

# Elementary Decomposition Mechanisms of Lithium Hexafluorophosphate in Battery Electrolytes and Interphases

Evan Walter Clark Spotte-Smith,<sup>†,‡,⊥</sup> Thea Bee Petrocelli,<sup>†,‡,¶,⊥</sup> Hetal D.  
Patel,<sup>†,‡</sup> Samuel M. Blau,<sup>§</sup> and Kristin A. Persson<sup>\*,‡,||</sup>

<sup>†</sup>*Materials Science Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road,  
Berkeley, CA, 94720 USA*

<sup>‡</sup>*Department of Materials Science and Engineering, University of California, Berkeley, 210  
Hearst Memorial Mining Building, Berkeley, CA, 94720 USA*

<sup>¶</sup>*Cabrillo College, 6500 Soquel Drive, Aptos, CA, 95003 USA*

<sup>§</sup>*Energy Storage and Distributed Resources, Lawrence Berkeley National Laboratory, 1  
Cyclotron Road, Berkeley, CA, 94720 USA*

<sup>||</sup>*Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley,  
CA, 94720 USA*

<sup>⊥</sup>*These authors contributed equally to this work*

E-mail: [kapersson@lbl.gov](mailto:kapersson@lbl.gov)

## Abstract

Electrolyte decomposition constitutes an outstanding challenge to long-life Li-ion batteries (LIBs) as well as emergent energy storage technologies, contributing to protection via solid electrolyte interphase (SEI) formation and irreversible capacity loss over a battery's life. Major strides have been made to understand the breakdown of

common LIB solvents; however, salt decomposition mechanisms remain elusive. In this work, we use density functional theory to explain the decomposition of lithium hexafluorophosphate ( $\text{LiPF}_6$ ) salt under SEI formation conditions. Our results suggest that  $\text{LiPF}_6$  forms  $\text{POF}_3$  primarily through rapid chemical reactions with  $\text{Li}_2\text{CO}_3$ , while hydrolysis should be kinetically limited at moderate temperatures. We further identify selectivity in the proposed autocatalysis of  $\text{POF}_3$ , finding that  $\text{POF}_3$  preferentially reacts with highly anionic oxygens. These results provide a means of interphase design in LIBs, indicating that  $\text{LiPF}_6$  reactivity may be controlled by varying the abundance or distribution of inorganic carbonate species or by limiting the transport of  $\text{PF}_6^-$  through the SEI.

Lithium-ion batteries (LIBs) have in recent years become a cornerstone energy storage technology,<sup>1</sup> 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 density<sup>2-5</sup> and longer cycle and calendar life<sup>6</sup> 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,<sup>7-9</sup> are an especially attractive target for research and development to expand the utility of LIBs.

In today’s commercial LIBs, the most common electrolytes are comprised of lithium hexafluorophosphate ( $\text{LiPF}_6$ ) dissolved in blends of cyclic carbonates, especially ethylene carbonate (EC), and linear carbonates such as ethyl methyl carbonate.<sup>10-14</sup> Carbonate/ $\text{LiPF}_6$  electrolytes have many desirable properties, including weak ion association and high  $\text{Li}^+$  conductivity,<sup>15-17</sup> but they are reactive at low potentials. When paired with graphite negative electrodes, carbonate/ $\text{LiPF}_6$  electrolytes decompose to form a relatively stable passivation film known as the solid electrolyte interphase (SEI),<sup>18-23</sup> which prevents continual electrolyte degradation while allowing reversible charging and discharging. On the other hand, conventional electrolytes based on EC and  $\text{LiPF}_6$  are essentially incompatible with high-energy density negative electrodes (e.g. Li metal,<sup>24,25</sup> Si<sup>26,27</sup>) and form unstable SEIs, resulting in

comparatively poor cycle and calendar life.<sup>28,29</sup>

Due to the significance of the SEI in preserving battery capacity, SEI formation from carbonate/LiPF<sub>6</sub> electrolytes has been extensively studied for decades.<sup>30-32</sup> Such studies have sought to reveal the fundamental processes involved in the exemplar carbonate/LiPF<sub>6</sub> 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,<sup>33,34</sup> short-chain organic molecules, oligomers/polymers, and inorganic carbonates (e.g. Li<sub>2</sub>CO<sub>3</sub>) and oxides (e.g. Li<sub>2</sub>O)<sup>19</sup> - have been experimentally characterized, and plausible elementary mechanisms for EC decomposition have been identified using density functional theory (DFT),<sup>35-37</sup> *ab initio* molecular dynamics (AIMD),<sup>38-40</sup> and chemical reaction network analysis.<sup>41-44</sup>



