10 bar to produce $LiPF_6$.

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$$LiF(in\ liq\ AHF) + PF_5(g) \underset{\text{in liq AHF}}{\rightleftharpoons} LiPF_6(s) \qquad \Delta H = -85\ kJ\ mol^{-1} \qquad (5)$$

Reaction (5) is carried out in Reactor 3 in the presence of liq. AHF (~96 wt. %) as a solvent to produce $LiPF_6$ crystals. The reaction reaches completion in about 5 h. Reactor 3 system is modeled as a series of CSTRs. Presence of HCl(g) in the reaction (5) is not shown as it acts as inert, which is collected at the top of the reactor, packaged and sold as a byproduct. Solvent AHF is removed by vaporization in Evaporator 1, then condensed and recycled. The dried product in Evaporator 1 consisting of $LiPF_6$ and 7% by weight of HF is sent to the crystallizer. Additional HF is added to the crystallizer such that HF content in the solution is around 75% by weight. The solution is cooled to –10 °C, where $LiPF_6$ crystals grow to form larger crystals of higher purity (~ 99.9%). HF separated in Evaporator 2 is then condensed and recycled. The product of Evaporator 2 is a solid mixture consisting of both 99.9% pure $LiPF_6$ crystals and LiF powder, which is separated through a vibrating sieve. LiF obtained is recycled. The recovery of $LiPF_6$ from Evaporator 2 is around 85% with a purity of 99.9%, where the impurities consists of both HF and LiF.

3.2. Process 2 (P2):

As HF is a highly toxic chemical, it is advisable to reduce the use of HF as much as possible. Using a solvent other than HF will greatly reduce the quantity used. Liquid SO_2 as an alternative solvent has the advantage of it's lower boiling point (-10°C vs. 19.5 °C for HF), which allows for easier separation from the product. This eliminates the need for additional processing and equipment such as the crystallizer.
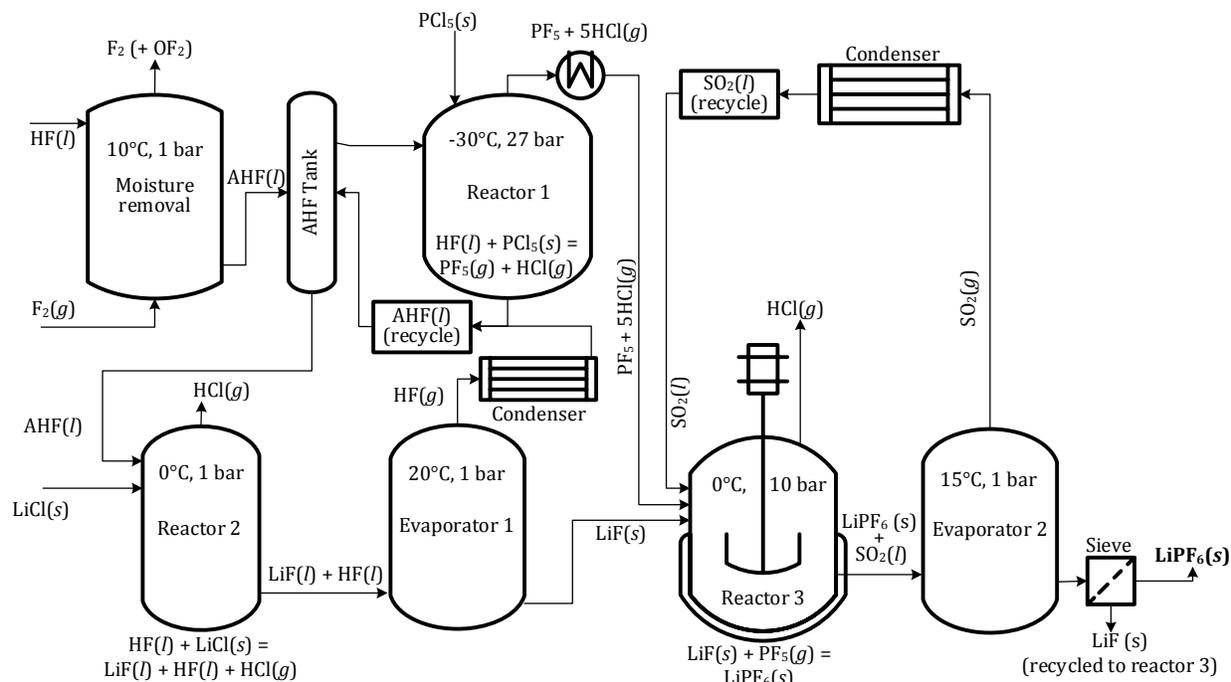
Figure 2 Process flow diagram for process 2 (P2)

P2, shown in Figure 2, uses the same starting materials as in P1, i.e. LiCl and PCl$_5$, and the processing steps of Reactor 1 and Reactor 2 remain the same as in process 1. The gaseous mixture (PF$_5$ and HCl) from Reactor 1 is passed to Reactor 3 and the excess HF is recycled. Reactor 2 produces a solution of LiF in HF. Now, as P2 uses liquid SO$_2$ as the solvent in Reactor 3, HF from the product of Reactor 2 is removed in Evaporator 1 (as shown in Figure 2) at 20 °C. The evaporated HF is condensed and recycled. The solid LiF powder from the Evaporator 1 is added to Reactor 3 along with liquid SO$_2$ (SO$_2$/LiF = ~8). Reactor 3 is maintained at 0 °C and 10 bar to facilitate the following reaction.

$$LiF\ (s) + PF_5(g) \rightleftharpoons LiPF_6(s) \qquad \Delta H = -85\ kJ\ mol^{-1} \qquad (6)$$
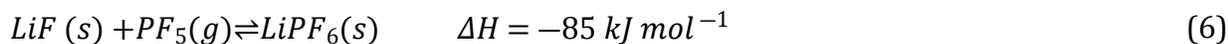
Reaction (6) reaches completion by the crystallization of LiPF$_6$ in ~5 h. Again, reactor 3 system is modeled as a series of multiple CSTRs. The slurry product of Reactor 3 consisting of crystal LiPF$_6$, unreacted LiF, and solvent liq. SO$_2$ is passed to the Evaporator 2. Evaporator

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2 operates at a reduced pressure of 1 bar and heats the feed to around 15 °C. This vaporizes

liq. SO_2, which is collected at the top in a condenser and recycled to Reactor 3. The dry

product in Evaporator 2 is sifted through a sieve to separate product $LiPF_6$ crystals from the

unreacted powder LiF, which is recycled to Reactor 3. The $LiPF_6$ obtained has a purity of

99.9% and an overall recovery of around 90% (higher than P1).

