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Analysis of fluoride compounds from Li-ion battery fires

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Abstract

Lithium-ion batteries are widely used and remain the dominant energy storage technology for modern electronics and electric vehicles. Despite their widespread adoption, these batteries pose safety risks, including fire hazards and thermal runaway. One aspect that has received relatively little attention in current research is the formation and impact of fluorinated compounds during battery degradation and thermal runaway events. This project aims to improve understanding of the role and formation of these compounds particularly hydrofluoric acid (HF) in lithium-ion batteries, through a comprehensive literature review complemented by a small scale simulation study. The main takeaways from the literature review are that thermal decomposition of LiPF_6 is central to HF formation, producing PF_5 , H_2O , POF_3 , and HF. The formation of HF induces a feedback cycle in which HF both forms from and accelerates further electrolyte breakdown. Electrolyte composition strongly affects these reactions. Solvent properties, especially permittivity, influence HF formation, with DMC showing higher thermal stability than EC, though EC is critical for solid electrolyte interphase formation. LiPF_6 modifies decomposition temperatures and gas evolution patterns. The main gas observed in thermal runaway are carbon oxides, hydrocarbons, fluorohydrocarbons, and oxygenated species. Radical reactions involving HF further contribute to fluorohydrocarbons formation, highlighting the complexity of these processes. Simulation results suggest that HF has no effect on ignition delay time but decreases flame speed, while CH_3F reduces ignition delay time and increases flame speed. Together, these findings emphasize the need for targeted strategies to control HF formation and mitigate its impact on battery safety.

Abbreviations

HF	Hydrogen Fluoride
LIB	Lithium-ion battery
EC	Ethylene carbonate
DMC	Dimethyl carbonate
DEC	Diethylene carbonate
TR	Thermal Runaway
NMC	Lithium nickel manganese cobalt oxide
LCO	Lithium cobalt oxide
LMC	Lithium methyl carbonate

Contents

1	Introduction	1
2	Methods	3
2.1	Literature review background	3
2.2	The battery	3
2.3	Simulation	5
3	Literature review	6
3.1	HF formation from the electrolyte salt	7
3.2	The electrolyte component chemistry	9
3.3	Gas emissions	11
3.4	Key findings from literature	11
4	Simulation result and discussion	12
4.1	Laminar Flame speed	12
4.2	Ignition delay time	14
4.3	Limitations	15
5	Conclusion	15
5.1	Outlook	16
	References	17

1 Introduction

The increased of usage of battery driven vehicles such as electric cars, bikes, scooters, etc., have made lithium-ion battery safety a larger concern. Those concerns include the risk for battery fire and thermal runaway. Where the increase in temperature can break down components of the battery, including the electrolyte which then can release harmful gases, which can trigger further combustion. This project's main focus is the formation, and accumulation of fluorinated compounds in lithium-ion batteries during fire and thermal runaway. Additionally, it examines how these compounds are formed through ageing processes and other damaging events.

Lithium-ion batteries (LIBs) are rechargeable batteries that utilise reversible reactions where lithium-ions intercalate, into an electric conduction solid, to store energy. These batteries are of particular interest in powering vehicles because of their valuable properties compared to other types of batteries. The properties includes higher specific energy, higher energy density, higher energy efficiency, longer cycle life, and longer calendar life compared to other batteries. The exact composition of the different components in a LIB can vary, but the general structure consists of a negative electrode (anode) conventionally made out of graphite, a positive electrode (cathode) made of either a metal oxide or phosphate, and an electrolyte consisting of organic solvent with a small amount of a lithium salt. [1]

Beyond this general structure there is a multitude of different types of LIBs that utilise different Li-ion cathode materials. Lithium cobalt oxide (LCO) offers high specific energy and is widely used in portable electronics, but its drawbacks include shorter cycle life, limited thermal stability, and modest power capability. Lithium manganese oxide (LMO) employs a spinel structure that lowers resistance and enables good current capability, while also providing improved safety and stability, though it suffers from reduced cycle and calendar life. LMO is often blended with nickel manganese cobalt (NMC) to combine stability with higher specific energy in electric vehicles. Lithium iron phosphate (LFP) has a high current rating, long cycle life, and good thermal stability, but has lower specific energy compared to other Li-ion batteries. NMC on its own combines high specific energy with balanced performance in power and safety, though it involves more complex material composition. Nickel cobalt aluminium (NCA) provides very high specific energy and power capability but requires careful management of safety and thermal behaviour. Lithium titanate (LTO), typically used as an anode material, delivers exceptional cycle life, fast charging, and high safety, but has a much lower energy density. [2]

There is also some alternatives to the lithium-ion battery that have similar good properties but in certain situations might be safer. One such alternative is Sodium-ion batteries. They are composed of a anode, cathode, electrolyte and separator. A positive thing with these batteries is that they can be discharged to zero volts making them safer to transport. However, two downsides is their lower energy density making one charge not last as long, current existing sodium-ion batteries has fewer charging cycles compared to LIBs. Furthermore, there are solid-state batteries that use solid electrolytes such as solid polymers and inorganic solid electrolytes. Their positives include higher energy density, faster charging charging cycles, and a lower risk of fire, but they are more difficult to produce economically in current battery producing facilities. Another option that still

utilize lithium are lithium-sulphur batteries, where the anode as lithium and the cathode has sulphur. The positive thing about these batteries are that sulphur is more abundant compared to the materials otherwise used such as nickel, manganese and cobalt, making them a more sustainable option. [3]

The purpose of the electrolyte in LIBs is to ensure the movement of the ions between the negative and positive electrode, where the Li^+ ions from the lithium salt are the charge carriers [4]. Because of the high energy density, the LIBs are sensitive to thermal events or thermal runaway. Thermal runaway is a chain reaction within the battery where an increase in temperature leads to the inner structure of the battery destabilizing and degrading, which in turn can result total failure of the battery. A general structure of the course leading to flame propagation of the battery i showed in Figure 1. The causing factor leading to a thermal runaway event can be mechanical, electrical and thermal abuse, all of which lead the battery to short-circuit, generating high heat causing a chain reaction. During the whole process, large amounts of flammable gas are released, increasing the pressure, making the battery at risk of explosion or fire. Along with the flammable gases there are also toxic gases being released, among which are fluorinated compounds. [5].

