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Elementary Decomposition Mechanisms of Lithium Hexafluorophosphate in Battery Electrolytes and Interphases

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should be kinetically limited at moderate temperatures. We further identify selectivity in the proposed autocatalysis of POF_3 , finding that POF_3 preferentially reacts with highly anionic oxygens. These results provide a means of interphase design in LIBs, indicating that LiPF₆ reactivity may be controlled by varying the abundance or distribution of inorganic carbonate species or by limiting the transport of PF_6^- through the SEI.

ithium-ion batteries (LIBs) have in recent years become a cornerstone energy storage technology,¹ powering personal electronics and a growing number of electric vehicles. To continue this trend of electrification in transportation and other sectors, LIBs with higher energy density²⁻⁵ and longer cycle and calendar life⁶ are needed, motivating research into novel battery materials. Battery electrolytes, which are typically the limiting factor in terms of LIB potential window and irreversible capacity loss,⁷⁻⁹ are an especially attractive target for research and development to expand the utility of LIBs.

primarily through rapid chemical reactions with Li₂CO₃, while hydrolysis

In today's commercial LIBs, the most common electrolytes are comprised of lithium hexafluorophosphate (LiPF₆) dissolved in blends of cyclic carbonates, especially ethylene carbonate (EC), and linear carbonates such as ethyl methyl carbonate.^{10–14} Carbonate/LiPF₆ electrolytes have many desirable properties, including weak ion association and high Li⁺ conductivity,^{15–17} but they are reactive at low potentials. When paired with graphite negative electrodes, carbonate/ LiPF₆ electrolytes decompose to form a relatively stable passivation film known as the solid electrolyte interphase (SEI),^{18–23} which prevents continual electrolyte degradation while allowing reversible charging and discharging. On the other hand, conventional electrolytes based on EC and LiPF₆ are essentially incompatible with high-energy density negative electrodes (e.g., Li metal,^{24,25} Si^{26,27}) and form unstable SEIs, resulting in comparatively poor cycle and calendar life.^{28,29}

Due to the significance of the SEI in preserving battery capacity, SEI formation from carbonate/LiPF₆ electrolytes has been extensively studied for decades.^{30–32} Such studies have sought to reveal the fundamental processes involved in the exemplar carbonate/LiPF₆ system and to identify opportunities for improvement through electrolyte engineering. An understanding of the decomposition of carbonate solvents, particularly EC, has been developed via a combination of experiment and theory. A wide range of decomposition products (including gases,^{33,34} short-chain organic molecules, oligomers/polymers, and inorganic carbonates (e.g., Li₂CO₃) and oxides (e.g., Li₂O)¹⁹) have been experimentally characterized, and plausible elementary mechanisms for EC decomposition have been identified using density functional

Received: October 17, 2022 Accepted: November 21, 2022





Figure 1. Hydrolysis of PF₅ to form POF₃ and 2HF. This mechanism is overall thermodynamically unfavorable and involves two reactions with high barriers ($\Delta G^{\ddagger} > 1.00 \text{ eV}$).

theory	(DFT),	^{35–37} ab	initio	molecular	dynamics
(AIMD),	^{38–40} and	chemical	reaction	network an	alysis. ^{41–44}

$$POF_3 + R_2CO_3 \rightarrow PF_2O_2R + RF + CO_2$$
(1)

$$PF_2O_2R + PF_5 \rightarrow RF + 2POF_3 \tag{2}$$

In comparison, there are many open questions concerning the decomposition of LiPF₆. It is widely accepted that LiPF₆ reacts to form LiF, which precipitates and contributes to the SEI.^{30,31,45,46} A range of other products, including POF₃,⁴⁷ difluorophosphoric acid (PF_2OOH) ,⁴⁸ and some organo-phosphorus compounds⁴⁹ have been identified by experimental spectroscopy. Moreover, LiPF₆ demonstrates thermal instability,^{50,51} and it has long been suggested that an autocatalytic mechanism involving POF_3 (eqs 1 and 2) is responsible.⁵² However, mechanistic explanations for LiPF₆ reactivity remain lacking. Most commonly, hydroly-sis^{7,45,46,51,53} is invoked to explain observed PF_6^- decomposition products (eqs 3 and 4 show an example mechanism). LiPF₆ has been shown to be unstable in the presence of water,¹⁴ yet hydrolysis alone is insufficient to explain the significant role of LiPF₆ in SEI formation. The DFT study of Okamoto⁵⁴ suggests that PF₆⁻ hydrolysis should be extremely slow, in agreement with longstanding experimental evidence.⁵⁵ Moreover, LIB electrolytes used in laboratory studies are often rigorously dried, allowing ~ 10 ppm of H₂O. Though exposure to high potentials on the positive electrode can both enable the formation of H_2O by reactions with EC^{56} and accelerate $PF_6^$ hydrolysis,⁵⁷ this cannot explain LiF formation or further LiPF₆ decomposition during early SEI formation before high potentials have been reached or in batteries without highvoltage positive electrodes.