3.3. Process 3 (P3):

Process 2 described above offers several advantages over P1 such as fewer equipment, fewer

processing steps, and reduction in the usage of hazardous HF. However, SO_2 is also a highly

controlled chemical in an industrial environment. Thus, using an organic solvent in place of

liq. SO_2 or HF will be significantly less hazardous and forms the basis of studying process 3

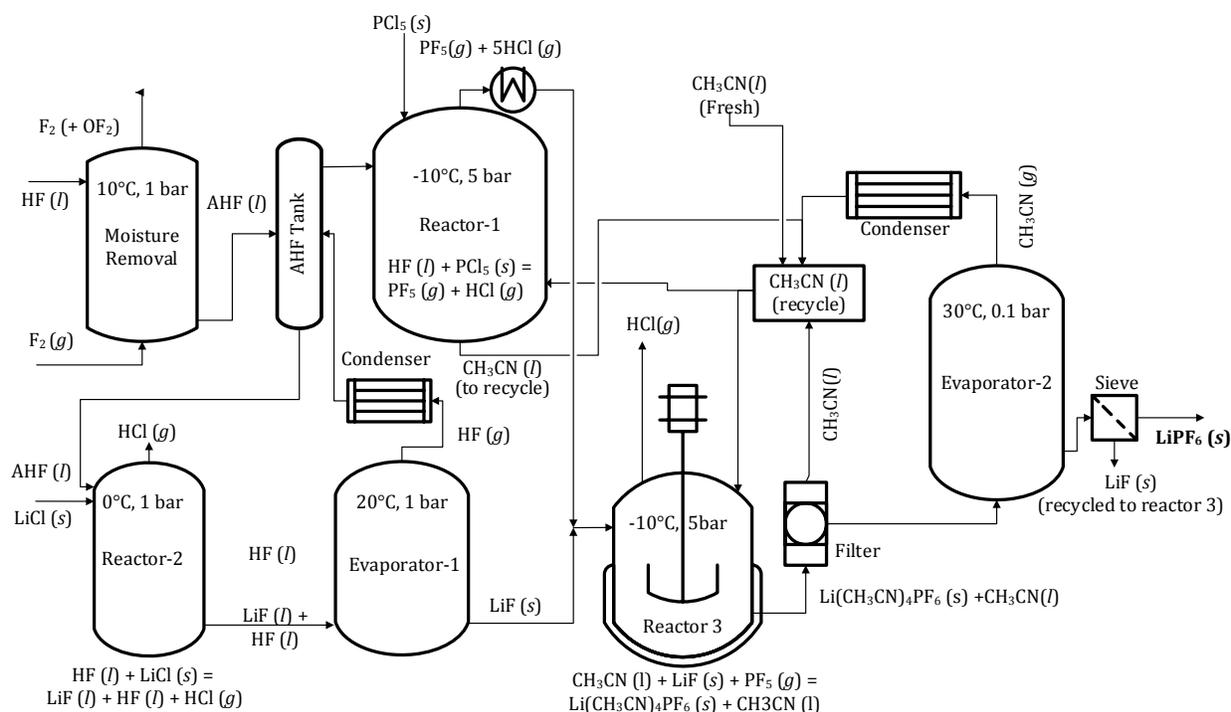(P3), where acetonitrile is used as a solvent.

Figure 3 Process flow diagram for process 3 (P3)

Again, P3 uses the same starting material as in P1 and P2, *i.e.*, LiCl and PCl$_5$ as shown in Figure 3. However, Reactor 1 in P3 is operated at -10 °C and 5 bar instead of -30 °C and 27 bar as in P1 and P2. Also, HF is added in stoichiometric quantity as required in reaction (3) to make PF$_5$. In order to facilitate the reaction with changed conditions, acetonitrile is added to Reactor 1 as a solvent such that the molar ratio of acetonitrile to PCl$_5$ is around 9. This is a significant departure from processes P1 and P2, where no solvent was used. The reaction reaches completion in ~ 1 h and the gaseous products (PF$_5$ and HCl) are added to Reactor 3, as shown in Figure 3. The solvent (i.e. acetonitrile) is then sent to the recycling unit. Similar to P2, LiF is produced from LiCl with excess HF in Reactor 2, which is subsequently removed in Evaporator 1. The dried LiF is added to Reactor 3 along with acetonitrile at -10 °C and 5 bar to facilitate reaction (6). Total acetonitrile added to Reactor 3 is such that the molar ratio of acetonitrile to LiF is around 8. The reaction reaches completion by the precipitation of a complex Li(CH$_3$CN)$_4$PF$_6$ in around 5 h. This precipitate is separated from the solvent in a filter, where the filtrate (i.e. liquid solvent is recycled). The precipitate is passed to Evaporator 2, where it is heated to around 30 °C to vaporize acetonitrile and obtain the dry LiPF$_6$ product. Since LiPF$_6$ begins to decompose at the boiling point of acetonitrile (82°C), the evaporator is operated at 0.1 bar and 30°C. The recovery of LiPF$_6$ in P3 is around 99% and is obtained in the product with a high purity (> 99.9%).

4. Approach and Assumptions

To analyze the relative technical challenges and economic restrictions of the three manufacturing processes, spreadsheet-based process models tracking material and energy balances, and cost calculations were developed. The inputs to these spreadsheet models are the process conditions (e.g. temperature and pressure), model parameters (such as reactor

residence times and conversions, equilibrium constants, and equipment efficiencies), and costs for materials and equipment. The process conditions, material properties, and model parameters were obtained from the literature and if they were not directly available, these were estimated from the experimental data presented in various patent publications.

In the economic model, the costs of equipment were estimated from the expressions provided in Turton et al.[51] and then adjusted to their 2017 value using CEPCI correction. The production cost was computed using the procedure proposed by Peters et al.[52] and presented in Ahmed et al.[53]. The values for various economic parameters (such as costs for contingency, royalties, installations, construction, etc. as percentages of equipment cost or capital cost) in the model were assumed based on the suggestions given by the authors of Peters et al.[52] and Ahmed et al. [53].

Material of construction for the equipment and fittings is very important both for safety and cost, especially because all three processes involve the use of fluoride compounds. For this, all the vessels such as reactors, evaporators, and heat exchangers were assumed to be made of stainless steel (SS) with Polytetrafluoroethylene (PTFE) coatings. The pumps and fittings were assumed to be made of PTFE [53-55]. The cost of equipment and pumps were estimated accordingly.

All the materials purchased from the market were assumed to be of very high purity (> 99.9 %) and not contain any unwanted impurities such as moisture or traces of other metals. However, HF is further treated to remove any traces of moisture in all three processes. Also, the costs for materials procurement were assumed to include the cost of transportation to the production site. Specifically, the cost of HF was assumed to include the costs of the mandated auxiliary facilities such as power source, cooling system, and medical supplies.

Furthermore, all 3 processes (P1 – P3) produce HCl, which is compressed and sold as a byproduct. The cost of compressing and packaging HCl as well as the credits from its sale were not considered; it was assumed that the revenue from the sale of HCl offsets the compression and packaging cost. To estimate the required electricity usage in the refrigeration cycle to meet the cooling duty, a coefficient of performance (COP) of 3 in all three processes was assumed. The greenhouse gas emissions in term of equivalent CO_2 was estimated from the EPA's (Environmental Protection Agency) greenhouse gas equivalencies calculator[56].

Finally, for the production of $LiPF_6$, a baseline plant capacity of 10,000 metric tons (MT) per year and a plant life of 10 years for the amortization of the capital investment were used.