In comparison, there are many open questions concerning the decomposition of LiPF<sub>6</sub>. It is widely accepted that LiPF<sub>6</sub> reacts to form LiF, which precipitates and contributes to the SEI.<sup>30,31,45,46</sup> A range of other products, including POF<sub>3</sub>,<sup>47</sup> difluorophosphoric acid (PF<sub>2</sub>OOH),<sup>48</sup> and some organophosphorus compounds<sup>49</sup> have been identified by experimental spectroscopy. Moreover, LiPF<sub>6</sub> demonstrates thermal instability,<sup>50,51</sup> and it has long been suggested that an autocatalytic mechanism involving POF<sub>3</sub> (Equations 1-2) is responsible.<sup>52</sup> However, mechanistic explanations for LiPF<sub>6</sub> reactivity remain lacking. Most commonly, hydrolysis<sup>7,45,46,51,53</sup> is invoked to explain observed PF<sub>6</sub><sup>-</sup> decomposition products (Equations 3-4 show an example mechanism). LiPF<sub>6</sub> has been shown to be unstable in the presence of water,<sup>14</sup> yet hydrolysis alone is insufficient to explain the significant role of LiPF<sub>6</sub> in SEI

formation. The DFT study of Okamoto<sup>54</sup> suggests that  $\text{PF}_6^-$  hydrolysis should be extremely slow, in agreement with longstanding experimental evidence.<sup>55</sup> Moreover, LIB electrolytes used in laboratory studies are often rigorously dried, allowing  $\sim 10$ ppm  $\text{H}_2\text{O}$ . Though exposure to high potentials on the positive electrode can both enable the formation of  $\text{H}_2\text{O}$  by reactions with EC<sup>56</sup> and accelerate  $\text{PF}_6^-$  hydrolysis,<sup>57</sup> this cannot explain LiF formation or further  $\text{LiPF}_6$  decomposition during early SEI formation before high potentials have been reached or in batteries without high-voltage positive electrodes.



In this work, we explore the decomposition mechanisms of  $\text{LiPF}_6$  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  $\text{POF}_3$ , but rather that  $\text{PF}_5$  can react rapidly with readily available  $\text{Li}_2\text{CO}_3$  during early SEI formation. This mechanism is entirely chemical in nature; it does not depend on electrochemical reduction or oxidation of  $\text{LiPF}_6$  and can occur at any depth of the SEI as long as the transport of  $\text{PF}_6^-$  to inorganic carbonate domains is feasible. Hence, the porosity, morphology, and transport properties of the SEI also become relevant factors. We then study  $\text{POF}_3$  autocatalysis, using  $\text{PF}_2\text{OOH}$  and  $\text{LiPF}_2\text{O}_2$  as model intermediates. Because  $\text{POF}_3$  adds selectively to highly charged oxygens in oxyanions,  $\text{LiPF}_2\text{O}_2$  is preferred over  $\text{PF}_2\text{OOH}$  in the absence of an oxidizing potential. Our calculations indicate that overall, the  $\text{POF}_3$  autocatalytic cycle is limited by a slow intramolecular fluorine transfer step. These findings answer longstanding questions regarding the decomposition of  $\text{LiPF}_6$  and suggest new routes for controlling salt reactivity during SEI formation.

We begin by considering the formation of  $\text{PF}_5$ , which is a key intermediate in essentially all  $\text{LiPF}_6$  reaction routes considered in the literature and in this work. We find that the