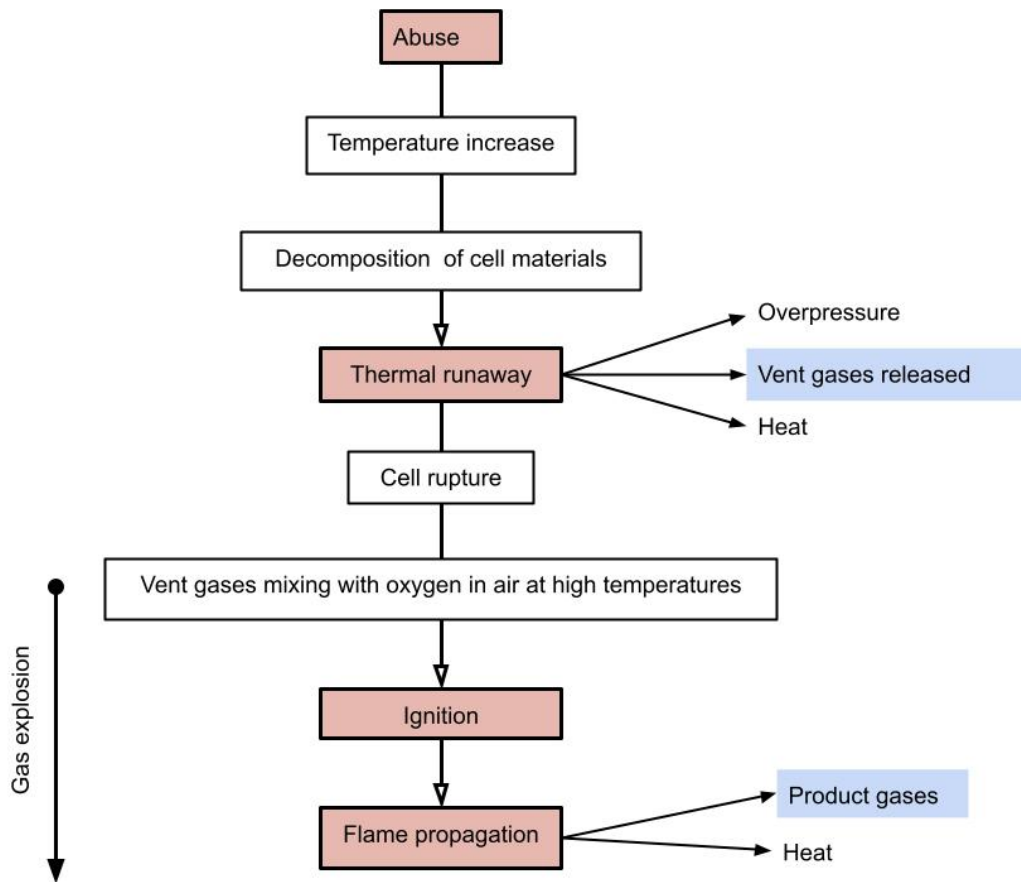


Figure 1: Flowchart of the battery breakdown process

The chemical processes involved in formation, decomposition and accumulation of fluorinated compounds from battery materials was investigated by performing a combined literature and simulation study. In existing literature there are different hypothesis regarding chemical reaction that lead to the formation of fluorinated compounds. Therefore a literature study was performed to get an understanding about what is known. This was done together with a simple simulation study to investigate the effect of different potential outcomes. The work was based on three objectives, the electrolyte leaking out at room temperature, electrolyte in gas form leaking out of a battery at around an environment of 200°C and lastly how HF is formed during full thermal runaway and fire in the battery. The simulations will be based of a 41Ah pouch-cell battery of the type NMC/LCO. The values for the battery such as the electrolyte composition, were based on experimental values from Essl et.al [6].

2 Methods

The method used in this project is a combined literature and simulation study to investigate formation of HF and fluoride chemistry regarding a specific LIB, from the study done by Essl et. al [6]. This was done by combining relevant general knowledge from other scientific articles and applying it to this specific case. Combustion simulations of ignition and flame propagation of gas mixtures that are released from the LIB was used to test different conditions and outcomes.

2.1 Literature review background

In the literature there are multiple hypothesis and multiple results for different reactions and different settings about how fluorinated compounds are formed, in particular HF. In this work different research was read to build an understanding of what is known about the course of these reactions and in what settings they occur. Most of the fluoride in the battery comes from LiPF_6 , therefore the focus was put on the fluoride from the electrolyte. The electrolyte can be released from the battery either from battery damage as liquid, and thereby HF could be formed from reactions outside of the battery, or the fluorinated compounds can undergo chemical processes inside of the battery and then be released as HF or as fluoroalkanes such as CH_3F . Another thing that was to be considered was the temperature in which these reactions happen, how the electrolyte impact the reactions, what would happen if the electrolyte was to be leaked into the environment and the impact water has if it comes in contact with the electrolyte. The literature of interests have been identified from the published article by Nilsson and Ahlberg Tidblad [7].

2.2 The battery

To have a good starting point for the simulations, the composition of the battery was taken from a study by Essl et al. to use as a reference point [6]. This particular battery was selected because of the extensive information given about the cell they investigated, something that is not as easily found in other literature. The information given from their article was used to calculate the gas composition that were used for the simulations, and to calculate the approximate amount of fluorinated compounds. In their experiments no

HF was measured. This was probably a result of their measuring equipment not being calibrated, and or optimized to detect HF. However, the assumption has been made that Fluorinated compounds must be present.

