Mechanism of Hydrofluoric Acid Formation in Ethylene Carbonate

Electrolytes with Fluorine Salt Additives

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ABSTRACT: We utilized density functional theory to examine HF generation in lithium-ion battery electrolytes from reactions between H₂O and the decomposition products of three electrolyte additives: LiPF₆, LiPOF₄, and LiAsF₆. Decomposition of these additives produces PF₅, AsF₅, and POF₃ along with LiF precipitates. We found PF₅ and AsF₅ react with H₂O in two sequential steps to form two HF molecules and POF₃ and AsOF₃, respectively. PF₅ (or AsF₅) complexes with H₂O and undergoes ligand exchange to form HF and PF₄OH (AsF₄OH) with an activation barrier of 114.2 (30.5) kJ mol⁻¹ and reaction enthalpy of 14.6 (-11.3) kJ mol⁻¹. The ethylene carbonate (EC) electrolyte forms a Lewis acid-base complex with the PF₄OH (AsF₄OH) product, reducing the barrier to HF formation. Reactions of POF₃ were examined and are not characterized by complexation of POF₃ with H₂O or EC, while PF₅ and AsF₅ complex favorably with H₂O and EC. HF formation from POF₃ occurs with a reaction enthalpy of -3.8 kJ mol⁻¹ and a 157.7 kJ mol⁻¹ barrier, 43.5 kJ mol⁻¹ higher than forming HF from PF₅. HF generation in electrolytes employing LiPOF₄ should be significantly lower than those using LiPF₆ or LiAsF₆ and LiPOF₄ should be further investigated as an alternative electrolyte additive.

Keywords: Electrolyte degradation; Hydrofluoric acid; Lithium-ion Battery; LiPOF₄; LiPF₆ decomposition; Density Functional Theory

1. Introduction

A major obstacle to the economical use of lithium ion batteries (LIBs) in a variety of mobile technologies, including portable electronics and especially electric vehicles is their limited service lifetimes. Commercial LIBs suffer from capacity fading – a loss in the battery's discharge capacity. Capacity fading in LIBs has been attributed to the degradation of the liquid electrolytes and lithium transition metal oxide cathodes during storage and charge/discharge cycling. Thus, understanding electrolyte degradation mechanisms is of considerable interest in the effort to reduce capacity fading and improve the performance and service lifetimes of LIBs due to the subsequent interactions of electrolyte degradation products with the solid-electrolyte interphase (SEI) in LIBs[1–6]. In this study we investigated the formation of HF in ethylene carbonate-based LIB electrolytes resulting from degradation of PF_5 , POF_3 , and AsF_5 electrolyte additives. This HF formed in the electrolyte as a result these degradation reactions may react with the SEI and contribute its formation, but this is beyond our current scope.

Common liquid electrolytes in LIBs tend to be mixtures of aprotic organic solvents, such as ethylene-carbonate (EC), dimethyl-carbonate (DMC), propylene carbonate (PC) and other carbonates. Because LIBs operate at temperatures below the melting point of EC (307-310K), mixtures of EC with DMC, PC, and other alkyl carbonates are used for EC-based electrolytes in LIBs to lower the mixtures' melting points and improve the stability of the electrolyte relative to redox reactions with the electrodes. These aprotic, organic liquid carbonate solvents possess large HOMO-LUMO gaps and, as a result, are stable with respect to reduction or oxidation over large voltage ranges. Consequently, these EC-based electrolytes possess large stability windows that allow them to be employed in LIBs over wide operating potentials and biases up to ~ 5 V, at which point they will decompose. Additionally, liquid carbonate electrolytes have ionic conductivities that are usually an order of magnitude greater than polymeric or solid-state electrolytes[6–8], which enable LIBs with these liquid electrolytes to possess higher power densities.

To achieve higher power densities and also increase the safety and service lifetimes of LIBs, lithium-salts are added to carbonate electrolytes. The desire to further improve the safety, service lifetime and power density of LIBs has motivated studies of various lithium-salt electrolyte additives[1,6,9–11]. Lithium hexafluorophosphate (LiPF_6) is comprised of a Li^+ ion and a PF_6^- counter ion and is currently the dominant electrolyte salt additive in commercial LIBs with organic, EC-based electrolytes because of its ability to enhance the ionic conductivity and electrochemical stability of the electrolyte relative to other additives. Although alternative salt additives have been investigated, they either do not achieve a superior combination of conductivity and stability over LiPF_6 [5,6,9] or are potentially unsafe. For example, LiAsF_6 exhibits similar improvements in electrolyte conductivity and electrochemical stability relative to LiPF_6 [1,5,6,11], but has not been employed in commercial LIBs due to concerns over As toxicity.

Unfortunately, LiPF_6 undergoes heterolytic dissociation at elevated temperatures to form a LiF precipitate and pentafluorophosphate (PF_5)[2,8,9]. Because Li^+ is sequestered in the LiF precipitate, this results in loss of working Li^+ . However,

the high polarity of EC-based electrolytes separates LiPF_6 as solvated Li^+ and PF_6^- ions at low temperatures and thus stabilizes Li^+ and PF_6^- relative to LiF and PF_5 . This limits PF_5 and LiF formation, and thus loss of working Li^+ , which improves the LIB lifetime[9,10,12]. However, lifetime issues still persist, especially concerning the degradation of the lithium transition metal oxide cathode, which is vulnerable to attack by hydrofluoric acid (HF) that has been proposed to form from the reaction of PF_5 with H_2O impurities[13]. Because lowering H_2O contamination in carbonate electrolytes below the concentrations typically present in commercial LIBs (greater than 20 ppm)[14] is impractical, some reaction between this H_2O and PF_5 is inevitable.