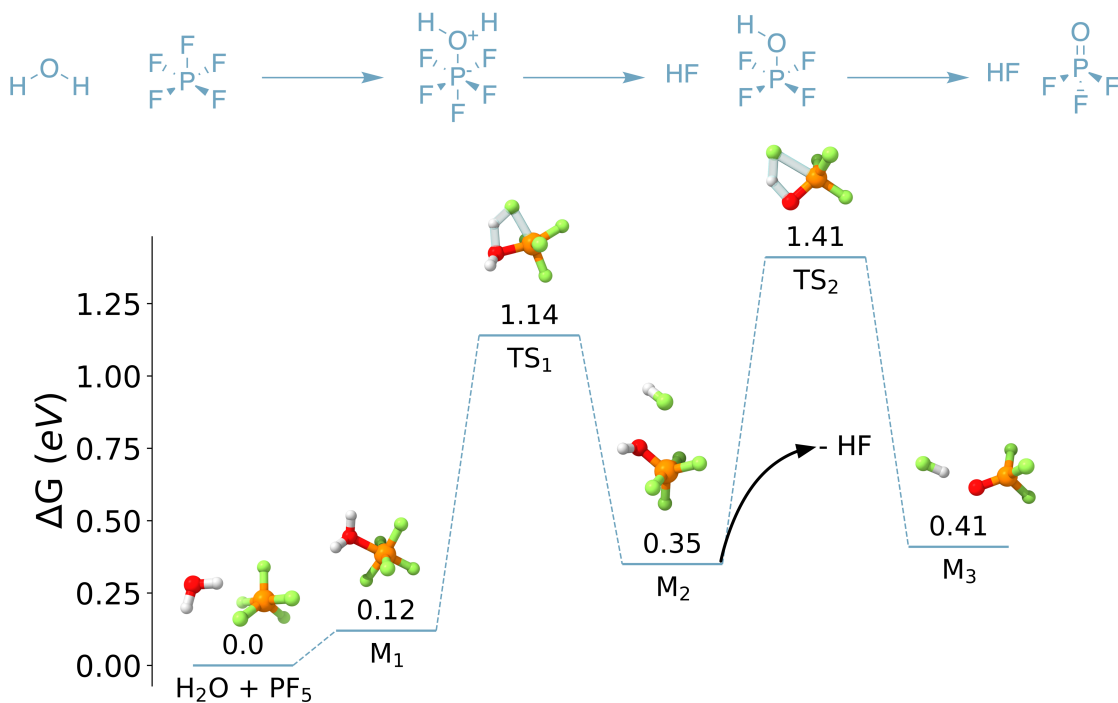


Figure 1: Hydrolysis of  $\text{PF}_5$  to form  $\text{POF}_3$  and  $2\text{HF}$ . This mechanism is overall thermodynamically unfavorable and involves two reactions with high barriers ( $\Delta G^\ddagger > 1.00$  eV).

elimination of  $\text{LiF}$  from  $\text{LiPF}_6$  to form  $\text{PF}_5$  (Equation 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  $\text{LiF}$ , whereas we expect that  $\text{LiF}$  will precipitate, forming solid deposits within the SEI. The elimination of  $\text{LiF}$  is more likely to occur when considering the possibility that  $\text{LiF}$  could be stabilized by precipitation. Okamoto<sup>54</sup> previously found that the deposition of solid  $\text{LiF}$  ( $\text{LiF}(\text{solv}) \longrightarrow \text{LiF}(\text{solid})$ ) has  $\Delta G = -1.17$  eV, which would make Equation 3 overall exergonic. More recently, Cao et al.<sup>58</sup> used DFT and AIMD to show that  $\text{LiPF}_6$  decomposition by either chemical or electrochemical means is greatly accelerated in the presence of existing  $\text{LiF}$ . Here, we report the reaction energies and energy barriers of  $\text{LiF}$  elimination reactions like Equation 3 without including the effect of a surface or  $\text{LiF}$  precipitation. However, we emphasize that these reactions, in general, should be more favorable than what is predicted based on calculations with molecular  $\text{LiF}$  in solution.

Even once  $\text{PF}_5$  is formed, Figure 1 confirms that, at our chosen level of theory, the direct

hydrolysis of  $\text{PF}_5$  by  $\text{H}_2\text{O}$  is unfavorable. Each of the three hydrolysis steps - the addition of  $\text{H}_2\text{O}$  to  $\text{PF}_5$  ( $\text{H}_2\text{O} + \text{PF}_5 \longrightarrow \text{M}_1$ ), the elimination of  $\text{HF}$  to form  $\text{PF}_4\text{OH}$  ( $\text{M}_1 \longrightarrow \text{M}_2$ ), and the elimination of another  $\text{HF}$  from  $\text{PF}_4\text{OH}$  to form  $\text{POF}_3$  ( $\text{M}_2 \longrightarrow \text{M}_3$ ) - is predicted to be endergonic. Further, the latter 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  $\text{LiPF}_6$  hydrolysis.

An alternate mechanism involves the reaction of  $\text{PF}_5$  with  $\text{Li}_2\text{CO}_3$  (Figure 2). Reactions between  $\text{LiPF}_6$  and inorganic carbonates have been proposed in the past<sup>59,60</sup> on the basis of the observed evolution of  $\text{CO}_2$  and  $\text{POF}_3$  upon mixing of  $\text{LiPF}_6$  and  $\text{Li}_2\text{CO}_3$ , but this route has largely been neglected in favor of hydrolytic mechanisms. Moreover, no elementary mechanism for the reaction between  $\text{LiPF}_6$ -like species and  $\text{Li}_2\text{CO}_3$  has been reported.

