



Mechanism of hydrofluoric acid formation in ethylene carbonate electrolytes with fluorine salt additives



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HIGHLIGHTS

- Increased Lewis acid–base interactions correspond to lower HF formation barriers.
- The barrier to HF generation from POF_3 is $10.4 \text{ kcal mol}^{-1}$ higher than from PF_5 .
- An ethylene carbonate molecule acts as a catalyst to HF formation from PF_5 .

ARTICLE INFO

Article history:

Received 21 May 2015

Received in revised form

13 July 2015

Accepted 30 July 2015

Available online 25 August 2015

Keywords:

Electrolyte degradation

Hydrofluoric acid

Lithium-ion battery

LiPOF_4

LiPF_6 decomposition

Density functional theory

ABSTRACT

We utilized density functional theory to examine HF generation in lithium-ion battery electrolytes from reactions between H_2O and the decomposition products of three electrolyte additives: LiPF_6 , LiPOF_4 , and LiAsF_6 . Decomposition of these additives produces PF_5 , AsF_5 , and POF_3 along with LiF precipitates. We found PF_5 and AsF_5 react with H_2O in two sequential steps to form two HF molecules and POF_3 and AsOF_3 , respectively. PF_5 (or AsF_5) complexes with H_2O and undergoes ligand exchange to form HF and PF_4OH (AsF_4OH) 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 PF_4OH (AsF_4OH) product, reducing the barrier to HF formation. Reactions of POF_3 were examined and are not characterized by complexation of POF_3 with H_2O or EC, while PF_5 and AsF_5 complex favorably with H_2O and EC. HF formation from POF_3 occurs with a reaction enthalpy of -3.8 kJ mol^{-1} and a $157.7 \text{ kJ mol}^{-1}$ barrier, 43.5 kJ mol^{-1} higher than forming HF from PF_5 . HF generation in electrolytes employing LiPOF_4 should be significantly lower than those using LiPF_6 or LiAsF_6 and LiPOF_4 should be further investigated as an alternative electrolyte additive.

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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 (307–310 K), 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

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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 (LiPF₆) is comprised of a Li⁺ ion and a PF₆⁻ 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 LiPF₆ [5,6,9] or are potentially unsafe. For example, LiAsF₆ exhibits similar improvements in electrolyte conductivity and electrochemical stability relative to LiPF₆ [1,5,6,11], but has not been employed in commercial LIBs due to concerns over As toxicity.

Unfortunately, LiPF₆ undergoes heterolytic dissociation at elevated temperatures to form a LiF precipitate and pentafluorophosphate (PF₅) [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 LiPF₆ as solvated Li⁺ and PF₆⁻ ions at low temperatures and thus stabilizes Li⁺ and PF₆⁻ relative to LiF and PF₅. This limits PF₅ 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 PF₅ with H₂O impurities [13]. Because lowering H₂O contamination in carbonate electrolytes below the concentrations typically present in commercial LIBs (greater than 20 ppm) [14] is impractical, some reaction between this H₂O and PF₅ is inevitable.

H₂O contamination has been suggested to drive the breakdown of LiPF₆ by hydrolysis to produce HF by the overall reaction [2,8,9].



LiPF₆ has been observed to thermally decompose at temperatures above 390 K [9], producing a LiF precipitate and PF₅ by the following reaction [9,10,12].



The generated PF₅ 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 LiPF₆ 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 PF₆⁻ ion pair compared to other liquid electrolytes. Thus, highly polar organic electrolytes hinder PF₅ 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 PF₅ and LiF products.

PF₅ produced by Reaction (2) and H₂O impurities in the electrolyte are expected to play a central role in producing HF via the reaction [16].



PF₅ 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 358 K and 373 K 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 LiPF₆, 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 PF₅ with H₂O and by the analogous reaction between AsF₅ and H₂O, where AsF₅ is produced along with LiF in electrolytes utilizing the LiAsF₆ additive. Additionally, we studied the formation of HF by a reaction between H₂O and POF₃, which is produced by Reaction (3). A previous computational study by Okamoto has examined the reaction between PF₅ and H₂O to develop an understanding of the role that POF₃ plays in EC ring opening reactions [16]. Here, we report a comprehensive study of HF formation in the liquid EC electrolytes that results from H₂O reacting with PF₅, AsF₅ or POF₃. This study focuses on determining the active mechanisms by which HF is formed from H₂O 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 PF₅, AsF₅, and POF₃. We investigated the mechanisms of HF formation resulting from reaction of PF₅, POF₃, and AsF₅ with H₂O 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 PF₅, POF₃, and AsF₅ electrolyte constituents with H₂O 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

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