The battery in question is a fresh high energy density 41 Ah Li-ion pouch cell, designed for electric vehicles. They measured the total mass before any measurements to be 865g. The cell consisted of an electrode stack sealed in laminated foil, there was 22 anode layers made of copper foils coated with graphite of both sides, 21 cathode layers made of aluminium foils coated with a mixture of NMC. and LMO on both sides, and 42 separator layers with a coating of Al_2O_3 facing the cathode side. F was detected in both the anode and cathode materials

The electrolyte was a mix of EC, DEC and DMC with 1 mol LiPF_6 per litre. (One mole of LiPF_6 is solvated in every litre of the solvent solution) Essl et. al [6] measured the molar ratios in the solvent to be 48 % EC, 48 % DEC and 4 % DMC. They approximate 14 % of the initial mass to be electrolyte plus LiPF_6 meaning that there was 125g of electrolyte with 44g of EC, 59g of DEC and 37g of DMC.

The values of the mass given by Essl et. al [6] in their article together with the molecular weight of the different compounds was used to calculate the composition in moles, using the relation: $\text{moles} = \frac{\text{Mass}}{\text{Molecular weight}}$. The values for the electrolyte composition is summarised in Table 1. Where the amounts in moles and grams are from Essl et al. [6], and the molecular weight is from the calculations explained above.

Table 1: Composition of the electrolyte [6].

Chemical substance	Amount in moles	Grams	Molecular weight
Ethylene carbonate (EC)	0.50	44	88.06
Diethyl carbonate (DEC)	0.50	59	118.13
Dimethyl carbonate (DMC)	0.041	3.7	90.08
LiPF_6	0.0974	14.8	151.905

Table 2 shows the amounts of gas production measured by Ess et. al [6] during thermal runaway for both 100% and 50% State of charge (SOC), where SOC is the remaining charge in the battery.

For the combustion simulations, three different cases were considered in addition to the gas composition measured experimentally by Essl et al. [6]. For during thermal runaway at 100% SOC. The first assumes that no fluorinated compounds are formed, the second assumes that all fluoride originating from the electrolyte is released as HF, and the third assumes that it is released as a fluorocarbon, specifically CH_3F . These cases were evaluated in the context of the experimentally measured gas mixture in order to assess the potential influence of the release of different fluorinated compounds. Information from the article was used to estimate the maximum HF, or CH_3F that could have possibly been released from the battery. The total weight of LiPF_6 as previously stated is 14.8 g, the molar masses of the different compounds is stated in Table 3.

The ratio between F_6 and the total is then $113.9904/151.905 \approx 0.750$, and the mass of F_6 is $14.8\text{g} \cdot 0.75 = 1.11\text{g}$. The amount of F in moles is then $\frac{11.11\text{ g}}{113.9904\text{ g/mol}} \cdot 6 = 0.584\text{ mol}$.

Table 2: Amounts of gas products released during thermal runaway for 100 % SOC and 50 % SOC measured by Essl et. al [6]

Gas	100% SOC (cv/mol)	30% SOC (cv/mol)
O ₂	0.00	0.00
H ₂	0.53	0.02
C ₂ H ₂	0.00	0.00
C ₂ H ₄	0.14	0.02
C ₂ H ₆	0.02	0.00
CH ₄	0.08	0.00
CO	0.38	0.03
CO ₂	0.89	0.25
DEC	0.06	0.11
DMC	0.00	0.00
EC	0.00	0.00
EMC	0.00	0.00
H ₂ O	0.17	0.09
C ₆ H ₁₄	0.00	0.00
HF	0.00	0.00
C ₄ H ₁₀	0.03	0.00
C ₃ H ₈	0.00	0.00
Gas Amount	2.31 mol	0.53 mol

Table 3: The molar masses of the different compounds in the electrolyte salt

Compound	Molar mass
Li	6.941 g/mol
P	30.974 g/mol
F ₆	18.9984 g/mol x 6 = 113.9904 g/mol
Total LiPF ₆	151.905 g/mol

Table 4 shows the molar ratios that was used as input for the simulations for gas products released during thermal runaway. The baseline composition is the non zero values converted from the concentration of the gas products Essl et. al measured, presented in Table 2. The amount of moles of F was used to calculate the molar ratio for the fluorinated species cases. The molar ratios was calculated from the total sum, and taking the ratio to the total for each of the compounds. Since the molar ratio is based on the molar ratio of fluoride the values for HF and CH₃F will be the same.

2.3 Simulation

For the simulations, the chemistry simulation software ANSYS Chemkin Pro was used. ANSYS Chemkin is widely recognized in industry for modeling complex chemical reaction systems and has been validated for a broad range of chemistry applications, offering fast and reliable simulation performance [8]. In combustion studies, it is primarily used to determine combustion characteristics such as ignition delay, burning velocity, and flame structure, as well as to assess the influence of fuel composition. The software operates by reading a detailed chemical reaction mechanism, which contains the list of species,

Table 4: Molar ratios that used as input for the simulation for gases released during thermal runaway.

Species	Baseline composition	Fluorinated species input
C ₂ H ₄	0.061	0.056
C ₂ H ₆	0.009	0.008
C ₄ H ₁₀	0.013	0.012
CH ₄	0.035	0.032
CO	0.165	0.152
CO ₂	0.385	0.356
DEC	0.026	0.024
H ₂	0.229	0.212
H ₂ O	0.074	0.068
HF/ CH ₃ F	—	0.082

elementary reactions with Arrhenius rate parameters, and thermodynamic data in NASA polynomial form. Using this information, Chemkin constructs and solves a system of coupled ordinary differential equations that describe the time-dependent evolution of temperature and species concentrations. Thermodynamic data are used to calculate equilibrium constants and enthalpy changes, while reaction rate coefficients govern the progress of individual reactions. In flame calculations, transport properties such as diffusion and thermal conduction can also be included. Outputs typically consist of species concentration profiles, ignition delays, flame speeds, and temperature histories, providing detailed insight into the kinetics and dynamics of the reacting system.