We find that  $\text{PF}_5$  reacts vigorously with  $\text{Li}_2\text{CO}_3$ . An initial addition step between the two reactants ( $\text{M}_4 \longrightarrow \text{M}_5$ ) has a low barrier of  $\Delta G^\ddagger = 0.04$  eV. Following reorganization of  $\text{Li}^+$  ( $\text{M}_5 \longrightarrow \text{M}_6$ ), the adduct ( $\text{M}_6$ ) then dissociates in a single concerted reaction, yielding  $\text{LiF}$ ,  $\text{CO}_2$ , and  $\text{LiPOF}_4$  with  $\Delta G^\ddagger = 0.19$  eV. Finally, to form  $\text{POF}_3$ ,  $\text{LiPOF}_4$  eliminates an additional molecule of  $\text{LiF}$  ( $\text{M}_7 \longrightarrow \text{LiF} + \text{POF}_3$ ), with  $\Delta G^\ddagger = 0.63$  eV,  $\Delta G = 0.28$  eV. We again note that we expect both  $\Delta G$  and  $\Delta G^\ddagger$  for  $\text{LiF}$  elimination reactions to be lowered if precipitation of  $\text{LiF}$  on a surface is allowed. Even without any corrections for the instability of molecular  $\text{LiF}$  produced in  $\text{M}_6 \longrightarrow \text{M}_7$  and  $\text{M}_7 \longrightarrow \text{LiF} + \text{POF}_3$ , this mechanism represents one of the most kinetically favorable elementary mechanisms for  $\text{PF}_5$  decomposition yet reported.

If it does not dissociate completely, the adduct  $\text{M}_5$  may instead eliminate  $\text{LiF}$  ( $\text{M}_5 \longrightarrow \text{M}_8$ ), though this reaction suffers from a high predicted barrier of  $\Delta G^\ddagger = 1.34$  eV. After  $\text{LiF}$  elimination, an additional oxygen from the carbonate group binds to phosphorus to form a ring complex  $\text{M}_9$ . By eliminating  $\text{CO}_2$ , either immediately ( $\text{M}_9 \longrightarrow \text{M}_{11}$ ,  $\Delta G^\ddagger = 0.81$  eV) or following the elimination of another  $\text{LiF}$  ( $\text{M}_{12} \longrightarrow \text{M}_{13}$ ,  $\Delta G^\ddagger = 0.36$  eV), this ring



complex also forms  $\text{LiPOF}_4$  ( $\text{M}_{11}$ ) or  $\text{POF}_3$  ( $\text{M}_{13}$ ).

The proposed mechanisms shown in Figure 2 rely only on  $\text{Li}_2\text{CO}_3$ , which should be abundant at the negative electrode, especially during early SEI formation.<sup>21,31,38,60-62</sup> The reaction of  $\text{PF}_5$  and  $\text{Li}_2\text{CO}_3$  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  $\text{PF}_5$  can occur anywhere in the SEI, so long as inorganic carbonates like  $\text{Li}_2\text{CO}_3$  are present. This being said, because  $\text{Li}_2\text{CO}_3$  is formed in the SEI as a result of electrochemical reduction of EC,<sup>38,44</sup> the overall rate of  $\text{POF}_3$  formation via the reaction of  $\text{PF}_5$  with  $\text{Li}_2\text{CO}_3$  will implicitly have a potential dependence.

While our focus in this work is on  $\text{LiPF}_6$  decomposition during SEI formation, it is worth noting that  $\text{Li}_2\text{CO}_3$  is an impurity formed during the synthesis of common transition metal oxide positive electrodes.<sup>59</sup> 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  $\text{POF}_3$  emerges rapidly by reaction with  $\text{Li}_2\text{CO}_3$  during SEI formation. This hints that the proposed autocatalytic mechanisms for  $\text{POF}_3$  (re)formation (Equations 1-2), which rely on  $\text{POF}_3$  and carbonate species, are chemically plausible.

To confirm the mechanism of  $\text{POF}_3$  autocatalysis at elevated temperature, we first consider the formation of  $\text{PF}_2\text{O}_2\text{R}$  species (Figure 3). Specifically, we explore the formation of  $\text{PF}_2\text{OOH}$  from  $\text{H}_2\text{CO}_3$  (Figure 3a) and  $\text{LiHCO}_3$  (Figure 3b) and the formation of  $\text{LiPF}_2\text{O}_2$  by  $\text{Li}_2\text{CO}_3$  (Figure 3c). In addition to their relevance for  $\text{POF}_3$  formation and  $\text{LiPF}_6$  decomposition,  $\text{PF}_2\text{O}_2\text{R}$  species and in particular  $\text{PF}_2\text{OOH}$  have been blamed as major contributors to the decomposition of SEI species and the loss of battery capacity.<sup>63,64</sup> Jayawardana et al. have argued that  $\text{PF}_2\text{OOH}$  should form at the positive electrode as a result of  $\text{PF}_6^-$  oxidation.<sup>63</sup> If  $\text{PF}_2\text{OOH}$  and related species could form at the negative electrode without high potentials, it could have significant implications for the stability of the SEI.