H_2O contamination has been suggested to drive the breakdown of LiPF_6 by hydrolysis to produce HF by the overall reaction[2,8,9]

LiPF_6 has been observed to thermally decompose at temperatures above 390K[9], producing a LiF precipitate and PF_5 by the following reaction[9,10,12]

The generated PF_5 has been suggested to then interact with various components of the electrolyte and undergo a number of possible electrolyte degradation reactions, including: hydrolysis, polymer initiating reactions with EC or other electrolyte molecules, and the generation of undesirable products such as phosphine oxides and alkyl fluorides, among others[10,11,15]. The thermal decomposition of LiPF_6 via Reaction (2) and resulting LiF precipitate formation was studied using density functional theory (DFT) molecular dynamics (MD) simulations[12,17], which predicted that highly polar electrolyte molecules, such as the organic liquid carbonates EC, dimethyl carbonate and propylene carbonate, most effectively solvate the Li^+ and PF_6^- ion pair compared to other liquid electrolytes. Thus, highly polar organic electrolytes hinder PF_5 formation and LiF precipitation by limiting interactions between the two solvated ions. However, if the two ions do react, the LiF product precipitates from the electrolyte onto the electrode surface, which lowers the LiF concentration in the electrolyte and shifts the equilibrium of Reaction (2) towards the PF_5 and LiF products.

PF_5 produced by Reaction (2) and H_2O impurities in the electrolyte are expected to play a central role in producing HF via the reaction[16]

PF_5 is difficult to isolate *in situ* during LIB operation, suggesting that it exists in low concentrations because it is either produced in small quantities or that it readily reacts and is consumed[2,4]. NMR and GC-MS characterization of Reaction (1) at temperatures of 358K and 373K demonstrate that electrolyte degradation is endothermic and slow in organic electrolytes with water impurities[9,17–19]. In addition to the deleterious effect this reaction has on decreasing the concentration of LiPF_6 , it also produces

HF, which has been suggested to react with lithium transition metal cathodes to degrade them and cause capacity fading in LIBs[2,8,18,20].

In this study, we employed DFT to investigate the mechanisms and energetics of reactions involving electrolyte salt additives that may generate HF. We examined HF generation from Reaction (3) between PF_5 with H_2O and by the analogous reaction between AsF_5 and H_2O , where AsF_5 is produced along with LiF in electrolytes utilizing the LiAsF_6 additive. Additionally, we studied the formation of HF by a reaction between H_2O and POF_3 , which is produced by Reaction (3). A previous computational study by Okamoto has examined the reaction between PF_5 and H_2O to develop an understanding of the role that POF_3 plays in EC ring opening reactions. [16] Here, we report a comprehensive study of HF formation in the liquid EC electrolytes that results from H_2O reacting with PF_5 , AsF_5 or POF_3 . This study focuses on determining the active mechanisms by which HF is formed from H_2O contaminants reacting with various electrolyte salts and developing an understanding of the roles that these reactions might play as well as the effects of bulk EC electrolyte in generating HF from PF_5 , AsF_5 , and POF_3 . We investigated the mechanisms of HF formation resulting from reaction of PF_5 , POF_3 , and AsF_5 with H_2O in EC-based LIB electrolytes as well as interactions between EC solvent molecules and these species, and how these interactions affect HF formation and electrolyte degradation. The study we report examined and compared various routes to HF formation, the effect of Lewis acid-base interactions on electrolyte decomposition as well as the roles of the central atom and the ligands of electrolyte species in HF formation in LIB electrolytes.

2. Computational Details

2.1 Molecular DFT Calculations - DFT calculations for examining reactions of the PF_5 , POF_3 , and AsF_5 electrolyte constituents with H_2O to form HF were performed using the M06[21] hybrid density functional combined with the 6-31++G(3d,p) basis set[22–24] as implemented in the GAMESS computational chemistry software package[25,26]. This basis set was chosen because it reproduces the reaction enthalpies of the 6-311++G(3d,p) triple zeta basis set within 4.2 kJ mol⁻¹. The M06 exchange-correlation DFT functional was selected because benchmarking has shown that it accurately reproduces experimental results for fluorine chemistry[27]. The Polarizable Continuum Model (PCM) implicit solvent model, with its parameters set to model EC solvent[28], was employed in all calculations performed to model bulk solvent effects.

For the reactions, all reactant and product structures were verified to have real frequencies, while transition states (TS) were verified to have a single imaginary frequency corresponding to the reaction coordinate determined via an Intrinsic Reaction Coordinate (IRC) calculation. The TS themselves were located using the Quadratic Approximation Method as implemented in GAMESS. See the Supporting Information (SI) for the coordinates of all calculated structures. Frequency calculations were performed at the M06/6-31++(3d,p) level of theory to determine zero point energies (ZPE) and thermal contributions to the enthalpy at 298K and 1 atm. Atomic charges were calculated using the CHELPG[29] electrostatic potential derived charges method at the

M06/6-31++G(3d,p)/PCM-EC level of theory. The bond strengths of the P-F and As-F bonds of the PF₅, PO₃F₃, and AsF₅ molecules were determined by calculating their bond dissociation enthalpies (BDE) in PCM modeling EC.

2.2 Use of Explicit Solvent Molecules in Addition to PCM Solvent - Previous studies[11,12,16] on the thermal decomposition of LiPF₆ to form LiF and PF₅ via Reaction (2) demonstrate that solvent effects play a significant role in LIB electrolyte chemistry, desirably solvating the reactant ion pair – Li⁺ and PF₆⁻ – and facilitating ion transport during operation. Additionally, the high polarity of the EC electrolyte, with a dipole moment of 4.81 μ/D[30], leads to strong solvent-solvent interactions in addition to electrolyte interactions with Li⁺ and PF₆⁻ and other electrolyte impurities. Consequently, to accurately describe HF formation careful consideration of the effects of solvent molecules on the reactions between electrolyte salts and H₂O is required, which had been neglected in previous studies of the reactions of PF₅ with H₂O. The effect of explicit EC solvent molecules on HF forming reactions is examined below.

When Reaction (2) is calculated using PCM implicit solvent, it is endothermic by 119.2 kJ mol⁻¹. However, modeling the solvent with one explicit solvent in addition to implicit solvent lowers the reaction enthalpy to 65.7 kJ mol⁻¹. Furthermore, adding a second and third explicit EC molecules causes the enthalpy of Reaction (2) to oscillate; it is endothermic by 76.6 and 67.8 kJ mol⁻¹ when two and three explicit EC molecules are included, respectively. Thus, the reaction enthalpy converges to a value within ~ 2.1 kJ mol⁻¹ of the reaction enthalpy obtained by using only a single explicit EC molecule. This highlights the importance of accurately capturing the solvent interactions that not only significantly affect the stabilities of Li⁺ and the PF₆⁻ counter ion, but also affect the stabilities of the LiF and PF₅ products, as demonstrated by this result.