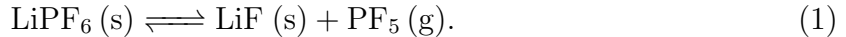
The chemical reaction mechanism applied in this work was the detailed kinetic mechanism developed by Nilsson et al. [7]. Calculations of the burning velocities of freely propagating premixed flames were performed using the PREMIX module in Chemkin. For these simulations, curvature and gradient parameters were set to 0.05 and 0.05, respectively, resulting in a computational grid of 300–450 points. Homogeneous ignition was simulated as a constant volume case using the SENKIN module, which integrated the governing kinetic equations until ignition was reached. These simulations provided predictions of flame propagation characteristics and ignition delay times for the studied fuel mixture.

3 Literature review

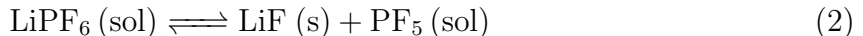
The purpose of this literature review is to gain understanding about how LiPF₆ decomposes and leads to the formation of HF in LIBs. Moreover, how these processes are affected by differing temperatures, what type of solvent is used for the batteries, and how the chemistry is altered by the present of water contaminants. Different settings in which HF can be formed are also of interest. One pathway is the electrolyte leaking out from the battery reacting with water, producing HF. Another is through reactions inside the battery itself, caused by water contamination during assembly. HF can also be generated and released as vent gases during thermal runaway, influencing the course of the event. During flame propagation or a battery fire HF may appear among the combustion products. The last setting involves HF formation occurring in oxygen-free conditions.

3.1 HF formation from the electrolyte salt

The most common salt used in LIBs is Lithium hexafluorophosphate, (LiPF_6) [9]. The reason for this is good electrochemical properties such as it's big electrochemical stability window, chemical inertness and high ionic conductivity [4]. LiPF_6 can thermally decompose and form the Lewis acid PF_5 . [9–12]:



LiF is insoluble in the organic electrolyte so in the context of the LIBs a more accurate representation would be the following, where LiPF_6 , and PF_5 are dissolved in the electrolyte while LiF remains precipitates as a solid phase [13].



Tebbe et al. [11] found this to be an equilibrium reaction and concluded that based on activation barriers it is also very likely for the products to react in the reverse reaction. However, they also concluded because LiF is insoluble in the organic electrolytes, the precipitations (i.e., the solid formation and settling out of LiF) of the LiPF_6 drives the reaction more forward compared to the expected amounts from the equilibrium equation. They found that this reaction start to happen at around 116°C . This also coincided with that Solchenbac et al. [14] found that the endothermic threshold for this reaction happens between 100 and 200°C depending on the conditions. Moreover, Sloop et. al [13] also found that because LiF is insoluble in the electrolyte the equilibrium position is determined by reaction temperature and pressure of PF_5 .

In addition to LiPF_6 thermically decomposing it can also react with H_2O [10]

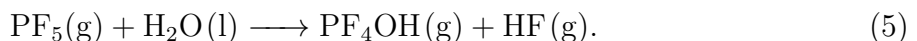


The source of the water could be: initial impurities in the processing of the battery, a result of normal usage, or from the environment if the electrolyte were to leak out [15]. Tebbe et al [11]. found this reaction to be endothermic for organic electrolytes with water impurities. Furthermore the hydrogen fluoride produced can further degrade components of the battery leading to more water impurities essentially creating a cycle [1]. Kawamura et al. [15] concluded that one LiPF_6 molecule reacts with two or more water molecules in the organic solvent.

The PF_5 formed in reaction 2 can further interact with these water impurities in a two step reaction [1, 11, 12]



Bertilsson et.al [12] found no resulting increase in the measured PF_5 which they concluded means that this part of the reaction happens very quickly, they also found that the range for when this starts to happen is around $100^\circ\text{C} - 170^\circ\text{C}$. Because of the low concentration of PF_5 in electrolyte and how its quickly it was consumed by hydrolysis Kawamura et. al [15] found PF_5 difficult to detect. The low concentration also suppressed the reaction with water in the electrolyte. The first step of reaction 4 is PF_5 being consumed by hydrolysis [11]

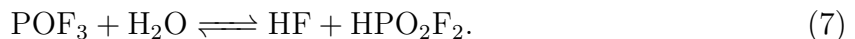


Tebbe et al. [11] suggested that this reaction is sluggish based on the values for activation energy of PF_5 and the low concentration of PF_5 . The second step of this occurs from decomposition of the PF_4OH .

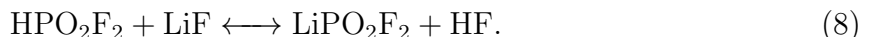


Tebbe et al. found that this reaction has a significantly lower reaction barrier compared to Reaction 5 since it only involves breaking a hydrogen bond.

Solchenbach et. al [14] inquired the conditions to produce PF_5 and POF_3 , and the effect of water containments. By measuring the amounts of them released from a dry and wet battery. Even with a drying set-up they still saw signs of PF_5 reacting with water to form POF_3 through reaction 4, pointing to high reactivity with water. With water added they saw a mass loss of 49 % compared to the theoretical 83 % based on reaction 3. Furthermore, They concluded that there is another thermally stable species, in addition to LiF . They found an option for their experiment is for HPO_2F_2 , that forms through



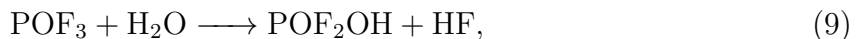
and then the HPO_2F_2 reacts with the rest of the LiF in the following reaction



The product LiPO_2F_2 has a melting point of 360 °C and therefore does not thermally decompose under the experimental conditions, remaining as a stable solid and contributing to the final mass observed.