$$PF_5 + H_2O \rightarrow POF_3 + 2HF \tag{4}$$

In this work, we explore the decomposition mechanisms of LiPF₆ using DFT at a high level of theory (see Supporting Information for details). We find that water is not necessary to explain the formation of LiF or POF₃ but rather that PF₅ can react rapidly with readily available Li2CO3 during early SEI formation. This mechanism is entirely chemical in nature; it does not depend on electrochemical reduction or oxidation of LiPF₆ and can occur at any depth of the SEI as long as the transport of PF_6^- to inorganic carbonate domains is feasible. Hence, the porosity, morphology, and transport properties of the SEI also become relevant factors. We then study POF₃ autocatalysis, using PF2OOH and LiPF2O2 as model intermediates. Because POF₃ adds selectively to highly charged oxygens in oxyanions, LiPF₂O₂ is preferred over PF₂OOH in the absence of an oxidizing potential. Our calculations indicate that overall, the POF₃ autocatalytic cycle is limited by a slow intramolecular fluorine transfer step. These findings answer longstanding questions regarding the decomposition of LiPF₆ and suggest new routes for controlling salt reactivity during SEI formation.

We begin by considering the formation of PF_5 , which is a key intermediate in essentially all LiPF₆ reaction routes considered in the literature and in this work. We find that the elimination of LiF from LiPF₆ to form PF₅ (eq 3) has no transition state but is endergonic, with $\Delta G = 1.04$ eV. However, we note that the product in this reaction is a solution-phase molecule of LiF, whereas we expect that LiF will precipitate, forming solid deposits within the SEI. The elimination of LiF is more likely to occur when considering the possibility that LiF could be stabilized by precipitation. Okamoto⁵⁴ previously found that the deposition of solid LiF (LiF(solv) \rightarrow LiF(solid)) has $\Delta G = -1.17$ eV, which would

$$\text{LiPF}_6 \rightleftharpoons \text{LiF}(s) + \text{PF}_5$$
 (3)

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Figure 2. Energy diagrams for the formation of POF₃ from PF₅ and Li₂CO₃. (a) LiPOF₄ forms via by simultaneous elimination of LiF and CO₂ from a PF₅-Li₂CO₃ adduct. LiPOF₄ can then eliminate LiF to form POF₃. (b) Alternative, less favorable mechanisms in which LiF is eliminated from the adduct without simultaneously eliminating CO₂.

make eq 3 overall exergonic. More recently, Cao et al.⁵⁸ used DFT and AIMD to show that LiPF_6 decomposition by either chemical or electrochemical means is greatly accelerated in the presence of existing LiF. Here, we report the reaction energies and energy barriers of LiF elimination reactions like eq 3 without including the effect of a surface or LiF precipitation. However, we emphasize that these reactions, in general, should be more favorable than what is predicted based on calculations with molecular LiF in solution.

Even once PF_5 is formed, Figure 1 confirms that, at our chosen level of theory, the direct hydrolysis of PF_5 by H_2O is unfavorable. Each of the three hydrolysis steps (the addition of

 H_2O to PF_5 ($H_2O + PF_5 \rightarrow M_1$), the elimination of HF to form PF_4OH ($M_1 \rightarrow M_2$), and the elimination of another HF from PF_4OH to form POF_3 ($M_2 \rightarrow M_3$)) is predicted to be endergonic. Further, the last two steps both have energy barriers $\Delta G^{\ddagger} > 1.00$ eV, agreeing with the experimental observation that hydrolysis is slow at room temperature. Significant thermal activation beyond temperatures reached in normal LIB cycling conditions would be required to enable LiPF₆ hydrolysis.

An alternative mechanism involves the reaction of PF_5 with Li_2CO_3 (Figure 2). Reactions between $LiPF_6$ and inorganic carbonates have been proposed in the past^{59,60} on the basis of



Figure 3. Reactions between POF₃ and simple inorganic carbonates (a) H_2CO_3 , (b) LiHCO₃, and (c) Li₂CO₃ to form CO₂ and either PF₂OOH or LiPF₂O₂. A trend between the partial charge of the reacting oxygen(s) and the reaction energies with POF₃ for each carbonate considered is shown in (d). A linear fit, $\Delta G = 4.39q + 4.47$, where q is the most negative oxygen partial charge, shows strong correlation ($R^2 = 0.96$) among the three carbonates.

the observed evolution of CO_2 and POF_3 upon mixing of $LiPF_6$ and Li_2CO_3 , but this route has largely been neglected in favor of hydrolytic mechanisms. Moreover, no elementary mechanism for the reaction between $LiPF_6$ -like species and Li_2CO_3 has been reported.