In order to establish an accurate solvation model for calculating the energetics of HF generation in LIB electrolytes we investigated the effect of the solvation model on the reaction of PF₅ with H₂O via Reaction (4)

With the inclusion of an explicit EC solvent molecule, Reaction (4) proceeds through the Lewis acid-base pair reactant complex where an oxygen lone pair of H₂O donates into an empty sp³d² orbital of the P center of the PF₅. The EC solvent directly affects this reaction to form HF because it acts as a Lewis base to form the PF₅-EC complex by donating one of its carbonyl O lone pairs into the empty sp³d² orbital of PF₅. Although this results in a dative complex that has a formation enthalpy similar to that of the PF₅·H₂O reactant complex, the high concentration of EC relative to H₂O significantly lowers the free energy of formation. Consequently, interactions of EC with the PF₅ and PF₄OH Lewis acids affect the reaction energetics. Thus, we examined Reaction (4) using different solvent models to determine the role of the electrolyte during HF formation.

Similar to Reaction (2), we investigated Reaction (4) with up to three explicit solvating EC molecules in PCM implicit solvent. PF₅ first complexes with H₂O to form the PF₅·H₂O complex, which converts the P center from trigonal bipyramidal to a distorted octahedron. PF₅·H₂O subsequently undergoes ligand exchange to form HF and PF₄OH via Reaction (4). When solvation is modeled

using only implicit solvent, (4) is endothermic by 38.9 kJ mol^{-1} and involves a reaction barrier of $131.4 \text{ kJ mol}^{-1}$, as shown in Table 1. Adding an explicit EC enables the PF_4OH product with a trigonal bipyramidal P center to complex with EC to form the more stable octahedral $\text{PF}_4\text{OH}\cdot\text{EC}$ complex. With one explicit EC, (4) is calculated to be endothermic by 14.6 kJ mol^{-1} and to occur with a $114.2 \text{ kJ mol}^{-1}$ activation barrier. Using three explicit EC molecules results in similar energies with (4) predicted to be endothermic by 11.3 kJ mol^{-1} and to involve a barrier of $115.9 \text{ kJ mol}^{-1}$. The slight lowering of the reaction enthalpy by 6.3 kJ mol^{-1} with the addition of three explicit solvating ECs relative to using one explicit EC likely results from the interactions between the solvent molecules themselves, partially overestimating the solvation effect produced by the polar EC-PCM implicit solvent model. These results show that the addition of explicit EC solvent not only stabilizes both the TS and the products relative to the PF_5 and H_2O reactants, but also qualitatively affects the properties of the products.

The equivalent reaction to (4), involving AsF_5 and AsF_4OH , proceeds through an analogous pathway. AsF_5 first dative bonds to H_2O to form an $\text{AsF}_5\cdot\text{H}_2\text{O}$ complex, which then undergoes ligand exchange to form HF and AsF_4OH . Including explicit EC in addition to the PCM continuum description of the solvent reduces the reaction energy and barrier to 7.5 kJ mol^{-1} and 49.0 kJ mol^{-1} , 32.2 and 19.7 kJ mol^{-1} lower than when the solvent is modeled only using implicit solvent. These results demonstrate the necessity of including an explicit solvent molecule in order to accurately capture the solvent effects that affect the energetics of HF generation from AsF_5 and H_2O .

We concluded that the effects of including explicit solvent for Reactions (2), (4), and (8) converge with three EC molecules and that a single explicit EC reproduces the results of the model with three explicit EC molecules to within 4 to 8 kJ mol^{-1} . Consequently, we employed a single explicit EC molecule in addition to PCM implicit solvent for all calculations examining HF formation reactions with H_2O because this captures the most relevant solvent effects of the more extensive electrolyte solvent model at a lower computational cost.

3. Results and Discussion

3.1 Salt Decomposition and LiF Formation - We examined LiF formation from LiPF_6 degradation via Reaction (2), and predict that (2) does not involve a TS and has a reaction enthalpy and barrier of 65.7 kJ mol^{-1} . This is consistent with the experimental observation that PF_5 forms at temperatures above 390K [9] and suggests that solvation effects play a significant role in LIB electrolyte chemistry, as shown by previous computational studies of LIB electrolytes[11,12,16]. Based on our calculated reaction enthalpy, we predict a Boltzmann factor in the concentrations of PF_5 and PF_6^- at 310K (typical of LIB operation) of $\sim 8 \times 10^{-12}$. This result indicates that (2) does not lead to significant dissociation of LiPF_6 because most LiF and PF_5 that does form by LiPF_6 dissociation likely reacts via the reverse of Reaction (2) to reform LiPF_6 because the reverse of Reaction (2) is barrierless and exothermic. However, because LiF is insoluble in the organic electrolyte, precipitation of LiF drives Reaction (2) forward to form

more LiF and PF₅ than would be expected based purely on the equilibrium of (2), although we expect PF₅ to be a low concentration contaminant species[31,32]. We predict that LiF precipitate formation from LiPOF₄ and LiAsF₆ also involve no TS and are endothermic by 78.2 and 78.7 kJ mol⁻¹ for LiPOF₄ and LiAsF₆, respectively. Consequently, we expect moderately lower rates of LiF formation for LiPOF₄ and LiAsF₆ relative to LiPF₆, given the ability of the methods to accurately predict relative reaction barriers and that the pre-exponential factors are comparatively similar.

3.2 PF₅ Decomposition and HF Generation – We first examined HF forming reactions that involve the most common electrolyte additive, LiPF₆. Following dissociation via Reaction (2), LiF precipitates from the electrolyte[31,32] while PF₅ remains solvated. The LUMO of PF₅ (see Figure S1 of the SI) is expected to accept the oxygen electron lone pairs of H₂O, present as an electrolyte contaminant, and EC. That is, PF₅ should act as Lewis acid to dative (dipolar) bond with Lewis bases, in particular, H₂O and EC. The formation of the PF₅·H₂O Lewis acid-base complex changes the phosphorous coordination in PF₅ from a trigonal bipyramidal coordination to a distorted octahedron (with an average F-P-O bond angle of 85.7 degrees). For PF₅·H₂O, we calculated a complexation enthalpy (at 298K) of -41.8 kJ mol⁻¹ and a P-O distance of 1.92 Å, indicating the formation of a P-O dative bond. Alternatively, for PF₅·EC we calculated a complexation enthalpy of -38.9 kJ mol⁻¹ and a P-O distance of 1.83 Å, also showing the formation of a dative bond between PF₅ and EC.