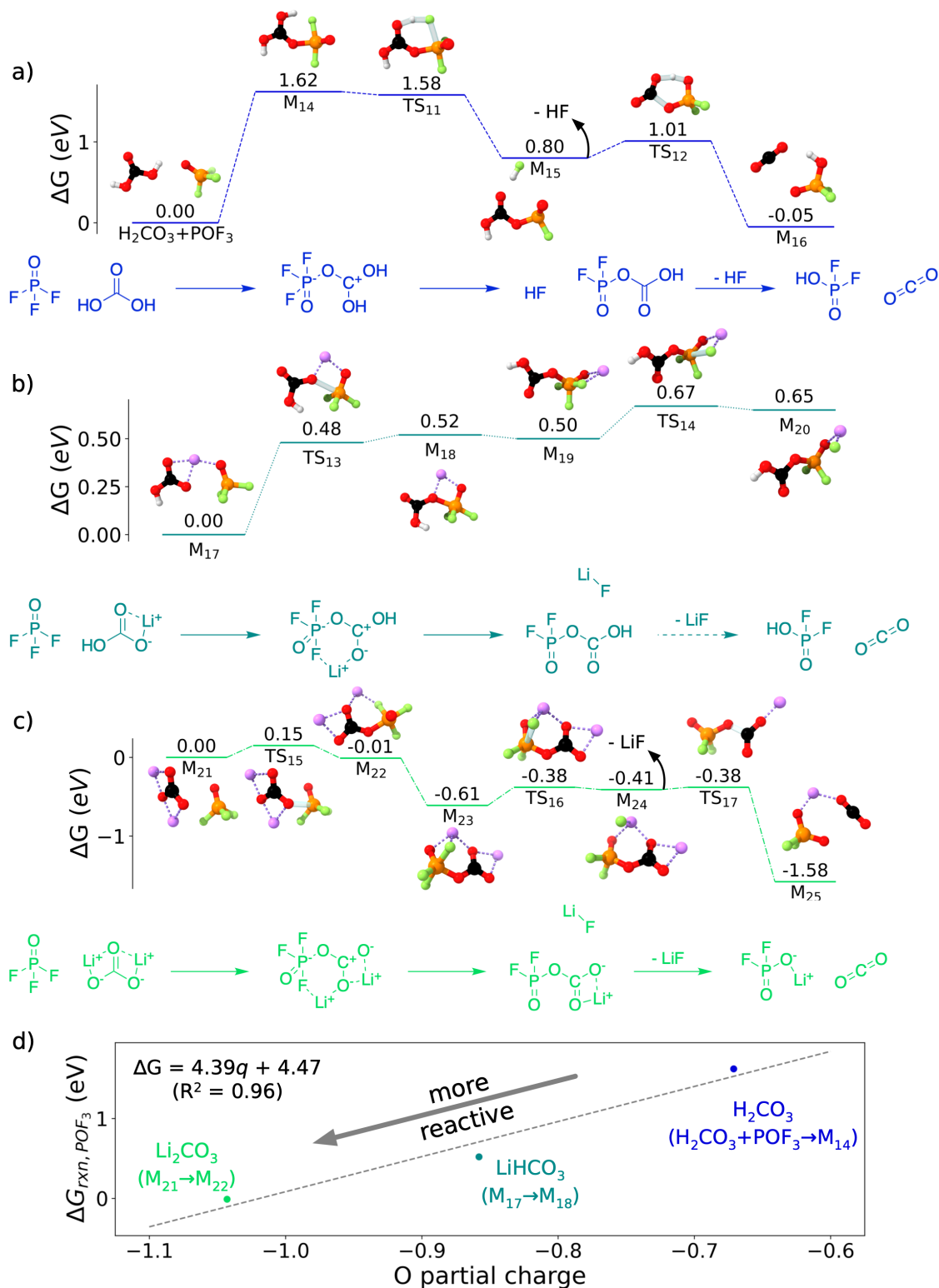


Figure 3: Reactions between  $POF_3$  and simple inorganic carbonates (a)  $H_2CO_3$ , b)  $LiHCO_3$ , and c)  $Li_2CO_3$ ) to form  $CO_2$  and either  $PF_2OOH$  or  $LiPF_2O_2$ . A trend between the partial charge of the reacting oxygen(s) and the reaction energies with  $POF_3$  for each carbonate considered is shown in d). A linear fit,  $\Delta G = 4.39q + 4.47$ , where  $q$  = the most negative oxygen partial charge, shows strong correlation ( $R^2 = 0.96$ ) among the three carbonates.