Solchenbach et. al [14] also compared the decomposition both when drying, and wetting the battery. They found that the dry LiPF_6 has a decomposition onset temperature of 165 °C, resulting product that was measured was PF_5 , HF and POF_3 from water impurities in the experiment. For the wet LiPF_6 the onset temperature is dropped to 90 °C and the main measured products was then instead POF_3 , HF , and LiPO_2F_2 . They were not able to differentiate PF_5 from POF_3 in their OEMS experiment.

Another alternative way for POF_3 to react with water is



that can in turn decompose further as either



or



POF_3 can decompose further in different ways



Kawamura et al. [15] studied the decomposition of LiPF_6 with water by measuring amount of water after storage at low temperatures. Part of their objective was to estimate the amount of PF_5 in reaction 1, The PF_5 comes from dissociation of non ionized LiPF_6 in

the electrolyte. Because of the very small amounts of PF_5 , and its high reactivity meant Kawamura et al. found it difficult to evaluate the concentration of PF_5 in the electrolytes. Therefore Kawamura et. al tried to find a empirical formula to describe it, using 1 and reaction 13 below.



Kawamura et al [15] did so by estimating the the reaction mechanism for how LiPF_6 reacts with water in reaction 3. They tried to apply the first order equation

$$-\frac{d[\text{H}_2\text{O}]}{dt} = k[\text{H}_2\text{O}][\text{LiPF}_6]. \quad (14)$$

This describes how quickly the water concentration decreases with time when water reacts with LiPF_6 , and the reaction constant k influence how quickly it happens. Kawamura et. al [15] found that their results did not fit the first order approximation, from the findings they concluded it probable that two or more water molecules reacts with one LiPF_6 in the solvent. Moreover they tried to apply a competitive successive reaction model if reaction 4 and reaction 9 happens simultaneously. However, this also did not fully fit their results. Kawamura et. al concluded that the mechanism between LiPF_6 must be complex, because both the degree of dissociation and electrolyte dissociation must be considered.

Kawamura et. al did find however, that their results could be matched up to first order approximation for the start of the reaction. Finally, They found that their experiment agrees with

$$-\frac{d[\text{H}_2\text{O}]}{dt} = k[\text{H}_2\text{O}]^2[\text{LiPF}_6]. \quad (15)$$

Moreover, kawamura et.al found the values for the rate constants at 30 °C over a long timespan to be, $2.2 \cdot 10^{-4}$ for PC+DEC, $1.6 \cdot 10^{-4}$ for PC+DMC, $7.8 \cdot 10^{-5}$ for EC+DEC, and $6.7 \cdot 10^{-5}$ EC+DMC. Concluding that the order of reaction rates are $1 \text{ M LiPF}_6/\text{PC} + \text{DEC} > 1 \text{ M LiPF}_6/\text{PC} + \text{DMC} > 1 \text{ M LiPF}_6/\text{EC} + \text{DEC} > 1 \text{ M LiPF}_6/\text{EC} + \text{DMC}$, which is inversely related to the dielectric constants of the solvents.

3.2 The electrolyte component chemistry

The electrolyte type that is of interest for this project is Lithium salts based organic carbonate electrolytes. These electrolytes are typically made up of linear carbonates such as DMC, DEC and EMC, together with cyclic carbonates such as EC and PC. EC is of particular importance because it forms a solid electrolyte interface (SEI) at the surface of the low-potential anode materials when it breaks down electrochemically, enabling the usage of graphitic carbon in the LIBs anode [4]. Because of the characteristics of both the linear and the cyclic carbonates combining them helps reducing harmful gaseous products formed during fire, particularly in a setting with a lack of oxygen [4]. The addition of the lithium salt changes the chemistry of the solvent, both physically and electromechanically characteristics [4].

The different organic carbonate solvents used for LIBs can influence the reaction kinetics between LiPF_6 with water. It could affect the chemical reaction rate, depending on the difference in reaction rates of different solvents, it could potentially even affect the full reaction mechanism [15].

Sloop et al. [13] found that ring opening polymerization of LiPF_6 produce LiF and PF_5 gas in reaction 2, even at temperatures below the decomposition temperature of 200 °C. In a solution of EC/DMC, Sloop et. al [13] found that because LiF is insolvable in the electrolyte LiPF_6 and PF_5 determine the equilibrium position in reaction 1. They found that the equilibrium shifts to the products when the PF_5 reacts with the solvents. Moreover, the evidence suggesting that the thermal decomposition of LiPF_6 can involve ring opening polymerization initiated by PF_5 is in agreement with Tebbe et. al [11] who stated similar findings.

Kawamura et.al [15] investigated the solvent effects and reactivity between LiPF_6 and water at 10°C, 20°C and 30°C . The solvent effect refers to how variations between solvents can influence chemical equilibrium and reaction rates. In some cases, even the reaction mechanism itself may change, depending on properties such as viscosity, permittivity, and solvation. They investigated the viscosity and permittivity of the carbonates EC, PC, DEC and DMC. They concluded that the order of viscosity in room temperature for the different electrolytes are the following: $\text{DMC} < \text{DEC} < \text{PC}$, where EC is solid at room temperature. Furthermore, they found that at 20 and 30 °C viscosity did not affect the reactivity between LiPF_6 and water. They found that permittivity had a bigger effect compared to viscosity. When the organic solvent nonionized LiPF_6 reacts with water, larger permittivity means less nonionized levels of LiPF_6 which in turn means that the larger permittivity makes it harder for the the LiPF_6 to react with the water. Speed of the reaction also depends on temperature. [15]. They also found that that was no reaction in the solvent EC+DMC at 0 °C.