Our results indicate that although both H₂O and EC form favorable complexes with PF₅ with similar energies, PF₅ primarily complexes with EC due to the high concentration of EC in the electrolyte relative to H₂O. This reduces the rate of HF generation in the electrolyte by limiting interactions between the PF₅ and H₂O present as a low concentration contaminant. This is of particular importance because degradation of the lithium transition metal oxide cathode by HF neutralization reactions produces H₂O, which increases its concentration in the electrolyte and thus, increases the rate of HF generation. Additionally, we calculated a charge on the central phosphorus atom of PF₅ of -1.31 e, as determined by a CHELPG population analysis and shown in Table 1, demonstrating that the highly electronegative F atoms of PF₅ withdraw electron density from the P center to make it highly electrophilic and likely to interact favorably with the lone pairs of EC or H₂O.

Following formation of the PF₅·H₂O complex, two HF molecules form according to Reaction (3). However, we find that Reaction (3) occurs as two sequential proton transfer reactions, Reactions (4) and (5), to form two HF molecules. We first examined Reaction (4), the ligand exchange reaction that converts PF₅·H₂O into HF and PF₄OH. We calculate the BDE of PF₅ is 560.7 kJ mol⁻¹, which is in agreement with previous computational results[33]. Our results predict that Reaction (4) is endothermic with a reaction enthalpy of 14.6 kJ mol⁻¹ and a reaction barrier of 114.2 kJ mol⁻¹ when referenced to the PF₅·EC complex; again, all reactions include one explicit EC molecule in addition to the PCM continuum solvent model. The low concentrations of both the PF₅ and H₂O and the 114.2 kJ mol⁻¹ activation barrier suggest that Reaction (4) to decompose PF₅ into PF₄OH and HF is sluggish,

even at temperatures realized in LIBs during operation. This is corroborated by the experimental observation that significant capacity loss from HF attack occurs over a time scale of months in LIBs that employ carbonate electrolytes with LiPF_6 additives¹³. Additionally, we expect PF_5 to exist in the electrolyte predominantly as a $\text{PF}_5\cdot\text{EC}$ complex, rather than as the uncomplexed, solvated species of our reference calculations. From the $\text{PF}_5\cdot\text{EC}$ complex with a solvating H_2O molecule we calculate a reaction barrier of $114.2 \text{ kJ mol}^{-1}$ and a reaction enthalpy of 14.6 kJ mol^{-1} , as shown in Figure 1.

As (4) proceeds from the reactant complex through the TS, as shown in Figure 2a, the P-O bond distance decreases from $1.92 \text{ \AA}$ to $1.73 \text{ \AA}$, while the P-F bond distance of the P-F bond undergoing dissociation increases from $1.60 \text{ \AA}$ to $1.95 \text{ \AA}$. This is characteristic of a ligand exchange reaction and demonstrates the simultaneous transformation of the P-O dative bond into a covalent bond and dissociation of a P-F bond, which occurs by proton transfer from the O of H_2O to a F of PF_5 to form HF, as shown in Figure 2b. Analysis of the product state structures shows that the O-H distance between the H of HF and the O of the OH ligand increases to $1.24 \text{ \AA}$, indicating that it is now a hydrogen bond rather than an O-H covalent bond. Meanwhile, the distance between the H and F atoms decreases from 2.29 in $\text{PF}_5\cdot\text{H}_2\text{O}$ to $1.14 \text{ \AA}$ in $\text{PF}_4\text{OH}\cdot\text{EC}$ – indicating the formation of HF. As the P-F bond dissociates, the P-center returns to the five-fold coordination it possessed in PF_5 , which allows P in PF_4OH to again act as a Lewis acid. Thus, PF_4OH complexes with the explicit solvating EC to form the $\text{PF}_4\text{OH}\cdot\text{EC}$ Lewis Acid-Base pair, in which EC acts as a Lewis base and PF_4OH acts as a Lewis acid in which the octahedrally coordinated P accepts the oxygen lone pair from the EC carbonyl. The dative bond stabilizes the $\text{PF}_4\text{OH}\cdot\text{EC}$ product to reduce the reaction enthalpy to generate HF by Reaction (4) (see Computational Details for an analysis of the effects of EC on Reaction (4)). These results predict that the EC electrolyte has a moderate catalytic effect on this reaction. Thus, while EC's polarity is desirable in improving the solvation of Li^+ to facilitate its transport in the electrolyte, its ability to form a Lewis acid-base complex promotes degradation of the electrolyte salt and formation of HF. Figure 3 shows the $\text{PF}_4\text{OH}\cdot\text{EC}$ product complex, which we verified using an IRC analysis that confirms that the TS shown in Figure 2 connects it with $\text{PF}_5\cdot\text{H}_2\text{O}$. Additionally, our results predict that the HF produced from Reaction (4) is hydrogen bonded to the O in the $\text{PF}_4\text{OH}\cdot\text{EC}$ complex, and dissociation of this $\text{PF}_4\text{OH}\cdot\text{EC}\cdot\text{HF}$ product to form $\text{PF}_4\text{OH}\cdot\text{EC}$ and a solvated HF is endothermic by only 8.8 kJ mol^{-1} , which is thermally accessible at room temperature. The above results show that Reaction (4) is the first HF formation step of PF_5 decomposition and HF generation in the overall reaction (3).

Reaction (5) forms HF by decomposition of the $\text{PF}_4\text{OH}\cdot\text{EC}$ complex by a subsequent proton transfer reaction analogous to Reaction (4); this is the second step in the two-step mechanism of PF_5 degradation by reaction with H_2O that comprises Reaction (3). We next investigated whether Reaction (5),

is an active route to forming additional HF.