We find that PF₅ reacts vigorously with Li₂CO₃. An initial addition step between the two reactants $(M_4 \rightarrow M_5)$ has a low barrier of $\Delta G^{\ddagger} = 0.04$ eV. Following reorganization of Li⁺ $(M_5 \rightarrow M_6)$, the adduct (M_6) then dissociates in a single concerted reaction, yielding LiF, CO₂, and LiPOF₄ with $\Delta G^{\ddagger} = 0.19$ eV. Finally, to form POF₃, LiPOF₄ eliminates an additional molecule of LiF $(M_7 \rightarrow \text{LiF} + \text{POF}_3)$, with $\Delta G^{\ddagger} = 0.63$ eV,

 $\Delta G = 0.28$ eV. We again note that we expect both ΔG and ΔG^{\ddagger} for LiF elimination reactions to be lowered if precipitation of LiF on a surface is allowed. Even without any corrections for the instability of molecular LiF produced in $M_6 \rightarrow M_7$ and $M_7 \rightarrow LiF + POF_3$, this mechanism represents one of the most kinetically favorable elementary mechanisms for PF₅ decomposition yet reported.

If it does not dissociate completely, the adduct M_5 may instead eliminate LiF ($M_5 \rightarrow M_8$), though this reaction suffers from a high predicted barrier of $\Delta G^{\ddagger} = 1.34$ eV. After LiF elimination, an additional oxygen from the carbonate group binds to phosphorus to form a ring complex M_9 . By eliminating



Figure 4. Possible routes for the re-formation of POF₃ from PF₂OOH (a) and LiPF₂O₂ (b). Both mechanisms are kinetically limited due to an extremely unfavorable intramolecular fluorine transfer step ($M_{26} \rightarrow M_{27}, M_{30} \rightarrow M_{31}$), which makes POF₃ autocatalysis unlikely at modest temperatures. Rate coefficients for the fluorine transfer step are provided in (c) for the PF₂OOH pathway and in (d) for the LiPF₂O₂ pathway.

CO₂, either immediately $(M_9 \rightarrow M_{11}, \Delta G^{\ddagger} = 0.81 \text{ eV})$ or following the elimination of another LiF $(M_{12} \rightarrow M_{13}, \Delta G^{\ddagger} = 0.36 \text{ eV})$, this ring complex also forms LiPOF₄ (M_{11}) or POF₃ (M_{13}) .

The proposed mechanisms shown in Figure 2 rely only on Li_2CO_3 , which should be abundant at the negative electrode, especially during early SEI formation.^{21,31,38,60–62} The reaction of PF₅ and Li_2CO_3 is also entirely chemical in nature; none of the reactions in Figure 2 depend on electrochemical oxidation or reduction. As a result, the decomposition should not depend explicitly on applied potential, the proximity to the anode surface, or the availability of electrons. We therefore predict that the decomposition of PF₅ can occur anywhere in the SEI, so long as inorganic carbonates like Li₂CO₃ are present. This being said, because Li₂CO₃ is formed in the SEI as a result of electrochemical reduction of PF₅ with Li₂CO₃ will implicitly have a potential dependence.

While our focus in this work is on LiPF_6 decomposition during SEI formation, it is worth noting that Li_2CO_3 is an impurity formed during the synthesis of common transition metal oxide positive electrodes.⁵⁹ Accordingly, the mechanisms described in Figure 2 could occur at the positive electrode as well as at the negative electrode or the SEI.

Figure 2 indicates that POF_3 emerges rapidly by reaction with Li_2CO_3 during SEI formation. This hints that the proposed autocatalytic mechanisms for POF_3 (re-)formation (eqs 1 and 2), which rely on POF_3 and carbonate species, are chemically plausible.