5. Results and discussion

The results obtained from the three process models of manufacturing $LiPF_6$ highlight respective process characteristics such as manufacturing cost, materials used, and energy required. In addition, the factors affecting these process characteristics have been studied in detail along with the relative differences among the three processes to derive insights for reducing the cost of production.

5.1. Material and energy requirement

A detailed breakdown of materials and energy required for all three processes (P1 – P3) is listed in Table 1. PCl_5 is a key starting material for all three processes and so, is needed in similar quantities, as seen in Table 1. The decreasing amount of PCl_5 used from P1 (50 MT day^{-1}) to P3 (43 MT day^{-1}) is because of the increasing molar yield of $LiPF_6$ with respect to PCl_5 from P1 (85%) to P3 (99%). LiCl is the other key starting material and is purchased in relatively smaller quantities. This is mainly because the associated product LiF (if unused) is

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recycled in all three processes. Among the three processes, the one with a relatively lower first pass conversion of LiF (*i.e.* P1) in Reactor 3 will require a smaller quantity of fresh LiF and consequently smaller quantity of LiCl. This is evident from the LiCl quantities required for the three processes shown in Table 1. Recall that P1 uses HF as a solvent for the production of $LiPF_6$. Thus, the amount of HF needed for P1 (83 MT day^{-1}) is significantly higher than P2 (28 MT day^{-1}) and P3 (25 MT day^{-1}). For this reason, the volume and cooling duty needed for moisture removal (in the moisture removal tank) is relatively higher for P1 (2 m^3) as compared to P2 (0.7 m^3) and P3 (0.64 m^3). Since the process conditions for reaction (3) are identical for P1 and P2, the volume, cooling duty, and power requirements for Reactor 1 in both P1 and P2 are similar. However, reaction (3) in P3 uses CH_3CN as a solvent leading to a higher volume and power requirements for Reactor 1 as compared to P1 and P2. As most of the CH_3CN is recycled in Reactor 1, at the required temperature, only a small quantity of fresh CH_3CN is required to be cooled. This reduces cooling duty needed in Reactor 1 of P3. Again, since the process conditions for reaction (4) are identical in all three processes, the volume, cooling duty, and power requirements for Reactor 2 are similar for P1, P2, and P3. However in P3, the amount of fresh HF required is relatively lower, resulting in lower cooling duty.

Table 1 List of material prices and breakdown of process loads and energy demand [10,000 MT year^{-1} of LiPF$_6$]

			P1	P2	P3
Materials purchased					
LiCl	$7 kg^{-1}	MT day^{-1}	5	6	9
PCl$_5$	$3.08 kg^{-1}	MT day^{-1}	50	48	43
HF	$1.1 kg^{-1}	MT day^{-1}	83	28	25
F$_2$	$6.5 MT^{-1}	MT day^{-1}	0.07	0.03	0.02
SO$_2$	$7 kg^{-1}	MT day^{-1}	-	1.2	-
CH$_3$CN	$2.68 kg^{-1}	MT day^{-1}	-	-	1.5
Moisture removal tank					
	Volume	m^3	2	0.71	0.64
	Cooling duty	kW	3583	1215	1104
	Electricity	kW	74	25	3.8
Reactor 1					
	Volume	m^3	27	25	273
	Cooling duty	kW	924	873	779
	Electricity	kW	96	91	571
Reactor 2					
	Volume	m^3	4	4	4
	Cooling duty	kW	8	9	4
	Electricity	kW	9	8	8
Reactor 3					
	Volume	m^3	849	770	1382
	# of reactors	#	9	8	14
	Cooling Duty	kW	237	224	204
	Electricity	kW	1719	1560	2756
Evaporator 1					
	Volume	m^3	5	3	3
	Heating duty	kW	57	34	31
Evaporator 2					
	Volume	m^3	6	4	0.76
	Heating duty	kW	99	55	39
Crystallizer					
	Volume	m^3	11	-	-
	Cooling duty	kW	102	-	-
	Electricity	kW	22	-	-
Filter					
	Area	m^2	-	-	8
	Max. velocity	m h^{-1}	-	-	0.2
	Electricity	kW	-	-	0.02

The three processes P1, P2, and P3 differ from each other based on the process conditions of Reactor 3 such as type of solvent, solvent to LiF ratio, pressure, and temperature. The pressure of Reactor 3 in P3 is 5 bar as compared to 10 bar for P1 and P2. Also, the solvent to LiF ratio for all three processes is different; 20 for P1 and 8 for P2 and P3. This difference in pressure and solvent-to-LiF ratio results in varying volumes of Reactor 3 for P1 ($849 m^3$), P2 ($770 m^3$), and P3 ($1382 m^3$). Consequently, the power requirement for Reactor 3 follows the same trend as volume in the three processes, i.e. 1719, 1560, and 2756 kW for P1, P2, and P3, respectively. Now, Evaporator 1 in P1 is located after Reactor 3, while it is placed before Reactor 3 in P2 and P3. This is the reason the heating load on P1 (57 kW) is much higher than P2 (34 kW) and P3 (31 kW). The difference in the size and heating duty for Evaporator 2 differs significantly across P1 ($6 m^3$ & 99 kW), P2 ($4 m^3$ & 55 kW), and P3 ($0.76 m^3$ & 39 kW). The volume of for Evaporator 2 in P3 is significantly less because the inlet feed is mainly the filtered precipitate and contains a very low quantity of liquid solvent. Recall that the change in temperature in Evaporator 2 for P1 is from -10 °C to 20 °C, but for P2 it is from 0 °C to 15 °C and for P3 it is from -10 °C to 30 °C. This results in a lower heating load for P2 and a higher load for P3 as compared to P1.

Overall, as observed from the aforementioned discussion and the data presented in Table 1, the three processes differ from each other based on energy required, number of processing steps, and type of solvents used. Now, as P3 uses the least amount of HF in the production of $LiPF_6$, it is the least hazardous process among all three.

5.2. Economic analysis

The procedure for estimating manufacturing cost is shown in Table 2 and consists of a number of parameters and involves computing a variety of costs such as capital investment, direct manufacturing, and general expenses.

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Table 2 List of parameters used for economic model

Assumption / Input Parameter	Estimated %	Of	Range %
1. Direct Costs			
A. Purchased Equipment	Model*		Model*
Installation	80%	Purchased Equipment	50-155%
B. Buildings, process and auxiliary	15%	Purchased Equipment	10-50%
C. Service facilities and yard improvements	50%	Purchased Equipment	40-80%
D. Land	8%	Purchased Equipment	4-8%*
2. Indirect Costs			
A. Engineering and supervision	10%	Direct Costs	5-20%
B. Construction expense and contractor's fee	10%	Direct Costs	5-25%
C. Contingency	5%	Fixed Cap. Investment	5-15%
3. Fixed Capital Investment = 1 + 2			
4. Working Capital	10%	Fixed Cap. Investment	10-20%
5. Total Capital Investment = 3 + 4			
I. Manufacturing Cost, $ year^{-1}			
A. Direct Product Costs			
Raw Materials	Model*		Model*
Operating labor	Model*		Model*
Direct supervisory and clerical labor	15%	Operating Labor	10-20%
Utilities	Model*		Model*
Maintenance and Repairs	5%	Fixed Cap. Investment	2-10%
Operating supplies	15%	Maintenance & Repairs	10-20%
Laboratory charges	10%	Operating Labor	10-20%
Patents and royalties	1%	Total Product Cost	0-6%
B. Fixed Charges			
Depreciation	Model*		Model*
Local taxes	4%	Fixed Cap. Investment	1-4%
Insurance	1%	Fixed Cap. Investment	0.6-1%
Rent	5%	Fixed Cap. Investment	5-12%
Financing	5%	Total Cap. Investment	5-10%
C. Plant Overhead Costs	5%	Total Product Cost	5-15%
II. General Expenses			
A. Administrative costs	4%	Total Product Cost	2-6%
B. Distribution and selling costs	6%	Total Product Cost	2-15%
C. R&D costs	5%	Total Product Cost	2-5%
III. Annual Cost, $ year^{-1} = I + II			