Our calculations predict that (5) proceeds through an activation barrier of 97.5 kJ mol^{-1} and is endothermic by 1.3 kJ mol^{-1} relative to the $\text{PF}_4\text{OH}\cdot\text{EC}$ reactant complex, as shown in Figure 3. At the TS (shown in Figure 4), the EC molecule has dissociated from the $\text{PF}_4\text{OH}\cdot\text{EC}$ reactant complex, increasing the P-O distance to $3.21 \text{ \AA}$, and the P-F bond has partially dissociated by lengthening to $2.17 \text{ \AA}$. Dissociation of the P-F bond results in POF_3 with a tetrahedral coordination and with HF hydrogen bonded to its oxygen atom. However, POF_3 does not form a dative complex with EC or H_2O , which would involve a significant energy penalty to hybridize with the P 3d orbitals while only enabling the formation of a relatively weak dative bond. Consequently, although Reactions (4) and (5) are both proton transfer reactions that dissociate P-F and O-H bonds to form HF, (5) differs from (4) in that the POF_3 resulting from (5) does not complex with EC and is tetrahedral, whereas the $\text{PF}_4\text{OH}\cdot\text{EC}$ product resulting from (4) does complex with EC and is octahedral. Dissociation of HF from the product complex of Reaction (5) to form a solvated HF only involves breaking a hydrogen bond and only requires 13.4 kJ mol^{-1} . The schematic potential energy surface (PES) of the two-step decomposition of PF_5 by reaction with H_2O to form POF_3 and two HF molecules is shown in Figure 1.

PF_5 and PF_4OH are both Lewis acids and form relatively stable Lewis acid-base complexes with H_2O and EC through their oxygen lone pairs with complexation enthalpies of -41.8 , -38.9 , and $-20.1 \text{ kJ mol}^{-1}$ for $\text{PF}_5\cdot\text{H}_2\text{O}$, $\text{PF}_5\cdot\text{EC}$, and $\text{PF}_4\text{OH}\cdot\text{EC}$, respectively. The reaction of PF_5 with H_2O to form two HF molecules (3) involves barriers for both steps – Reactions (4) and (5) – as shown in Figure 1. The first step, Reaction (4), has a larger barrier ($114.2 \text{ kJ mol}^{-1}$) than Reaction (5) (97.1 kJ mol^{-1}) and is thus the rate-limiting step for HF generation by this mechanism. These results indicate that the concentration of PF_4OH in the electrolyte is low because it is an intermediate product formed by the rate-limiting step and is rapidly transformed into the products through a lower barrier step. Our calculations predict that PF_5 reacts with H_2O to generate HF, especially at elevated operating temperatures. However, the barrier to these reactions is relatively high, while the concentration of H_2O is low and H_2O must compete with EC to form the initial reactant complex. The relatively slow generation of HF predicted by these results is consistent with experimental observation[13,16].

3.3 POF_3 Decomposition and HF Generation – POF_3 is the product of PF_5 hydrolysis via Reactions (4) and (5) and has been suggested to further react with H_2O impurities to generate additional HF, which reacts with the cathode to reduce LIB service lifetimes[11,15]. However, POF_3 is a weak Lewis acid compared to PF_5 and - as mentioned above - does not dative bond to EC or H_2O in our calculations, in contrast to $\text{PF}_4\text{OH}\cdot\text{EC}$. This is a result of the relatively weak dative bonds not providing sufficient stabilization to compensate for the promotion energy required to form sp^3d^2 hybridized orbitals, whereas the P-O covalent bond with the OH ligand in $\text{PF}_4\text{OH}\cdot\text{EC}$ is strong enough to stabilize the hybridization required to form PF_4OH , which possesses an empty sp^3d^2 orbital to accept the carbonyl lone pair of EC. Consequently, the P center of POF_3 does not act as an acceptor for the oxygen lone pairs of either EC or H_2O , in contrast to our predictions for PF_5 described above. Additionally, we calculated a $595.8 \text{ kJ mol}^{-1}$ BDE for the P-F bond in POF_3 , 35.1 kJ mol^{-1} greater than for the P-F bond in PF_5 , as shown in Table 2. This suggests that HF generation

from POF_3 degradation involves greater energetic barriers than HF generation from PF_5 . Consequently, we examined the reaction of POF_3 with H_2O to determine whether this reaction is a kinetically viable route for HF formation.

Reaction of H_2O with POF_3 to form two HF molecules might occur via two subsequent ligand exchange reactions, analogous to the mechanism of HF formation by reaction of H_2O with PF_5 . The first step in this reaction to form HF is

We calculate a lower positive charge on the central P atom of POF_3 (1.19 e) compared to PF_5 (1.31 e), as expected given the higher electronegativity of F relative to O and that PF_5 has five F ligands. This suggests that the P of POF_3 is less electrophilic than the P of PF_5 . Furthermore, POF_3 is tetrahedrally coordinated and its P is sp^3 hybridized while PF_5 is bipyramidal and its P is sp^3d^2 hybridized. As a result, and in contrast to PF_5 , POF_3 does not possess a low lying LUMO to accept the oxygen lone pairs of H_2O or EC to form stable dative bonded complexes with them. Furthermore, the LUMO of POF_3 (see Figure S1 of the SI) is more diffuse than that of PF_5 , suggesting that a higher degree of spatial overlap exists between the POF_3 LUMO and the HOMO of EC or H_2O , which in both cases is an oxygen lone pair. We also calculate that the LUMO of POF_3 lies $102.1 \text{ kJ mol}^{-1}$ higher in energy than the LUMO of PF_5 , as shown in Table 2, also suggesting that POF_3 is a poor Lewis acid and should form weaker Lewis acid-base complexes with EC and H_2O than PF_5 , if it dative bonds at all. Our calculations confirm this. Optimization of the IRC reactant complex results in the reactants approaching two separated solvated species, with the P-O distance of $2.98 \text{ \AA}$ between POF_3 and H_2O , indicating only a weak electrostatic interaction rather than the formation of a dative bond. Consequently, we expect the reactants of Reaction (6) will preferentially remain isolated as solvated electrolyte species rather than form a $\text{POF}_3\cdot\text{H}_2\text{O}$ reactant complex – in contrast to the formation of the $\text{PF}_5\cdot\text{H}_2\text{O}$ complex.