Kawamura et al. [15] focused on the viscosity and permittivity for different electrolytes and concluded that although electrolyte with larger viscosity should make it more difficulty for LiPF_6 to react with water, the impact of the viscosity was seemingly low and did not greatly effect how LiPF_6 reacts with water. What can be seen to have an effect is the relative permittivity of the mixed solvents, the permittivity decreases in the following order $\text{EC} + \text{DMC} > \text{EC} + \text{DEC} > \text{DC} + \text{DMC}$. They essentially found the larger the permittivity is the more difficult it is for the reactions with the salts to occur, making permittivity more important then viscosity. Kawamura et al. [15] found the order of the reaction rates for the different solvents are in the inverse order of their dielectric constants. From this they concluded that solvents with high electric constants suppress the reaction between LiFP_6 and water

Sloop et. al [13] also investigated the relation to the different organic electrolytes, and found that DMC has better thermal stability compared to EC. Their results propose that the preferred path for the PF_5 to take is to react with EC.

Lamb et al. studied different solvents and how they decomposed both isolated, and with the LiPF_6 salt added [10]. They also found DMC to be the most stable, and found the stability to be unchanged when with the added salt, with little gas produced for both.

When isolated found low levels of gas evolution around 130 °C and 140 °C but stable after. With DEC it was found to have a similar progression up until liquid-vapour pressure equilibrium at around 180 °C, after which it undergoes thermal decomposition starting at 305 °C. DEC with the salt present was found to be considerable more unstable with the decomposition onset temperature down to 170 °C, and with the salt it undergoes close to complete decomposition. EC as a solvent is almost always included [10], and without the salt they found evidence of EC decomposition temperature to be 190 °C, with the salt the EC undergoes a sharper transition, with full decomposition promptly after reached onset temperature. For EMC they found no sign of decomposition until rapid decomposition at around 170 °C. [10].

3.3 Gas emissions

To get a context of when the fluorinated compounds can be formed, have to look at other gases that are produced when the electrolytes thermally decompose. Liao et al. [1] experimentally evaluated gas emissions from thermal decomposition of 1 M LiPF₆ in an EC/DMC (1:1 v:v) electrolyte. They identified an exothermic threshold at 183 °C. Above 215 °C, gas evolution increased sharply suggesting that more complex electrothermal reactions dominate at higher temperatures.

At 230 °C Liao et al. [1] saw that significantly more gas species were emitted compared to 155 °C, and decomposition continued to intensify with temperature. The highest CO₂ release occurred around 300 °C in 60 minute experiments. The main gaseous products were carbon oxides, hydrocarbons, fluoroalkanes, and smaller amounts of C₂H₄O₂ and C₂H₆O. They proposed that free lithium ions and electrons can break solvent alkyl bonds, generating CH₃·, C₂H₄, and C₂H₆ radicals. These hydrocarbon radicals then react with fluorine containing species from LiPF₆ decomposition to form fluoroalkanes. For example, a decrease in C₂H₄ volume concentration coincided with a large increase in C₂H₅F at 300 °C, indicating that HF reacted with C₂H₄ to form C₂H₅F.

They further suggested a cyclic process: HF breaks down LiPF₆, producing more HF through hydrolysis with water. Meanwhile, oxygen- and hydrogen-containing gases generated during electrolyte decomposition can react further to form water, which then sustains hydrolysis of LiPF₆. Finally, Liao et al. concluded that the gases formed during electrolyte decomposition closely resemble those detected during full thermal runaway in LIBs with similar electrolyte compositions.

3.4 Key findings from literature

The literature consistently shows that the decomposition of LiPF₆ is central to HF formation in LIBs. Thermal decomposition produces PF₅, which is highly reactive and difficult to detect because it is quickly consumed, primarily through hydrolysis with water to form POF₃ and HF. The insolubility of LiF drives the equilibrium toward further decomposition, especially above 100 to 200 °C. Water plays a critical role: whether as residual impurities, introduced during battery assembly, or formed in situ during decomposition, it lowers onset temperatures and can create a feedback cycle where HF both arises from and accelerates further salt breakdown.

Electrolyte composition strongly influences these processes. Solvent properties such as permittivity affect both reaction rates and mechanisms, with higher permittivity generally suppressing HF formation. Among the carbonate solvents, DMC exhibits higher thermal stability, while EC, though less stable, is essential for SEI formation. The addition of LiPF_6 modifies these stabilities, often reducing decomposition onset temperatures and altering gas evolution patterns.

Gas analysis studies highlight that electrolyte breakdown produces a mixture of carbon oxides, hydrocarbons, fluorohydrocarbons, and oxygenated species, with emissions intensifying sharply above 200 °C. Radical chemistry particularly the interactions of HF and hydrocarbons further contributes to fluorohydrocarbon formation. Importantly, many of these products mirror those observed in full thermal runaway, suggesting that electrolyte decomposition experiments can serve as a reference case for understanding fire and vent-gas scenarios.

The reviewed work reveals HF as both a product and driver of electrolyte degradation, linking salt chemistry, solvent effects, impurities, and high temperature gas evolution in a self reinforcing cycle. This makes HF central to understanding both the degradation processes during normal ageing and the hazards associated with thermal runaway and combustion in LIBs.

4 Simulation result and discussion

In this section the result for laminar flame speed and ignition delay time from the simulation study will be presented and discussed. The simulations used values for the combustion products determined experimentally by Essl et al. [6] together with theoretical values for added HF and CH_3F .