To confirm the mechanism of POF₃ autocatalysis at elevated temperature, we first consider the formation of PF₂O₂R species (Figure 3). Specifically, we explore the formation of PF₂OOH from H₂CO₃ (Figure 3a) and LiHCO₃ (Figure 3b) and the formation of LiPF₂O₂ by Li₂CO₃ (Figure 3c). In addition to their relevance for POF₃ formation and LiPF₆ decomposition, PF₂O₂R species and in particular PF₂OOH have been blamed as major contributors to the decomposition of SEI species and the loss of battery capacity.^{63,64} Jayawardana et al. have argued that PF₂OOH should form at the positive electrode as a result of PF₆⁻ oxidation.⁶³ If PF₂OOH and related species could

form at the negative electrode without high potentials, it could have significant implications for the stability of the SEI.

Figure 3a shows a mechanism for a chemical reaction between H_2CO_3 and POF_3 . The initial addition reaction between POF_3 and H_2CO_3 ($H_2CO_3 + POF_3 \rightarrow M_{14}$) is thermodynamically unfavorable ($\Delta G = 1.62 \text{ eV}$). Subsequent reactions to form HF, CO_2 , and PF_2OOH do not face significant barriers and should occur rapidly. The reaction between POF_3 and LiHCO_3 (Figure 3b) follows a similar mechanism. The addition step ($M_{17} \rightarrow M_{18}$) is also endergonic ($\Delta G^{\ddagger} = 0.48 \text{ eV}$, $\Delta G = 0.52 \text{ eV}$), though we suggest that it could be accessed at moderate temperatures. Addition by LiHCO₃ is followed by the elimination of LiF ($M_{19} \rightarrow M_{20}$), which is analogous to the elimination of HF in Figure 3a ($M_{14} \rightarrow M_{15}$). Following the complete removal of LiF, M_{20} can undergo the same concerted proton transfer and CO_2 elimination shown in Figure 3a ($M_{15} \rightarrow M_{16}$).

In contrast, POF₃ adds easily to Li_2CO_3 (Figure 3c, $M_{21} \rightarrow$ M_{22}), with $\Delta G^{\ddagger} = 0.15$ eV and $\Delta G = -0.01$ eV. We explain the difference in the thermodynamics of the reactions between POF₃ and H₂CO₃, LiHCO₃, and Li₂CO₃ by considering atomic partial charges (Figure 3d). POF₃ is reactive toward the highly anionic oxygens in Li₂CO₃ but not toward the less charged oxygens in LiHCO₃ and H₂CO₃. The difference in behavior can also be rationalized in terms of acid-base chemistry. POF₃ and PF₅ (both Lewis acids) prefer to react with CO_3^{2-} (a Lewis base) over HCO_3^{-} (depending on context, either a weak acid or a weak base) and H_2CO_3 (an acid). We find similar trends for the reaction between PF_5 and inorganic carbonates (Supporting Information Figure S1). Moreover, we suggest (Supporting Information Figure S2) that the reactivity of phosphorus fluorides with anionic oxygens and Lewis bases is at least somewhat general and is not specific to Li₂CO₃. Though PF₂OOH formation via LiHCO₃ is possible, the difficulty of addition with protonated carbonates suggests that, barring electrochemical processes, LiPF₂O₂ should be more abundant at the negative electrode than PF2OOH. Nonetheless, the prediction that PF2OOH and LiPF2O2 can form at or near the SEI without the need for cross-talk from the positive electrode motivates further efforts to understand the interactions between these species and other SEI components.

Mechanisms for the re-formation of POF₃, completing the autocatalytic cycle in eq 2, are shown in Figure 4. Following a similar trend to that shown in Figure 3d, the attack of PF_5 by the acidic PF₂OOH (Figure 4a, PF₂OOH + PF₅ \rightarrow M₂₆) is thermodynamically unfavorable, while LiPF₂O₂ can favorably add to PF_5 (Figure 4b, LiPF₂O₂ + PF₅ \rightarrow M₂₉). After the initial addition, an intramolecular fluorine transfer is required; for both PF₂O₂R species considered, this step is thermodynamically unfavorable and suffers from a high barrier ($M_{26} \rightarrow M_{27}$, $\Delta G^{\ddagger} = 0.95$ eV; $M_{30} \rightarrow M_{31}$, $\Delta G^{\ddagger} = 1.76$ eV). While both intramolecular fluorine transfer reactions are kinetically limited at room temperature (Figure 4c,d), the reaction without Li⁺ can occur at elevated temperature (especially T > 150 °C). After fluorine transfer, the two mechanisms in Figure 4a,b diverge. In Figure 4a, a concerted proton transfer and elimination step occurs $(M_{27} \rightarrow M_{28})$, yielding POF₃ and PF₄OH. PF₄OH can subsequently eliminate HF to form POF₃, as shown in Figure 1. In Figure 4b, a four-member O-P-O-P ring is formed $(M_{32} \rightarrow M_{33})$ and POF₃ is eliminated $(M_{33} \rightarrow$ M_{34}), leaving LiPOF₄ which could then form LiF and POF₃ as previously discussed.