We have calculated Reaction (6) of POF_3 with H_2O to produce HF and POF_2OH . The schematic PES for Reaction (6) is shown in Figure 1. We find that (6) proceeds through a TS lying $157.7 \text{ kJ mol}^{-1}$ above the separated, solvated reactants; 43.5 kJ mol^{-1} higher than the barrier to form HF from PF_5 , via Reaction (4). The reaction is approximately thermalneutral with a calculated enthalpy of reaction that is exothermic by only 3.8 kJ mol^{-1} relative to the isolated reactants, whereas Reaction (4) was endothermic by 14.6 kJ mol^{-1} . The increase in activation barrier for HF formation reduces the Boltzmann factor in the rate constant at 310K by 4.7×10^{-8} relative to that of Reaction (4). In addition, the TS – shown in Figure 5 – of Reaction (6) has longer P-F and H-F bonds of $2.01 \text{ \AA}$ and $1.35 \text{ \AA}$, respectively, than these bonds in the TS of Reaction (4). This indicates that POF_3 decomposition involves a late TS and a higher barrier, which is a result of the increase in the bond strength of the P-F bond of POF_3 compared to the P-F bond of PF_5 . The higher predicted barrier and associated slower HF formation kinetics results in a significant improvement over the current state-of-the-art salt additive, PF_6^- . **Consequently, degradation of a POF_3 electrolyte constituent by reaction with H_2O is predicted to result in significantly slower formation rates of HF and POF_2OH compared to PF_5 degradation.**

As expected, Reaction (6) does not produce a dative complex between POF_2OH and EC, in contrast to the $\text{PF}_4\text{OH}\cdot\text{EC}$ complex formed by Reaction (4) that stabilizes the products and thus enhances HF formation. The P center of POF_3 transitions from tetrahedral to five-fold coordination as Reaction (6) proceeds to the TS, and returns to being tetrahedrally coordinated in the POF_2OH product state. Consequently, the TS involves the energetic penalty of mixing in the P 3d orbitals, explaining the higher barrier than that of Reaction (4). Similar to POF_3 , the P of POF_2OH is sp^3 coordinated and does not possess an empty orbital to accept lone pairs from either H_2O or EC. Optimization of a contact complex between POF_2OH and EC results in the two components drifting apart towards separate, solvated species with a P-O distance of 3.11 Å, indicating that POF_2OH , like POF_3 , does not act as a Lewis acid to complex with EC or H_2O . It has been previously reported that POF_2OH may subsequently react sequentially with two additional H_2O molecules to form H_3PO_4 and two HF molecules[34]. However, both POF_2OH and H_2O as a contaminant are present in the electrolyte at very low concentrations, and thus, these reactions are unlikely. Consequently, we limit our investigation of further HF formation to the self-decomposition of POF_2OH , analogous to the above case of PF_4OH dissociation by Reaction (5). Although formation of POF_2OH involves a significantly higher barrier than Reaction (4), we also examined HF formation as a result of dissociation of the POF_2OH product of Reaction (6).

Although formation of POF_2OH involves a significantly higher barrier than Reaction (4), we also examined HF formation as a result of dissociation of the POF_2OH product of Reaction (6). This HF formation proceeds via the following reaction

We predict that Reaction (7) proceeds through an activation barrier of $141.4 \text{ kJ mol}^{-1}$ and is endothermic by 73.6 kJ mol^{-1} . The TS of Reaction (7), shown in Figure 6, is stabilized by formation of a complex between PO_2F and an EC solvent molecule, while the TS of Reaction (5) was predicted to not form a complex. The barrier for Reaction (7) is only 3.8 kJ mol^{-1} lower than the first activation barrier, which suggests that within the resolution of our model and method, either Reaction (6) or (7) will be rate-limiting. Although our calculations show that an EC donates a carbonyl oxygen lone pair to the P atom at the TS and product PO_2F to create a tetrahedral P center and stabilize the TS and products, the barrier and endothermicity are still relatively high. Our calculations predict that the length of the P-O dative bond that forms as the reaction proceeds increases from 1.54 Å at the TS to 1.74 Å at the product state, indicating that EC stabilizes the TS of Reaction (7). The higher activation energies reduces the Boltzmann factors in the rate constants of Reactions (7) and (5) by 4.0×10^{-8} at 310K. Thus, we expect significantly lower rates of HF formation from reaction of H_2O with POF_3 than with PF_5 , possibly allowing a battery with POF_3 electrolyte species to operate without significant HF formation. As a result, we recommend investigating LiPOF_4 – a potential electrolyte salt comprised of Li^+ and POF_4^- – as an alternative to LiPF_6 for use in LIBs. LiPOF_4 has been reported to be inexpensive to synthesize[35], and while LiF formation may still occur for LiPOF_4 in a similar manner to Reaction (1), POF_3 would be formed rather than PF_5 , which we expect would lead to reduced electrolyte and cathode degradation.

3.4 AsF₅ Decomposition and HF Generation – In addition to investigating PF₅ and POF₃, we also studied HF generation resulting from reaction between H₂O and AsF₅, which would be produced from decomposition of the potential electrolyte additive LiAsF₆ analogous to Reaction (1). LiAsF₆ is a salt comprised of Li⁺ and AsF₆⁻ and was studied alongside LiPF₆ as an electrolyte additive and showed improvements in LIB operation similar to LiPF₆, but has not been used in commercial LIBs due to concerns about the toxicity of As. We predict that LiAsF₆ dissociates into LiF and AsF₅ with a reaction enthalpy of 78.7 kJ mol⁻¹, similar to the energy to form LiF and POF₃ in an EC electrolyte from LiPOF₄, and ~ 13 kJ mol⁻¹ higher than the enthalpy to form LiF from LiPF₆. Similar to the cases of PF₅ and POF₃, we examined HF generation as a result of a ligand exchange reaction between the AsF₅ and H₂O.

Our calculations show that HF generation from AsF₅ is characterized by the formation of a strong AsF₅·H₂O dative complex, which converts the As center from the trigonal bipyramidal coordination of AsF₅ to a distorted octahedral coordination, similar to the PF₅·H₂O Lewis acid-base complex for Reaction (4). We predict a 448.9 kJ mol⁻¹ BDE for the As-F bond of AsF₅, 111.7 kJ mol⁻¹ lower than the BDE for the P-F bond in PF₅.