Figure 3a shows a mechanism for a chemical reaction between  $\text{H}_2\text{CO}_3$  and  $\text{POF}_3$ . The initial addition reaction between  $\text{POF}_3$  and  $\text{H}_2\text{CO}_3$  ( $\text{H}_2\text{CO}_3 + \text{POF}_3 \longrightarrow \text{M}_{14}$ ) is thermodynamically unfavorable ( $\Delta G = 1.62$  eV). Subsequent reactions to form HF,  $\text{CO}_2$ , and  $\text{PF}_2\text{OOH}$  do not face significant barriers and should occur rapidly. The reaction between  $\text{POF}_3$  and  $\text{LiHCO}_3$  (Figure 3b) follows a similar mechanism. The addition step ( $\text{M}_{17} \longrightarrow \text{M}_{18}$ ) is also endergonic ( $\Delta G^\ddagger = 0.48$  eV,  $\Delta G = 0.52$  eV), though we suggest that it could be accessed at moderate temperatures. Addition by  $\text{LiHCO}_3$  is followed by the elimination of LiF ( $\text{M}_{19} \longrightarrow \text{M}_{20}$ ), which is analogous to the elimination of HF in Figure 3a, ( $\text{M}_{14} \longrightarrow \text{M}_{15}$ ). Following the complete removal of LiF,  $\text{M}_{20}$  can undergo the same concerted proton transfer and  $\text{CO}_2$  elimination shown in Figure 3a ( $\text{M}_{15} \longrightarrow \text{M}_{16}$ ).

In contrast,  $\text{POF}_3$  adds easily to  $\text{Li}_2\text{CO}_3$  (Figure 3c,  $\text{M}_{21} \longrightarrow \text{M}_{22}$ ), with  $\Delta G^\ddagger = 0.15$  eV and  $\Delta G = -0.01$  eV. We explain the difference in the thermodynamics of the reactions between  $\text{POF}_3$  and  $\text{H}_2\text{CO}_3$ ,  $\text{LiHCO}_3$ , and  $\text{Li}_2\text{CO}_3$  by considering atomic partial charges (Figure 3d).  $\text{POF}_3$  is reactive towards the highly anionic oxygens in  $\text{Li}_2\text{CO}_3$ , but not towards the less charged oxygens in  $\text{LiHCO}_3$  and  $\text{H}_2\text{CO}_3$ . The difference in behavior can also be rationalized in terms of acid-base chemistry.  $\text{POF}_3$  and  $\text{PF}_5$  (both Lewis acids) prefer to react with  $\text{CO}_3^{2-}$  (a Lewis base) over  $\text{HCO}_3^-$  (depending on context, either a weak acid or a weak base) and  $\text{H}_2\text{CO}_3$  (an acid). We find similar trends for the reaction between  $\text{PF}_5$  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  $\text{Li}_2\text{CO}_3$ . Though  $\text{PF}_2\text{OOH}$  formation via  $\text{LiHCO}_3$  is possible, the difficulty of addition with protonated carbonates suggests that, barring electrochemical processes,  $\text{LiPF}_2\text{O}_2$  should be more abundant at the negative electrode than  $\text{PF}_2\text{OOH}$ . Nonetheless, the prediction that  $\text{PF}_2\text{OOH}$  and  $\text{LiPF}_2\text{O}_2$  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.