4.1 Laminar Flame speed

Laminar flame speed refers to the rate at which a flame front propagates through a pre-mixed air–fuel mixture. It is an important because it varies depending on what material is burning and under what conditions. For example, whether combustion occurs inside an intact battery or after electrolyte leakage. The electrolyte composition strongly influences combustion behaviour since it alters several physical and chemical properties. Here HF has a potential to be influential because it is highly reactive and may significantly affect flame propagation. Higher flame speeds generally indicate a greater tendency for unstable combustion pathways, meaning that the specific compounds involved can determine whether the situation is more or less severe than expected.

Figure 2 shows simulated the relationship between flame speed and equivalence ratio. The data is presented for scenarios without any fluorinated compounds and with the addition of HF, and CH_3F respectively.

For all three cases the the flame speed increases with equivalence ratio until al reaches a maximum around $\phi \approx 1.1$. Among the three cases, the case that includes CH_3F in the simulation reaches the highest peak and overall higher flame speed. While HF reaches

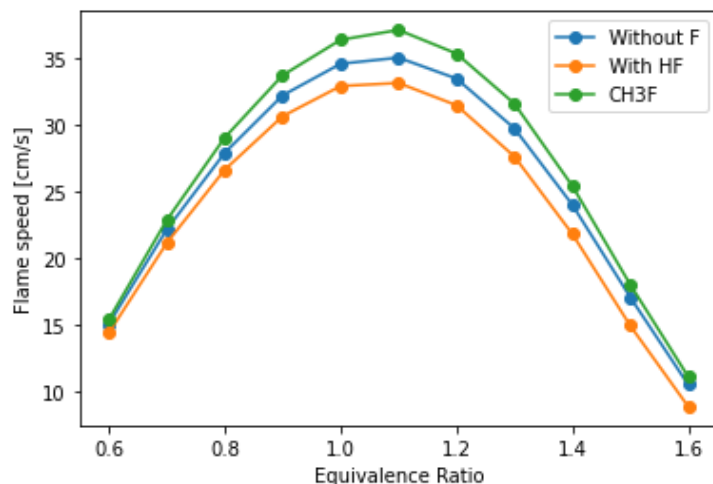


Figure 2: Relationship between laminar flame speed and equivalence ratio.

the lowest. The speed of CH_3F reaches about 40 cm/s, nothing added about 35 cm/s, and the HF slightly under that at around 32 cm/s.

The varying equivalence ratio shows that flame speed is highest slightly above 1, close to stoichiometric conditions where fuel and oxygen are present in the correct proportion. Flame speed decreases for both lean mixtures ($\phi < 1$) and rich mixtures ($\phi > 1$). The selected range of ϕ values was broad enough to capture different behaviours while remaining within the simulation's time constraints. In more isolated cases, such as inside a battery, limited oxygen supply can lead to richer mixtures, whereas in open air the mixture tends to be lean. The resulting curve aligns with expectations, showing a peak in flame speed near $\phi \approx 1.1$ for hydrocarbons.

This behaviour of the different fuel mixtures can be explained by differing behaviours for and CH_3F in high temperatures regarding radical chemistry. HF can be involved in multiple chain-terminating reactions consuming radicals such as $\text{OH}\cdot$ and $\text{H}\cdot$, while CH_3F instead contribute to the formation of more radicals, such as $\text{CH}_3\cdot$ and $\text{F}\cdot$. A few fundamental reactions HF is involved in are the following:



Something to be added here is the fact that HF can further break down LiPF_6 which releases more HF then in turn would slow down the process even further.

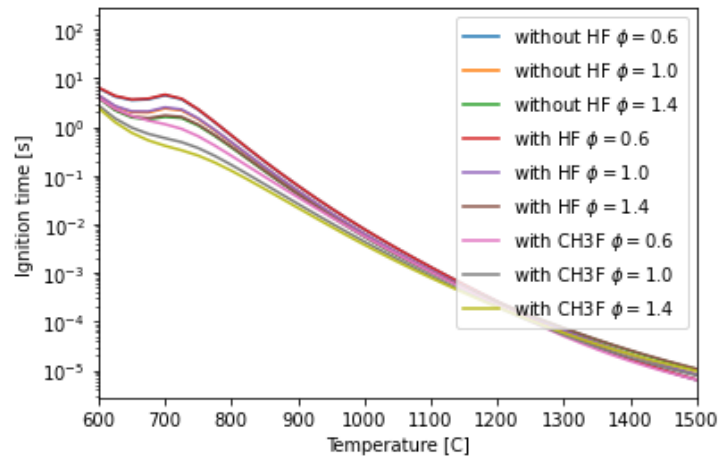
Something that is relevant for flame speed is how the solvent impact the reactivity. As both Kawamura et. al [15] and Sloop et. al [13] pointed out the type of solvent can

drastically change things like reactivity and decomposition temperature.

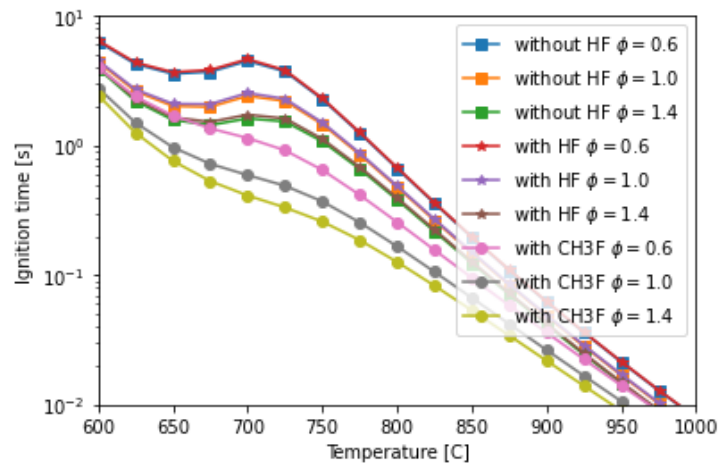
4.2 Ignition delay time

Ignition delay time (IDT) is the time that it takes for a fuel and oxidizer mixture to ignite for a certain temperature and pressure [16]. This is an important parameter for LIBs because it determines how fast the species ignite and therefore gives insight to the likelihood of fire and thermal runaway.