A population analysis predicts that the charges on the As and P centers of AsF₅ and PF₅ are 1.40 e and 1.31 e, respectively. Thus, the F atoms withdraw more electron density from the As center compared to the P center, creating a more electropositive As center. Additionally, a comparison of the HOMO-LUMO gap of the PF₅, POF₃, and AsF₅ species, shown in Table 1, demonstrates a relatively low-lying LUMO of AsF₅ (shown in Figure S1 of the SI) with an energy 55.6 kJ mol⁻¹ lower than the LUMO of PF₅. This allows for a closer energetic overlap between the oxygen lone pairs and the LUMO. Consequently, we expect AsF₅ to act as a stronger Lewis acid than PF₅ and form stronger dative complexes with EC and H₂O. Our calculations confirm this hypothesis; the formation of the AsF₅·H₂O complex is exothermic by 81.2 kJ mol⁻¹, nearly 42 kJ mol⁻¹ more stable than the PF₅·H₂O complex. Furthermore, we calculated an As-O bond distance for AsF₅·H₂O of 1.99 Å, indicating the formation of an As-O dative bond. In addition to complexing with H₂O, AsF₅ will also complex with EC to form AsF₅·EC; the formation of the AsF₅·EC complex is exothermic by 62.8 kJ mol⁻¹, as shown in Figure 1. However, the concentration of EC is ~10⁵ times higher than that of H₂O in LIB electrolytes so that an 18.4 kJ mol⁻¹ more stable complex does not lead to H₂O outcompeting EC to complex with AsF₅. Thus, we expect AsF₅ to be primarily complexed with EC, which reduces the rate of HF formation in electrolytes that utilize the AsF₆⁻ counter ion.

After formation of the AsF₅·H₂O complex, the ligand exchange reaction leads to formation of HF and AsF₅ degradation through

We calculated an activation barrier of 30.5 kJ mol⁻¹ and reaction enthalpy of -11.3 kJ mol⁻¹ relative to the AsF₅·EC complex. The low barrier ensures that this reaction is fast, even without the possibility that the transient non-equilibrium partitioning of excess energy from complex formation will be deposited into the reaction coordinate. The lower activation barrier for HF formation from

the ligand exchange between H₂O and AsF₅ relative to the reactions between H₂O and both PF₅ and POF₃ results from the lower As-F bond enthalpy relative to that of P-F in PF₅ and POF₃.

Our results predict that EC dative bonds with the AsF₄OH product of Reaction (8) to stabilize it by forming an AsF₄OH·EC complex (see Computational Details for an analysis of the effect of EC on Reaction (8)). This complex maintains an octahedral coordination of the As center upon reaction and drives Reaction (8) forward, analogous to the stabilization of the PF₄OH·EC product of Reaction (4). These comparisons show that interactions with the EC electrolyte stabilize the TS and products of (8) relative to the reactant state and thus lower the activation barrier and predict a reaction that is exothermic rather than endothermic. Additionally, the HF formed by Reaction (8) is hydrogen bonded to the O in the AsF₄OH·EC complex, and we predict a dissociation enthalpy of 10.0 kJ mol⁻¹ to solvate the HF from this AsF₄OH·EC-HF complex. Our results show that AsF₅ readily reacts with H₂O by a ligand exchange reaction through proton transfer to form HF and an AsF₄OH·EC complex.

The AsF₄OH·EC produced by Reaction (8) can itself undergo decomposition to form additional HF via another proton transfer reaction

Similar to the case of Reaction (5), which produced HF by reaction of PF₅ with H₂O, our calculations predict that EC dissociates from AsF₄OH·EC with a dissociation enthalpy of -62.3 kJ mol⁻¹ and that the resulting AsF₄OH undergoes an intramolecular proton transfer form HF and AsOF₃. Reactions (8) and (9) make up a two-step reaction that converts AsF₅ with H₂O into AsOF₃ and two HF molecules. However, we calculate a barrier and reaction enthalpy for Reaction (9) of 158.6 kJ mol⁻¹ and 117.2 kJ mol⁻¹, respectively, as shown in Figure 1.

Although AsF₅ reacts with H₂O to rapidly form HF and AsF₄OH via (8), subsequent reaction by (9) to generate a second HF occurs with a barrier of 158.6 kJ mol⁻¹, which is inactive at the typical temperatures realized in LIBs. Due to the high barrier of the second reaction step, AsF₄OH·EC complexes and a single HF molecule would predominantly form in electrolytes containing LiAsF₆, as AsF₄OH·EC is the first stable intermediate on the PES and is formed via a low barrier reaction and converted to AsOF₃ and a second HF molecule via a high barrier reaction. Consequently, our results predict that electrolytes with LiAsF₆ replacing LiPF₆ will have lower concentrations of HF than LIBs utilizing LiPF₆ - because PF₅ reacts with H₂O to form two HF molecules rather than just one - but higher HF concentrations than those utilizing LiPOF₄ as the electrolyte salt additive, where the first step to form HF possesses a high barrier and is kinetically inactive at operating conditions.

4. Conclusions

In this study, we examined HF generation in lithium ion battery electrolytes from reactions between H₂O contaminants and the decomposition products PF₅, POF₄ and AsF₅ of the three electrolyte additives LiPF₆, LiPOF₄, and LiAsF₆. The initial precipitation of LiF from these additives to form PF₅, POF₃ and AsF₅ from these salts has been previously shown to be dominated by the choice

of electrolyte solvent; we predict LiF precipitate formation enthalpies of 65.7, 78.2, and 78.7 kJ mol⁻¹ in EC electrolyte for LiPF₆, LiPOF₄, and LiAsF₆, respectively. We investigated the ligand exchange reaction mechanisms between the LiF precipitate products: PF₅, POF₃, and AsF₅, and H₂O to form HF in the electrolyte, which subsequently reacts with transition metal oxide cathodes to degrade them and shorten LIB lifetimes.