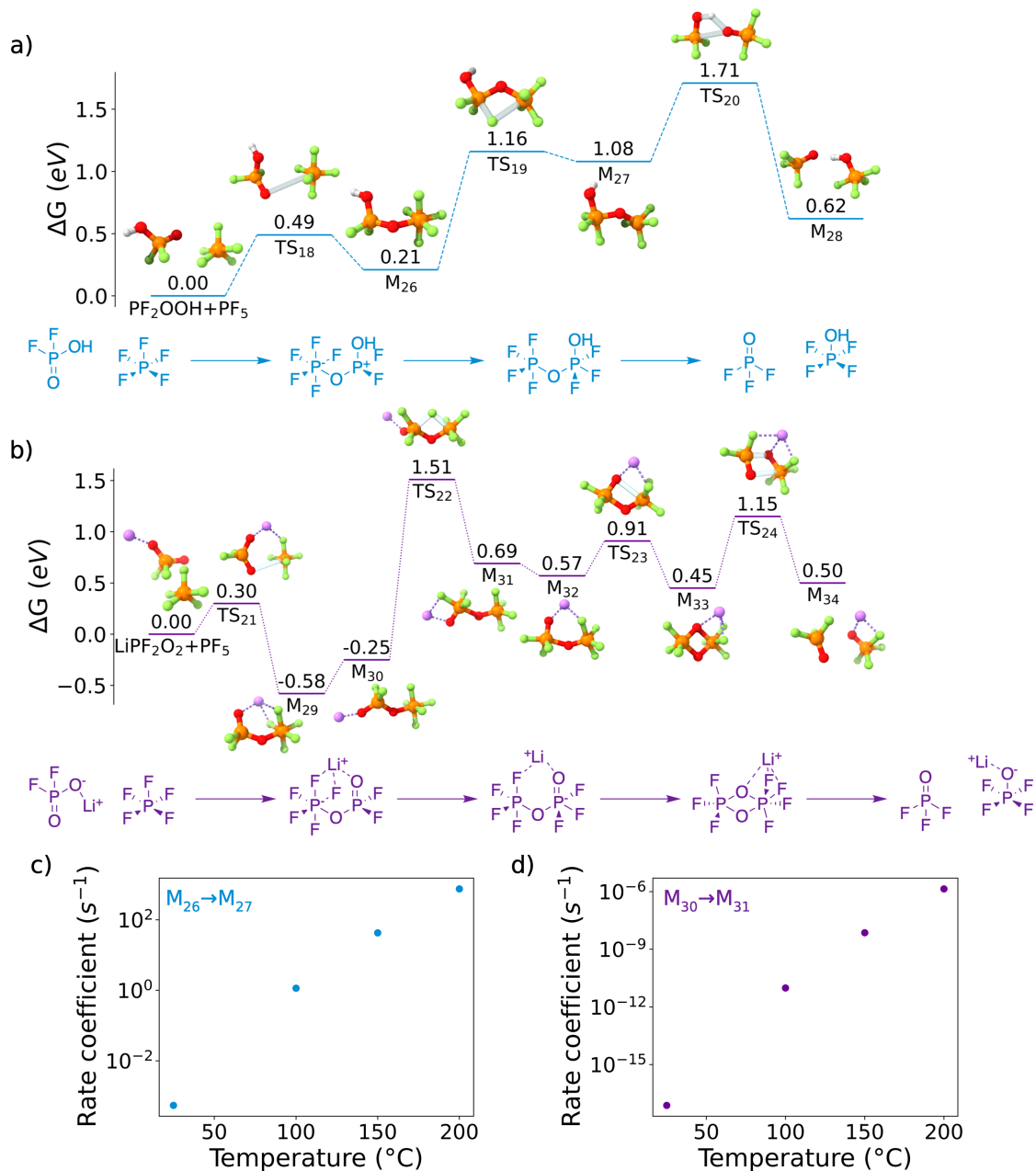


Figure 4: Possible routes for the reformation of POF<sub>3</sub> from PF<sub>2</sub>OOH (a) and LiPF<sub>2</sub>O<sub>2</sub> (b). Both mechanisms are kinetically limited due to an extremely unfavorable intramolecular fluorine transfer step (M<sub>26</sub> → M<sub>27</sub>, M<sub>30</sub> → M<sub>31</sub>), which makes POF<sub>3</sub> autocatalysis unlikely at modest temperatures. Rate coefficients for the fluorine transfer step are provided in c) for the PF<sub>2</sub>OOH pathway and in d) for the LiPF<sub>2</sub>O<sub>2</sub> pathway.

Mechanisms for the reformation of  $\text{POF}_3$ , completing the autocatalytic cycle in Equation 2, are shown in Figure 4. Following a similar trend to that shown in Figure 3d, the attack of  $\text{PF}_5$  by the acidic  $\text{PF}_2\text{OOH}$  (Figure 4a,  $\text{PF}_2\text{OOH} + \text{PF}_5 \longrightarrow \text{M}_{26}$ ) is thermodynamically unfavorable, while  $\text{LiPF}_2\text{O}_2$  can favorably add to  $\text{PF}_5$  (Figure 4b,  $\text{LiPF}_2\text{O}_2 + \text{PF}_5 \longrightarrow \text{M}_{29}$ ). After the initial addition, an intramolecular fluorine transfer is required; for both  $\text{PF}_2\text{O}_2\text{R}$  species considered, this step is thermodynamically unfavorable and suffers from a high barrier ( $\text{M}_{26} \longrightarrow \text{M}_{27}$ ,  $\Delta G^\ddagger = 0.95$  eV;  $\text{M}_{30} \longrightarrow \text{M}_{31}$ ,  $\Delta G^\ddagger = 1.76$  eV). While both intramolecular fluorine transfer reactions are kinetically limited at room temperature (Figure 4 c-d), the reaction without  $\text{Li}^+$  can occur at elevated temperature (especially  $T > 150^\circ\text{C}$ ). After fluorine transfer, the two mechanisms in Figure 4a-b diverge. In Figure 4a, a concerted proton transfer and elimination step occurs ( $\text{M}_{27} \longrightarrow \text{M}_{28}$ ), yielding  $\text{POF}_3$  and  $\text{PF}_4\text{OH}$ .  $\text{PF}_4\text{OH}$  can subsequently eliminate HF to form  $\text{POF}_3$ , as shown in Figure 1. In Figure 4b, a four-member O-P-O-P ring is formed ( $\text{M}_{32} \longrightarrow \text{M}_{33}$ ) and  $\text{POF}_3$  is eliminated ( $\text{M}_{33} \longrightarrow \text{M}_{34}$ ), leaving  $\text{LiPOF}_4$  which could then form  $\text{LiF}$  and  $\text{POF}_3$  as previously discussed.