Figure 3 shows the relationship between ignition delay time and temperature similarly from before, simulation of combustion products determined by Essl et al. [6], simulated for three cases: as they are, with HF added, and CHF_3 added. For all three done for equivalence ratio $\phi = 0.6, 1.0, 1.4$. Figure 3a shows the full temperature interval, while Figure 3b shows a temperature interval between 600 °C and 1000 °C for better visibility.



(a)



(b)

Figure 3: Ignition delay time for equivalence ratios 0.6, 1.0 and 1.4 without HF, with HF and with CHF_3

The figure generally illustrate a small peak in ignition time at 700 °C, where for no F and HF has it is more defined compared to CHF_3 . One can also see that CHF_3 lowered the

ignition delay time with around one magnitude, while HF had seemingly no effect.

Since HF requires other compounds to decompose before it can participate in radical reactions, its presence does not affect ignition time, as those reactions have already occurred by the time HF is involved. Compared then to the CH_3F that has weaker bonds compared in particular to methane, which has the highest molar ratio after CO_2 and CO , and is more unstable contributing to quicker ignition. Moreover, CH_3F contributes to other pathways and the potential of other radicals forming. However they partly should if it decomposes into F, then those partake in the some of the same radical reactions as HF.

The differences between the three cases, for both flame speed and ignition time are not very large and represent only a small part of the overall picture. Kawamura et al. [15] showed that the choice of solvent adds significant complexity, which is not accounted for in these simulations. The simulations also assume a homogeneous setting, while real systems are less uniform.

4.3 Limitations

In general, this is a highly uncertain field where much ongoing research is still developing, and as a result, parts of the literature may be inaccurate or imprecise. As previously mentioned, detecting certain compounds particularly HF and highly reactive species such as PF_5 is very challenging. This highlights the need for more targeted experiments in which setups are carefully calibrated for specific conditions before drawing conclusions about the broader picture.

Because this is an active research area, it is also possible that relevant and potentially contradicting studies have been published after the timeframe considered here. Most of the reviewed articles were published within the last 20 years, with half of them within the last 5 years, meaning that some perspectives may already be outdated or incomplete.

Another potential source of error lies in the interpretation of the literature itself. Important details may have been overlooked, overemphasized, or simplified in the process of summarizing, which could obscure a more nuanced understanding of the topic.

Finally, while the simulations presented provide useful insights into certain effects of HF, they remain simplified representations and cannot capture the full complexity of the processes involved.

5 Conclusion

This review analysed the effect of fluorinated compounds during lithium-ion battery fire, by doing a combined literature review and small simulation study. LiPF_6 thermal decomposes in organic electrolytes to form mainly PF_5 that reacts with water to form POF_3 and HF. Decomposition start to happen at between 160°C to 200°C or depending on setting and measuring setup. The decomposition of PF_5 seems to be very complicated. Products including PF_5 and HF being difficult to detect complicate the way to quantify the amounts that are being produced during thermal decomposition. Something that plays an important role for the decomposition of the is water impurities, where water is essentially

necessary for the formation of HF. Something that impacts both decomposition and how well hydrolysis happens is the type of electrolyte. More in particular what type of solvent is used. At the same time the chemistry of the solvents can also be altered by the presence of LiPF_5 , where the most stable solvent is DMC that seemingly have the same attributes whether the salt is solvated in it or not. The polarity of the solvents seem to be more important compared to viscosity, particularly close to room temperature. Hydrogen fluoride plays a particularly complex role, as it can decompose the salt to generate additional HF, creating a self-sustaining cyclic process.

The main gas products are carbon oxides, hydrocarbons, and fluorinated species. Their composition and amounts depend on temperature, solvent type, and water content, with higher temperatures favouring more reactive and fluorinated species. In particular, HF formation promotes further decomposition, highlighting its central role in the gas evolution during battery abuse or thermal runaway.

Simulations showed that HF lowered the the flame speed, and had seemingly no affect on ignition delay time. CH_3F instead increased the flame speed and lowered the ignition delay time. This implies that if HF is one of the gas products it could lead to a less volatile situation. Compared to CH_3F that could escalate it with the higher flame speed it would propagate faster through the fuel which means it could spread faster, and with a faster ignition speed there could be less time to take action in a dangerous situation such as putting out a fire. Although HF is reactive its presence can stabilize the gas mixture creating an interesting situation where the evolution of the flame may be slowed down.

5.1 Outlook

To strengthen this project, it would be valuable to expand the simulations to include a broader range of species as well as combinations of species. However, this would require a more detailed understanding of how these compounds interact in order to better estimate the ratios of gases produced. Achieving this understanding calls for studies that focus specifically on detecting and quantifying individual species particularly highly reactive ones such as HF, PF_5 , and POF_3 . These compounds are often overlooked in experimental studies, yet they have demonstrated measurable effects, and it remains unclear whether their presence ultimately increases the overall hazard.

Another important step would be to extend both simulations and experimental measurements to lower temperatures, closer to room or typical operating conditions. This would provide a more realistic picture of the processes relevant under normal battery use.

The role of the electrolyte also deserves further attention. Current electrolytes contain complex and highly reactive components, making their stability a critical safety concern. More research is needed to evaluate the long term stability of these electrolytes, in particular to understand how to minimize or control water impurities, and which electrolyte has the optimal balance between stability and efficiency, and how drastically the presence of the lithium salt affect their chemistry.

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