Total Product Cost ($ kg^{-1}) = Annual Cost ($ year^{-1})/Production Rate (kg year^{-1})

Model* - computed in the process model

Table 3 Breakdown of manufacturing costs [10,000 MT year^{-1} of LiPF$_6$]

		P1	P2	P3
Manufacturing cost	$ kg^{-1} LiPF$_6$	29	26	20
Sale Price	$ kg^{-1} LiPF$_6$	31	28	22
Purchased equipment	$	25,931,100	20,808,900	26,925,300
Materials purchased	$ year^{-1}	90,800,000	71,322,300	72,449,700
Material recycling	$ year^{-1}	98,606,500	99,453,900	47,618,000
Operating labor	$ year^{-1}	1,974,100	1,969,000	1,969,000
Electricity	$ year^{-1}	2,045,500	1,419,000	2,349,600
Water	$ year^{-1}	469	221	134
Natural gas	$ year^{-1}	21,200	11,700	9,500

The cost of manufacturing LiPF$_6$ is the least for P3 ($20 kg^{-1} LiPF$_6$) as compared to P1 ($29

kg^{-1} LiPF$_6$) and P2 ($26 kg^{-1} LiPF$_6$). Assuming a profit of 7.5% on the total manufacturing cost

would raise the sale price of the LiPF$_6$ to $31 kg^{-1} LiPF$_6$ for P1, $28 kg^{-1} LiPF$_6$ for P2, and $22

kg^{-1} LiPF$_6$ for P3. Table 3 lists a breakdown of this manufacturing cost for all three processes

in terms of costs for equipment, materials procurement, labor, etc. for the baseline

production plant of capacity 10,000 MT year^{-1}. Smaller size and fewer number of equipment

needed, as shown in Figure 2 and discussed in the process description, results in a low

equipment purchase cost for P2 ($ 20.8M vs. $ 25.9M for P1 and $ 26.9M for P3). As

acetonitrile is used as the solvent in P3, instead of HF in P1, a solvent filter is used in place of

the crystallization tank. The size of HF processing equipment (i.e. moisture removal tank and

Evaporator 1) in P3 is smaller than that in P1 and comparable to that in P2. The pressures of

Reactor 1 and 3 in P3 are much lower than in P1. The lower pressure of Reactors 1 and 3 in

P3 (i.e. 5 bar and 5 bar vs. 27 bar and 10 bar in P1) increases the size of the equipment but

also reduces the overall cost of the equipment, because the equipment is designed for a lower

stress. These factors contribute together to bring the total purchased equipment cost of P3

almost similar to, yet less than that of P1. It is noteworthy to see that the cost of the Reactor

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3 systems (series of CSTRs) contributes up to 75-85% of the total equipment cost. Also, we notice from Table 3 that the cost of operating labor is similar, because the number of processing steps among the three processes is not significantly different.

Breakdown of Manufacturing costs ($/year)
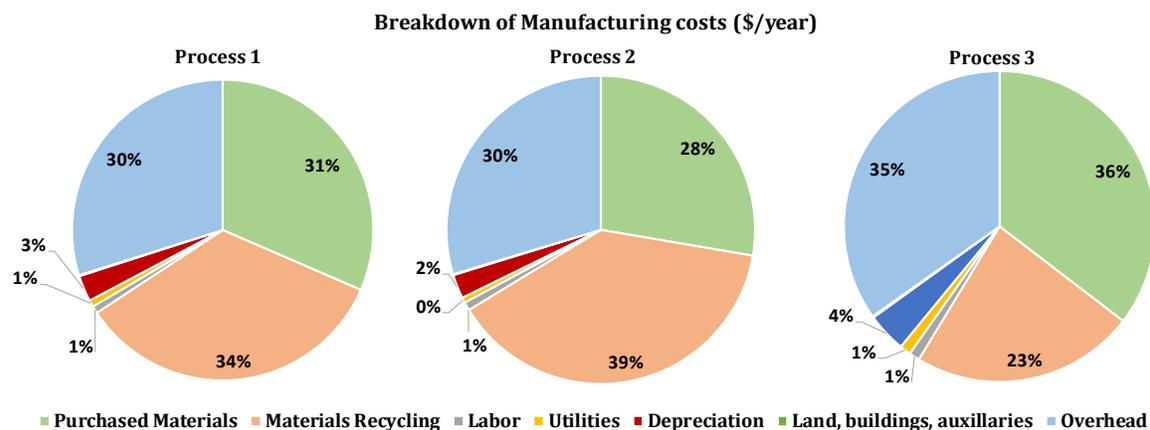
Figure 4 Breakdown of LiPF$_6$ manufacturing costs

Figure 4 shows that the cost of equipment (depreciation) and labor together account for less than 5% of the overall manufacturing costs in all three processes. The difference in the cost for utilities (electricity, water, and natural gas), shown in Table 3, follows our discussion presented in the previous section and collectively contribute to less than 1% of the manufacturing cost (Figure 4). The cost of purchasing raw materials contributes significantly to the manufacturing cost (31%, 28%, and 36% for P1, P2, and P3, respectively), as shown in Figure 4. Table 3 shows that the primary cause for the difference in manufacturing costs is the total cost of materials (purchased + recycled) for the three processes P1 ($19 kg^{-1} LiPF$_6$), P2 ($17 kg^{-1} LiPF$_6$), and P3 ($12 kg^{-1} LiPF$_6$). The cost of material recycling contributes significantly to this difference. Also, a lower cost of the solvent acetonitrile, relative to HF and liq. SO$_2$ is reflected in the difference of manufacturing costs. The cost of solvent recycling is estimated using separate spreadsheet-based process models for a representative process.

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Multiple methods are available for the purification and recycling of solvents. The cost of solvent recycling is subject to the uncertainty in the process selection and the prices of required materials. As the focus of this study is to estimate the cost of manufacturing $LiPF_6$, a representative recycling process is assumed using appropriate variation for each material. Appendix A presents a brief overview of the representative process considered for estimating the cost of solvent recycling in this study. For this assumed process, the cost of solvent recycling could vary from $0.5 - $6/kg of solvent recycled based on the price of ion exchange resin. The estimated costs of recycling HF, SO_2, and acetonitrile obtained from economic analysis of recycling process are $1.5, $2.0, and $0.5/kg of solvent recycled. The uncertainty in the price of solvent recycling and it significance to the overall cost of $LiPF_6$ points to the need for further study in understanding and reducing the cost of solvent recycling, and the importance of finding low cost solvents to reduce the cost of manufacturing $LiPF_6$.