Our mechanism confirms the previously reported autocatalytic formation of  $\text{POF}_3$ . We find, in agreement with earlier experimental studies,<sup>50,52</sup> that this cycle requires significant thermal activation ( $T \sim 150^\circ\text{C}$ ). This is primarily due to a sluggish intramolecular fluorine transfer and, specifically for the mechanism requiring  $\text{PF}_2\text{OOH}$  as an intermediate, the high barrier for HF elimination to reform  $\text{POF}_3$ . While we have found a mechanism for  $\text{POF}_3$  autocatalysis that does not require any water, the significantly lower barrier for the pathway involving  $\text{PF}_2\text{OOH}$  indicates that  $\text{LiPF}_6$  thermal decomposition could be initiated and accelerated by  $\text{LiPF}_6$  hydrolysis,<sup>47</sup> which is accessible at elevated temperature.

To conclude,  $\text{LiPF}_6$  is an exceptional salt that is likely to play a major role in the LIB market for years to come. While some decomposition of  $\text{LiPF}_6$  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  $\text{LiPF}_6$  using first-principles DFT simulations. Our results imply that under normal battery cycling conditions,

the major decomposition mechanism of  $\text{LiPF}_6$  does not depend on water or on electrochemical salt reduction. Rather,  $\text{LiPF}_6$  forms the expected products  $\text{LiF}$ ,  $\text{POF}_3$ ,  $\text{LiPF}_2\text{O}_2$ , and potentially  $\text{PF}_2\text{OOH}$  via entirely chemical reactions with inorganic carbonates (especially  $\text{Li}_2\text{CO}_3$ ). These reactions can likely occur in the solution phase or in nanocrystalline or amorphous regions of the SEI (see Supporting Information Table S1).  $\text{PF}_5$  and  $\text{POF}_3$  show a strong affinity to react with highly anionic oxygens and Lewis bases, suggesting that that efforts to control the reactivity of  $\text{LiPF}_6$  should focus on limiting the exposure of  $\text{PF}_5$  to oxyanion and other basic species, including and especially inorganic carbonates like  $\text{Li}_2\text{CO}_3$ , 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 e.g. time-resolved spectroscopy with varying amounts of inorganic carbonates and  $\text{LiPF}_6$ ) and theory (via kinetic simulations, e.g. kinetic Monte Carlo). More challenging, but no less worthwhile, would be to confirm if the decomposition of  $\text{LiPF}_6$  in a battery is primarily chemical or electrochemical in nature. This could be accomplished by tracking the rate of decomposition of  $\text{LiPF}_6$  in the presence of inorganic carbonate species in a reductively stable solvent under varying applied potentials. While we have focused here primarily on  $\text{LiPF}_6$  decomposition in EC-based electrolytes, we suspect that  $\text{LiPF}_6$  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  $\text{LiPF}_6$  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  $\text{LiPF}_6$  decomposition products (especially  $\text{PF}_2\text{O}_2\text{R}$  species) and other SEI species (e.g. organic carbonates), as well as the formation mechanisms of organophosphorus compounds and phosphate polymers in the SEI, should also be conducted.

## Author Contributions

Conceptualization: E.W.C.S.-S., K.A.P.; Formal analysis: E.W.C.S.-S., T.B.P., H.D.P.; Funding acquisition: E.W.C.S.-S., H.D.P., S.M.B., K.A.P.; Investigation: E.W.C.S.-S., T.B.P., H.D.P.; Resources: K.A.P.; Supervision: E.W.C.S.-S., K.A.P.; Visualization: E.W.C.S.-S.; Writing - original draft: E.W.C.S.-S., T.B.P.; Writing - review & editing: all authors.

## Competing Interests Statement

The authors declare no competing financial interests.

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## Supporting Information Available

Data availability statement; computational methods; discussion of additional reaction mechanisms for  $\text{LiPF}_6$  decomposition.

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