Our mechanism confirms the previously reported autocatalytic formation of POF₃. We find, in agreement with earlier experimental studies, ^{50,52} that this cycle requires significant thermal activation ($T \sim 150$ °C). This is primarily due to a sluggish intramolecular fluorine transfer and, specifically for the mechanism requiring PF₂OOH as an intermediate, the high barrier for HF elimination to re-form POF₃. While we have found a mechanism for POF₃ autocatalysis that does not require any water, the significantly lower barrier for the pathway involving PF₂OOH indicates that LiPF₆ thermal decomposition could be initiated and accelerated by LiPF₆ hydrolysis,⁴⁷ which is accessible at elevated temperature.

To conclude, $LiPF_6$ is an exceptional salt that is likely to play a major role in the LIB market for years to come. While some decomposition of LiPF₆ is desirable to form a functional SEI, continued breakdown can severely limit the life of LiBs. In this work, we identified a novel and facile elementary decomposition mechanism of LiPF₆ using first-principles DFT simulations. Our results imply that under normal battery cycling conditions, the major decomposition mechanism of LiPF₆ does not depend on water or on electrochemical salt reduction. Rather, LiPF₆ forms the expected products LiF, POF₃, LiPF₂O₂, and potentially PF₂OOH via entirely chemical reactions with inorganic carbonates (especially Li₂CO₃). These reactions can likely occur in the solution phase or in nanocrystalline or amorphous regions of the SEI (see Supporting Information Table S1). PF₅ and POF₃ show a strong affinity to react with highly anionic oxygens and Lewis bases, suggesting that efforts to control the reactivity of LiPF_6 should focus on limiting the exposure of PF5 to oxyanion and other basic species, including and especially inorganic carbonates like Li₂CO₃, in the SEI as well as on the surface of positive electrodes. This consideration may include morphological control, such as reducing porosity and/or abundance of inorganic species in the outer regions of the SEI.

In the future, theoretical studies should be combined with experimental spectroscopy to validate the mechanisms reported here. It should be possible to compare rate laws obtained by experiment (via, for example, time-resolved spectroscopy with varying amounts of inorganic carbonates and $LiPF_6$) and theory (via kinetic simulations, for example, kinetic Monte Carlo). More challenging but no less worthwhile would be to confirm if the decomposition of $LiPF_6$ in a battery is primarily chemical or electrochemical in nature. This could be accomplished by tracking the rate of decomposition of LiPF₆ in the presence of inorganic carbonate species in a reductively stable solvent under varying applied potentials. While we have focused here primarily on LiPF₆ decomposition in EC-based electrolytes, we suspect that LiPF₆ could chemically react in a range of solvents via mechanisms similar to what we have described, provided that those solvents reduce and decompose to form oxyanions with highly charged reactive oxygens or sufficiently strong Lewis bases. The extent of LiPF₆ decomposition will depend on the availability of these basic and oxyanion species. Additional investigations into solvent degradation and SEI formation in EC-free (and especially carbonate-free) electrolytes should be conducted to assess if the mechanism that we have described here is general or specific to carbonate-based solvents. Detailed study of the elementary reaction mechanisms between LiPF₆ decomposition products (especially PF2O2R species) and other SEI species (e.g., organic carbonates), as well as the formation

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mechanisms of organophosphorus compounds and phosphate polymers in the SEI, should also be conducted.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.2c02351.

Data availability statement, computational methods, and discussion of additional reaction mechanisms for $LiPF_6$ decomposition (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is intellectually led by the Silicon Consortium Project directed by Brian Cunningham under the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy, Contract DE-AC02-05CH11231 with additional support from the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. E.W.C.S.-S. is supported by the Kavli Energy Nanoscience Institute Philomathia Graduate Student Fellowship. H.D.P. is supported by the United States Department of Defense National Defense Science and Engineering Graduate Fellowship. S.M.B. is supoported by the Laboratory Directed Research and Development Program of Lawrence Berkeley National Laboratory under U.S. Department of Energy Contract DE-AC02-05CH11231. T.B.P. conducted this work as part of the Community College Internship program under the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists. Access to and assistance using the Schrödinger Suite of software tools, including Jaguar and AutoTS, were generously provided by Schrödinger, Inc. Data for this study were produced using computational resources provided by the Eagle and Swift highperformance computing (HPC) systems at the National Renewable Energy Laboratory and the Lawrencium HPC cluster at Lawrence Berkeley National Laboratory.

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