5.3. Sensitivity analysis

Considering the significance of the cost of materials and solvent recycling, its impact on the overall cost of manufacturing is shown in Figure 5. The sensitivity of manufacturing cost to the cost of solvent recycling is shown in Figure 5 (a). The slopes indicate that P1 and P2 are more sensitive to the cost of solvent recycling than that for P3. The effect of material prices for the 3 key starting materials (i.e. HF, PCl_5, and LiCl) on the cost of manufacturing are as shown in Figures 5 (b) – (d). The cost of the product $LiPF_6$ is more sensitive to the price of PCl_5 than HF and LiCl. Clearly, the choice and price of raw materials is critical to the final cost of manufacturing.

The product cost for P1 is most sensitive to the price of HF (Fig. 5(c)), mainly because P1 uses much more solvent HF than the processes P2 and P3.
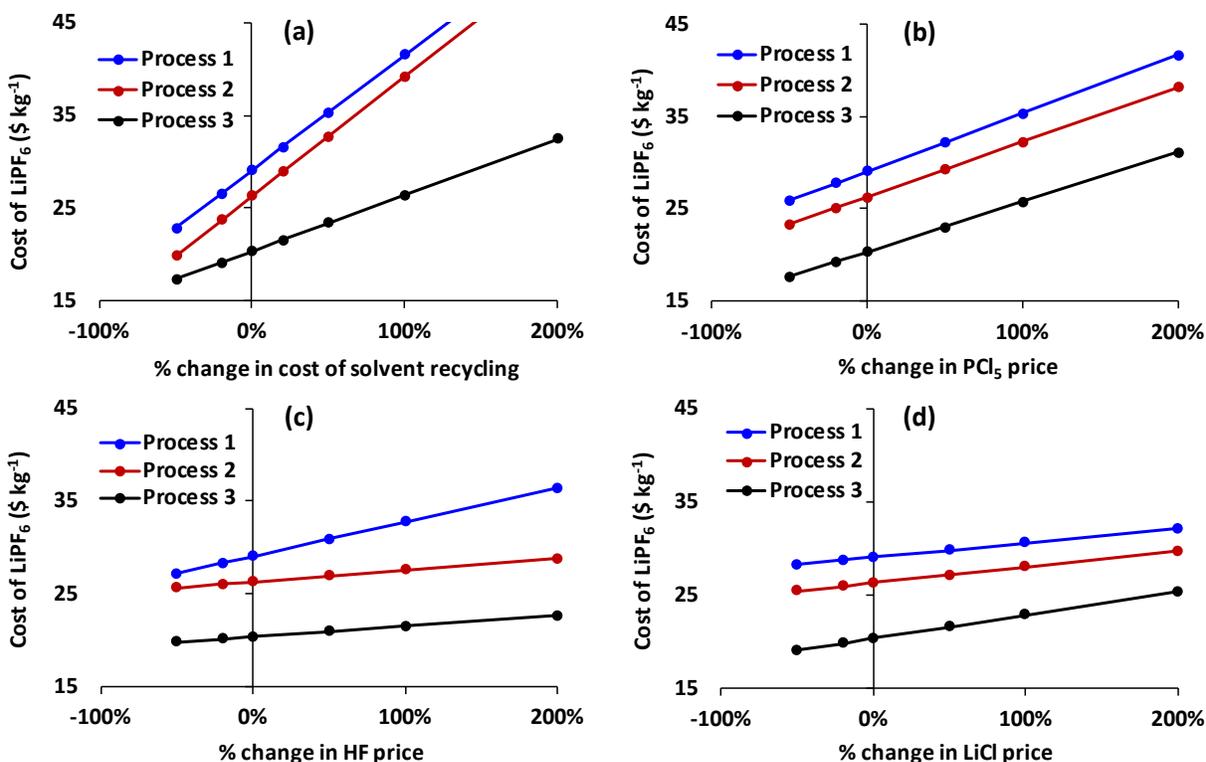

Figure 5 Sensitivity of manufacturing cost to material and solvent recycling prices

This study assumed that the raw materials were commercially purchased and so the $LiPF_6$ manufacturer has very little control on their prices. However, a production process for $LiPF_6$ that is integrated with the production of one or more of these raw materials will give the manufacturer control over the cost, but will require more capital investment. Such an integrated production will likely benefit from both economies of scale and process integration.
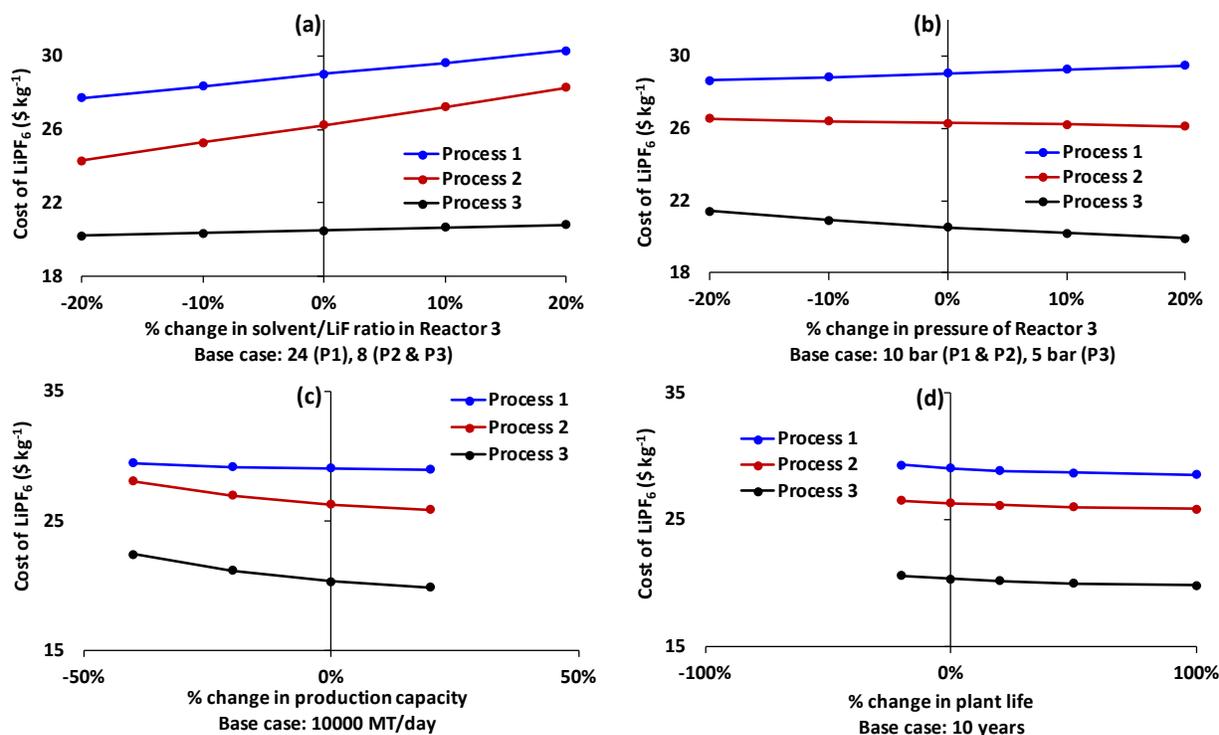
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Figure 6 Sensitivity of manufacturing cost to process and design parameters

The solvent to LiF molar ratios in processes P1 (20), P2 (8), and P3 (8) can be manipulated to significantly impact the cost of materials purchased (or recycled), equipment size, and processing load. The effect of changing solvent to LiF ratio on the cost of $LiPF_6$ shows, Figure 6(a), that a higher ratio (more solvent) increases the product cost. Of the three processes, P2 is the most sensitive to the solvent use.