We predict significant Lewis acid-base interactions between the PF₅ and especially AsF₅ Lewis acids and the EC and H₂O Lewis bases, whereas POF₃ does not exhibit these Lewis acid-base interactions with either the EC electrolyte or H₂O. Rather, geometry optimization of the contact reactant complex between POF₃ and H₂O drifts apart towards separated, solvated species. Additionally, we predict the P-F bond in POF₃ is stronger than the P-F bond in PF₅ and significantly stronger than the As-F bond in AsF₅. This suggests a greater energetic penalty to form HF from POF₃, and a significantly lower barrier to form HF from AsF₅. This is consistent with our calculations that predict a high barrier for HF generation from POF₃ of 157.7 kJ mol⁻¹, and suggests that LiPOF₄ is a viable alternative to the state-of-the-art electrolyte additive, LiPF₆. On the other hand, the first ligand exchange reaction between H₂O and PF₅ has a barrier of 114.2 kJ mol⁻¹, which is still low enough that it reacts to form HF, albeit relatively slowly. Furthermore, because the transition state for POF₃ to react with H₂O to form POF₂OH involves a five-fold coordinated P center and thus an energy penalty to hybridize P from sp³ to sp³d, it involves a significantly higher barrier (157.7 kJ mol⁻¹) to HF generation than the 114.2 kJ mol⁻¹ barrier to generate HF from PF₅. As a result of the 43.5 kJ mol⁻¹ higher activation barrier, we predict a reduction in the Boltzmann factor of the rate constant by ~10⁻⁸ for HF generation at 310K from POF₃ relative to PF₅.

We predict that AsF₅ is a stronger Lewis acid than either PF₅ or POF₃, and that formation the AsF₅·H₂O dative complex is exothermic by 81.2 kJ mol⁻¹. This complex then reacts to form HF with an activation barrier of 30.5 kJ mol⁻¹, relative to the AsF₅·EC reactant complex, suggesting that LIB electrolytes containing LiAsF₆ will suffer capacity fading and a shortened service due to relatively facile HF generation in the electrolyte.

These results explain the mechanisms by which the LiPF₆, LiAsF₆ and LiPOF₄ salt additives decompose in carbonate electrolytes. Our results predict that PF₅, formed by decomposition of LiPF₆ in typical LIB electrolytes, will react with H₂O to produce HF, which degrades transition metal oxide cathodes. However, we find that the barriers for the reaction of POF₃ with H₂O are relatively high leading to significantly slower generation of HF. Consequently, based on its stability with respect to generating HF, we suggest that LiPOF₄ should be investigated further as a potential electrolyte salt for LIBs to mitigate HF formation in liquid carbonate based electrolytes. However, its implementation will ultimately depend on whether it performs adequately in terms of Li⁺ conductivity and SEI formation.

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Table 1 : The Effect of Solvent Model on the Energetics of HF Generation by Reaction 2

Species and Solvent Model	Activation Barrier (kJ mol ⁻¹)	Reaction Enthalpy (kJ mol ⁻¹)
PF ₅ – Implicit	131.4	39.7
PF ₅ - 1 EC + PCM	114.2	14.6
PF ₅ - 2 EC + PCM	115.5	12.6
PF ₅ - 3 EC + PCM	115.9	11.3
POF ₃ – Implicit	151.5	-15.1
POF ₃ - 1 EC + PCM	157.7	-3.8
POF ₃ - 2 EC + PCM	148.5	-10.5
POF ₃ - 3 EC + PCM	145.2	-9.2
AsF ₅ – Implicit	68.6	39.7
AsF ₅ - 1 EC + PCM	30.5	-11.3
AsF ₅ - 2 EC + PCM	33.9	-12.6
AsF ₅ - 3 EC + PCM	31.8	-13.4

Table 2: Properties of POF₃, PF₅, and AsF₅ and Their Lewis Acid-Base Complexes with H₂O

Species	P or As Charge (e)	LUMO Energy Relative to H ₂ O HOMO (kJ mol ⁻¹)	O-P or O-As Distance in Complex (Å)	Complexation Energy (kJ mol ⁻¹)
POF ₃	1.19	1255.2	2.98	6.7
PF ₅	1.31	1153.1	1.92	-41.8
AsF ₅	1.40	1097.5	1.99	-81.2

Figure 2. (a) The structure of the TS of Reaction (4) in PCM with a solvating EC (not shown) is illustrated. This ligand exchange reaction produces HF and involves a barrier 114.2 kJ mol⁻¹ and a reaction enthalpy is 14.6 kJ mol⁻¹, referenced to the PF₅·EC complex. The red, white, purple and orange atoms are O, H, F and P. (b) A 180°

schematic illustration of Reaction (4) showing the ligand exchange reaction involving the simultaneous dissociation of the P-F and O-H bonds and formation of the P-O and HF bonds.

Figure 3. (a) The $\text{PF}_4\text{OH} \cdot \text{EC}$ product of Reaction (4), (the HF product is not shown). The red, white, purple, orange and black atoms represent O, H, F, P and C. (b) Illustration showing the Lewis acid-base complex between PF_4OH and EC, which returns the P atom to an octahedral-like coordination.

Figure 4. The (a) transition state of Reaction (5) (the spectating EC molecules is not shown). The red, white, purple and orange atoms represent O, H, F and P. (b) Illustration of the ligand exchange reaction that forms HF. As the reaction approaches the TS, $\text{PF}_4\text{OH} \cdot \text{EC}$ dissociates, while at the TS the P-F and O-H bonds dissociates as the H-F and P=O π -bond forms. Reaction (5) has an activation energy of 97.5 kJ mol^{-1} and reaction enthalpy of 17.6 kJ mol^{-1} , referenced to the $\text{PF}_4\text{OH} \cdot \text{EC}$ reactant complex.

Figure 5. (a) Structure of the TS of Reaction (6) is shown where H_2O reacts with POF_3 through ligand exchange to form HF and POF_2OH . The red, white, purple, orange and black atoms represent O, H, F, P and C. (b) Schematic illustration of the ligand exchange reaction where the H-F and P-O bonds form as the P-F and OH bonds dissociate. Reaction (6) has an activation energy of $157.7 \text{ kJ mol}^{-1}$ and is exothermic by 3.8 kJ mol^{-1} , referenced to the solvated reactants.

Figure 6. (a) The structure of the TS for Reaction (7) is shown where the red, white, purple, orange and black atoms represent O, H, F, P and C. (b) A schematic illustration of the HF formation reaction involving dissociation of the P-F and O-H bonds and simultaneous formation of the H-F and P-O bonds. Reaction (7) is predicted to occur with an activation energy of $141.4 \text{ kJ mol}^{-1}$ and reaction energy of 73.6 kJ mol^{-1} , referenced to the $\text{PF}_2\text{OOH}\cdot\text{EC}$ complex.