Recall that lower pressure of Reactor 3 in P3, as compared to P1 and P2, resulted in its larger volume but lower cost. For this reason, the impact of change in pressure of Reactor 3 on the cost of manufacturing is further explored. Figure 6 (b) shows only a small effect of pressure on the cost of product. This is mainly because the change in pressure directly impacts the cost of equipment, and since that cost is spread over several years it accounts for < 4% of the manufacturing cost.

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To explore the impact of economies of scale and period of capital cost amortization, the sensitivity of production cost to production capacity and plant life is studied in Figure 6 (c) and (d), respectively. Although the change in the cost of manufacturing with change in either the production capacity or the plant life is apparent, it is not very significant. A 20% change in the production capacity results in less than 4% change in the manufacturing cost, as seen from Figure 6 (c). However, further reducing the production capacity to 40% reflects a bigger change in the cost of $LiPF_6$ of more than 10%.

5.4. Battery Pack Cost

BatPaC, the modeling tool developed at Argonne National Laboratory, enables the design of automotive lithium ion batteries, using specifications such as the energy storage capacity, the electrode chemistry combination, and a host of other parameters and constraints[3]. The model then estimates the cost of this battery when produced in large volume, typically 100,000 packs per year. The price of the electrolyte, hence the price of $LiPF_6$, is needed to determine the cost of the battery pack.

The following discussion relates to establishing the relationship between the price of $LiPF_6$ and the cost of a battery pack. For the purposes of this analysis, the battery pack was defined as made of NMC622-graphite electrodes, capable of storing 60 kWh of energy.

The default electrolyte used in BatPaC (called Gen2) consists of 1.2 M solution of $LiPF_6$ dissolved in a mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) in a ratio of 3:7 by weight. In addition to Gen2, three other electrolytes were also considered in this study. These are: E1 consisting of 1M solution of $LiPF_6$ in a mixture of EC and diethyl carbonate (DEC) in the ratio of 3:7 by weight; E2 consisting of 1M solution of $LiPF_6$ in equal parts by weight mixture of EC, DEC, and dimethyl carbonate (DMC); and E3 consisting of 1M

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solution of $LiPF_6$ in a mixture of EC, propylene carbonate (PC), and DMC in the ratio of 2:1:4 by weight. The cost of the four electrolytes (i.e. Gen2, E1, E2, and E3) are estimated for different costs of $LiPF_6$ and used as input to the BatPaC to determine the battery cost in $ kWh^{-1}. Figure 7 shows the effect of varying $LiPF_6$ cost on the cost of battery pack in $ kWh^{-1}. The slopes of the curves in Figure 7 show that the cost of the battery increases ~13 cents for every $1 increase in the cost of $LiPF_6$. The analysis of the $LiPF_6$ production in this paper indicated the cost of $LiPF_6$ to be in the range of $20-30 kg^{-1}. The default cost of the electrolyte solution used in BatPaC is $17 L^{-1}, which translates to ~$85 kg^{-1} of $LiPF_6$ (assuming the price of EC, DEC, DMC, and PC as $1.3, $2.1, $0.8, and $1.3 per kg, respectively), which leads to a battery cost of $8617 $pack^{-1}$.

A reduction in the cost of $LiPF_6$ from $85 kg^{-1} to $20 kg^{-1}, reduces the battery cost by ~$8 kWh^{-1} for Gen2 and ~$7 kWh^{-1} for the other electrolytes, *i.e.* E1, E2, and E3. A $8 kWh^{-1} or 6% savings in the cost of the battery would be a significant step in approaching the USABC target of $100 kWh^{-1}. Also, reducing the cost of $LiPF_6$ will be important once the costs of other battery components (e.g. active materials) are reduced. In terms of absolute cost savings, ~$7-8 kWh^{-1} savings are equivalent to ~$400 per battery pack, which amounts to ~$40M in annual savings for a plant producing 100,000 battery packs per year.
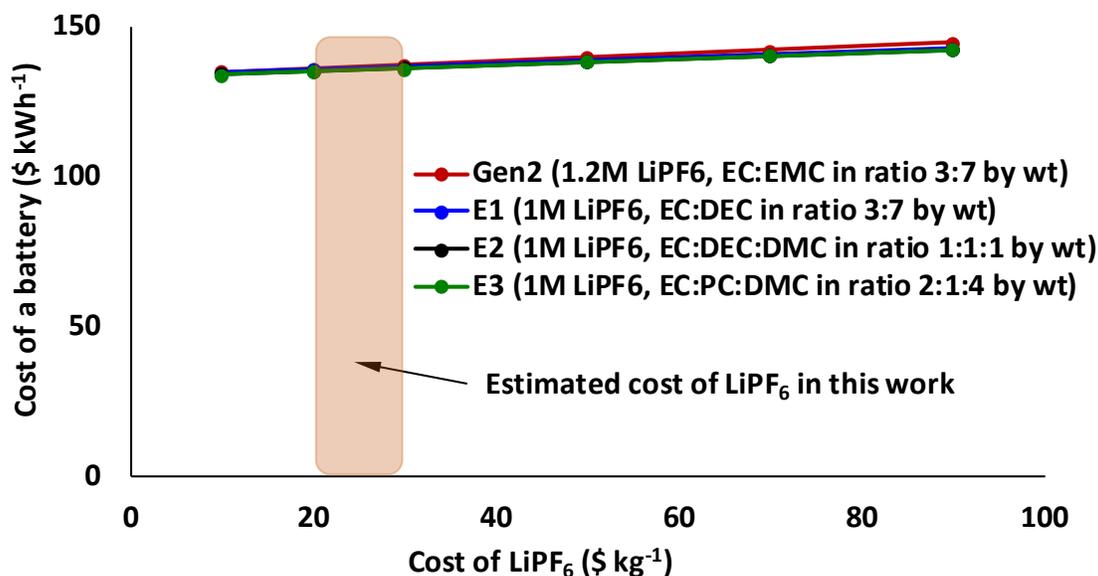
Figure 7 Impact of the cost of LiPF$_6$ on the cost of a 60 kWh lithium ion battery pack.
(NMC622-Graphite electrodes, plant capacity of 100,000 packs year^{-1})

5.5. Environmental analysis

Table 4 Breakdown of annual energy and water usage

Basis: 1 day & plant capacity: 10000 mtpa		Process 1	Process 2	Process 3
Electricity	kWh	51,201	44,910	89,013
Max. Temperature	K	283	283	303
Min. Temperature	K	243	243	263
Heating Duty	kWh	5,736	3,670	2,104
Cooling Duty	kWh	123,907	58,539	52,094
Water Requred	Gal	434	205	124

The environmental impact of the processes were compared based on emissions, electricity

used, heating and cooling duties for all three processes. Table 4 lists the heating and cooling

duties for the three processes, along with the electricity used and temperature ranges. It is

clear from the aforementioned discussions that the process volume and equipment

capacities for P3 are relatively higher than P1 and P2. As a result, more power is required for

the agitators and pumps in P3 and especially, for the agitator of Reactor 3. This is evident

from the electricity required for the three processes, as observed in Table 4. The cooling duty

is mainly controlled by the amount of fresh HF added to the process. As seen from Table 1,

P1 uses significantly higher fresh HF (83 MT day^{-1}) as compared to P2 (28 MT day^{-1}) and P3

(25 MT day^{-1}). This clearly results in higher cooling duty required for P1, as seen in Table 4.

Also, the load on evaporators is much higher in P1 as compared to P2 and P3, as seen in Table

1, which results in a higher heating duty required for P1. Water is used to heat the gaseous

products from Reactor 1 in all three processes. Since the heat load for this heat exchanger is

very low, the total water used for the production of $LiPF_6$ is insignificant to cause any impact

to the environment.

5.5.1. Cooling and Heating Methods

In the base case scenario of this study (Scenario A), the cooling load is assumed to be met by

using the grid electricity in a refrigeration cycle with COP = 3. It is further assumed that the

heating duty for evaporators is supplied by burning natural gas. For this scenario in all three

processes, the greenhouse gas (GHG) emissions were estimated using the GHG emissions in

CO_2 equivalencies calculator available on the webpage of Environmental Protection Agency

(EPA)[56]. Figure 8 shows the level of emissions for all three processes with three different

production capacities. Although P3 uses the least hazardous solvent (acetonitrile) as

compared to P1 (HF) and P2 (liq. SO_2), it has the highest emissions because it uses the most

electricity. For scenario B, it is assumed that the heating duty for all three processes is

primarily supplied by hot air, which is heated by using electricity instead of natural gas.

Table 5 lists the emissions for all three processes at different production capacities and both

scenarios. As the heating duties are relatively low, the difference in emissions between the

two scenarios is quite small (less than 4%).

Table 5 GHG emissions in equivalent CO_2 (MT day^{-1})

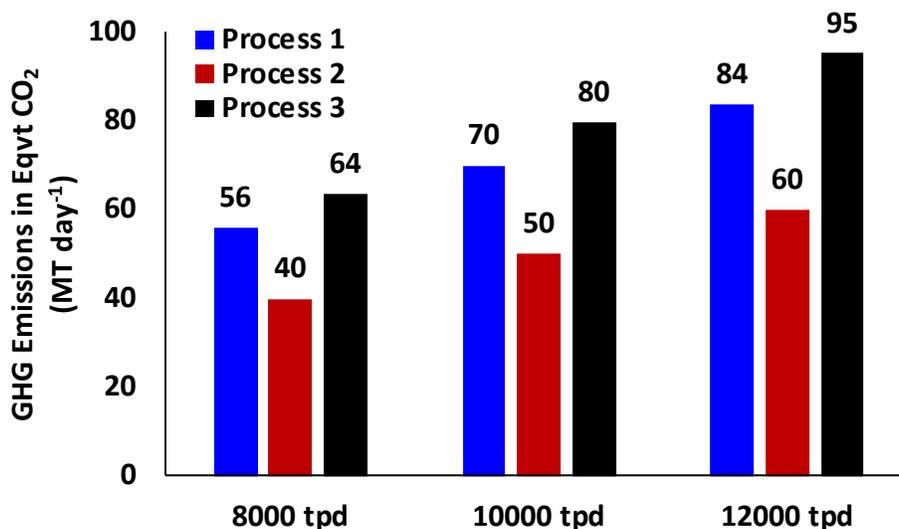|	8000 tpd		10000 tpd		12000 tpd	
	Scenario A	Scenario B	Scenario A	Scenario B	Scenario A	Scenario B
Process 1 (MT of CO_2/day)	56	58	70	73	84	87
Process 2 (MT of CO_2/day)	40	41	50	52	60	62
Process 3 (MT of CO_2/day)	64	65	80	81	95	97

Figure 8 GHG emission chart for the three processes at different plant capacities in terms of equivalent CO_2

Although P3 uses the least hazardous solvent of the three, it has the highest GHG emissions in terms of equivalent CO_2.

6. Conclusions

The production of $LiPF_6$ was studied to estimate the manufacturing cost, energy demand, and environmental impact. For this, detailed process models and flowsheets were presented for three different process pathways. Here, the primary difference among the three processes was the use of solvent, where the first process used HF as solvent while the other

two processes used liq. Sulfur dioxide and acetonitrile. Lithium chloride and phosphorus

pentachloride were used as the starting materials for all three processes.

The manufacturing cost of $LiPF_6$ with a baseline plant capacity of 10,000 MT day^{-1} was

estimated to be \$29 kg^{-1} of $LiPF_6$ for process 1, \$26 kg^{-1} of $LiPF_6$ for process 2, and \$20 kg^{-1}

of $LiPF_6$ for process 3. The main contributor to the total equipment cost is Reactor 3, which

was modelled as a series of CSTRs and accounts for up to 85% of the total equipment cost.

However, the cost of equipment contributes less than 4% of the overall manufacturing cost

of $LiPF_6$. The major contributors to the manufacturing cost (60 – 65%) are the cost for

procuring raw materials and the cost for solvent recycling. Further studies to explore

avenues for cost reduction in solvent recycling are recommended. The collective cost of

operating labor, utilities, and purchased equipment is < 10% of the manufacturing cost.

The parametric sensitivity study highlights that the manufacturing cost is very sensitive to

both the cost of solvent recycling and the price of raw materials (PCl_5, LiCl, and HF). Here,

cost of manufacturing for process 1 and 2 increases more rapidly with increase in the cost of

solvent recycling as compared to process 3. The process 1 was identified to be more sensitive

to the price of HF relative to others. An integrated synthesis approach for $LiPF_6$ along with

one or more of its raw materials will have a significant advantage in governing the raw

material prices and consequently, the cost of manufacturing. Reducing the amount of solvent

added to a reactor (i.e. solvent to LiF ratio in Reactor 3) reduces the cost of manufacturing.

This impact of solvent reduction is insignificant in process 3 because of the low cost solvent

used. The study of economies of scale (plant capacity) and amortization period showed the

effect is insignificant. However, for cases where production capacity was reduced below

20%, the manufacturing cost increases rapidly. The results show potential savings of ~\$8

kWh^{-1} (or \$40M year^{-1}) in the battery cost from the reduction in the cost of making LiPF$_6$, which will play a crucial role in achieving the target of \$100 kWh^{-1}.

Considering the environmental impact of producing LiPF$_6$, it was found that process 1 needs significantly more cooling (124 MWh vs. 58.5 and 52.1 MWh) because of handling larger quantity of HF (83 MT day^{-1} vs. 28 and 25 MT day^{-1}). Here, process 3 is the most and process 2 is the least energy intensive among the three with total electricity requirement of 106 MWh per day for process 1 and 64 MWh per day for process 2, as compared to 92.5 MWh per day for process 1. Consequently, process 3 is least environmentally friendly with GHG emissions in equivalent CO$_2$ of around 80 MT day^{-1}. To sum it all, process 3 is the most preferable method for producing LiPF$_6$, because it uses the least hazardous material (i.e. acetonitrile vs. HF and liq. SO$_2$) as the solvent and has the lowest manufacturing cost.

Acknowledgments

Abbreviations

AHF	anhydrous hydrogen fluoride
BEV	Battery Electric Vehicle
DEC	diethyl carbonate
EC	ethylene carbonate
PC	Propylene carbonate
EMC	Ethyl methyl carbonate
DEC	Diethyl carbonate
DMC	Dimethyl carbonate
DOE	U.S. Department of Energy
GHG	greenhouse gas
PTFE	polytetrafluoroethylene
USABC	U.S. Advanced Battery Consortium
CEPCI	Chemical Engineering Plant Cost Index
CSTR	Continuous Stirred Tank Reactor
GWh	Giga-watthour
NCM	Nickel Cobalt Manganese oxide

Appendix A. Material recycling process

The cost of removing moisture, impurities, and recycling different materials is estimated using separate spreadsheet-based process models. Out of the several plausible processes for material purification and recycling, a representative process as shown in Fig. A1 is assumed to support the techno-economic analysis presented in this study. Detailed economic analysis

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as presented in the manuscript is performed to estimate the cost of recycled materials. These cost estimates are used as inputs to the $LiPF_6$ production model. In order to understand the recycling process, an example of HF recycling in P1 is explained in the following. Similar strategy is adopted to estimate the cost of recycling other solvents in P2 and P3.

Spent HF is defined as the residual solvent sent to purification and recycling unit after its use in a unit operation. In P1, spent HF is obtained from reactor 1, evaporator 1, and evaporator 2. These different streams of HF are first condensed and cooled to the temperature of 273 K. The liquid HF is then subjected to a 2-stage ion-exchange unit filled with commercial ion-exchange resins. Some examples for such resins include the Dowex series
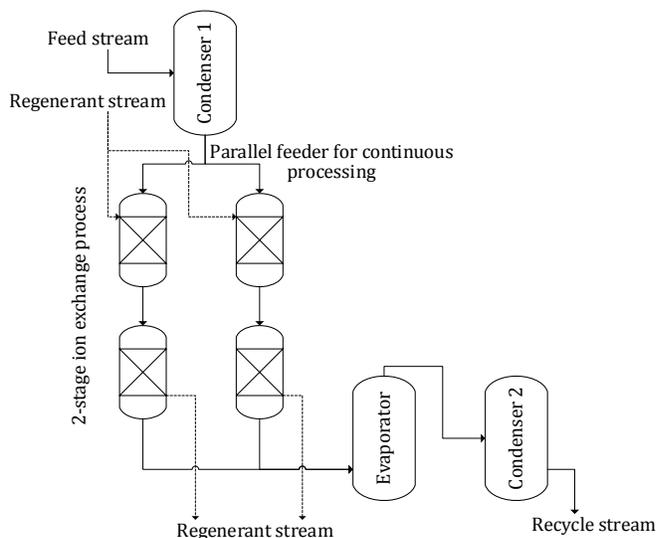
Figure A. 1Process flow diagram of an ion-exchange based process for solvent recycling

manufactured by Dow Chemicals Ltd. and Amberlite series manufactured by Rohm and Haas. Trace amount of metallic impurities accumulated in the solvent is removed in this stage. Multiple parallel lines of these 2-stage ion-exchange units are used to make the process continuous. In case of HF, the residence time of HF in each stage of the ion-exchange column is 1 h. The solvent from the ion-exchange step is evaporated and re-condensed to obtain a pure solvent, which is recycled to the respective process (P1, P2, or P3).

A cost estimation procedure similar to the one explained in the main text is followed to estimate the cost of purifying and recycling solvents. It was observed that the capital cost amounted to < 1% of the overall process cost. The major cost component driving the overall

cost of recycling is the cost of purchased materials, which is mainly governed by the price of commercial resin used. This cost analysis showed that the solvent recycling cost varies from $0.5 – 6/kg of solvent recycled, as mentioned in the main text of the paper. Within the uncertainties of assumed prices for materials (i.e. ion-exchange resins) the estimated costs for recycling HF, liq. SO_2, and acetonitrile are $1.5, $2, and $0.5/kg of solvent recycled.
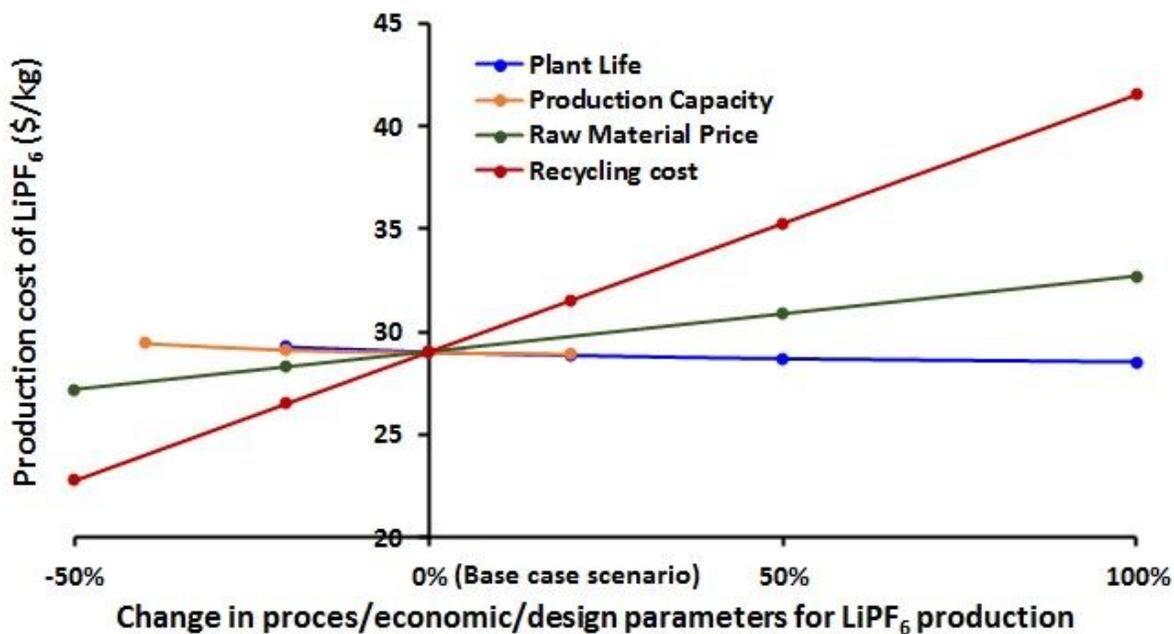
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Sensitivity of LiPF$_6$ production cost to various process, economic, and design parameters estimated from detailed techno-economic modeling of 3 different production processes.

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