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Further insights into structural diversity of phosphorus-based decomposition products in lithium ion battery electrolytes *via* liquid chromatographic techniques hyphenated to ion trap - time of flight mass spectrometry

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Keywords

Lithium ion battery electrolyte, organo(fluoro)phosphates, LC-IT-TOF-MS, non-target analysis

Abstract

This study illustrates the high complexity of phosphorus-based decomposition products in thermally treated state-of-the-art lithium ion battery (LIB) electrolytes. Liquid chromatographic techniques hyphenated to ion trap time of flight mass spectrometry reveals 122 different organophosphate (OP) and organofluorophosphate (OFP) species, the majority of them not reported in literature so far. The application of hydrophilic interaction liquid chromatography and reversed-phase chromatography enables the investigation of the acidic as well as nonacidic spectrum of aging products. Furthermore, the generation of high structure certainty by consideration of (i) mass accuracy of the precursor ions and subsequent MS^{2/3} fragments, (ii) fragment intensity distribution in the mass spectra as well as (iii) retention times in HILIC and RP separation allows a target analysis in further work in the LIB electrolyte context. In an ethyl methyl carbonate-based battery electrolyte 82 OP compounds, 27 OFPs and 13 cyclic O(F)Ps are identified. Additionally, the formation of 8-membered organo(fluoro)phosphate rings in lithium ion battery electrolytes is reported for the first time. Since the high toxic potential of organo(fluoro)phosphates emerged interest in safety assessments of electrolytes, the knowledge of possibly formed substances supports further quantification approaches and toxicological assessments compared to non-target investigations.

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1 Introduction

Since its market introduction in the early 1990s, the lithium ion battery (LIB) took over the market of energy storage in portable electronics like power tools, laptops and smartphones. Nowadays, the demand is still rising due to upscaling of LIBs for e.g. stationary energy storage systems (EES), plug-in hybrid electric vehicles (PHEVs) or fully electrified vehicles (EVs).^{1,2} In particular, LIBs offer a high operating cell voltage (>3.5 V) and specific energy / energy density on cell level (260 Wh kg⁻¹ / 700 Wh L⁻¹) compared to other battery systems, accompanied with outstanding energy efficiency and cycle life.^{3,4} Recently, improvements in gravimetric and volumetric energy densities research aligned to new, high capacity and high voltage electrode materials is nescessary.^{5–7} In theory, the LIB is based on redox reactions between two electrodes, referred to as anode and cathode, whereas, as anode commonly carbonaceous materials are used and as cathode materials lithium transition metal oxides (Li*TMO*₂; *TM*: Mn, Co, Ni).^{5,8} Additionally, an separator which is soaked with electrolyte is located between the electrodes.⁹

The state-of-the-art electrolyte formulation is based on lithium hexafluorophosphate (LiPF₆) as conducting salt, dissolved in a mixture of a linear and a cyclic organic carbonate solvent (e.g. ethyl methyl carbonate and ethylene carbonate, respectively). They exhibit the best compromise in terms of viscosity, conductivity, temperature range and stability, however, suffering from high reactivity of LiPF₆ to moisture as well as its redox instability.^{10–13} Electrolyte decomposition is one of various and highly complex degradation mechanism reported in battery cell components which is often referred to as aging. Additionally, among other also in literature reported degradation mechanisms were (i) particle cracking, (ii) transition metal dissolution, (iii) metallic lithium deposition or iv) contact losses to the current collectors of the respective active material.^{14–16} One electrolyte-based aging phenomenon that is actually desired is the formation of interphases at the respective electrodes like the solid electrolyte interphase (SEI) on the anode¹⁷ or the cathode electrode interphase (CEI) on the cathode which are mainly generated during the first charging process of the battery cell.¹⁸ These interphases are electronically insulating but ionically conductive, thus, ensuring Li ion movement and protecting the electrolyte from further oxidation/reduction at the respective electrode surfaces. Their composition and physicochemical properties have a crucial influence on the performance and lifetime of a LIB cell.19-21

However, the instability of electrolytes leads to undesirable side reactions. Plakhotnyk et al. showed a reaction route for the decomposition of LiPF₆ where the assumed equilibrium of LiPF₆ and LiF/PF₅ is disrupted by trace amounts of water reacting with PF₅ to highly reactive POF₃ and hydrofluoric acid (HF).²² After further conversions with water and organic carbonates, the reaction cascade concludes in the formation of organofluorophosphate (OFP) and organophosphate (OP).^{23,24} Mechanism of formation of these phosphorus esters has been reported in recent years.^{25–29} This decomposition behavior is an aging process in LIBs, whereas organo(fluoro)phosphate (O(F)P) products excite interest regarding their toxicity and the safety of LIBs due to their structural similarity to pesticides and nerve agents.²⁵ Especially OFP possess the same characteristic P-F bond as chemical warfare agents (CWA) which interact irreversibly with the catalytic active site of the acetylcholinesterase enzyme (AChE).³⁰ The inhibition of the catalytic triad, and therefore the cleaving of acetylcholine at the synapses, results in the permanent stimulation of neuromuscular junctions ending up to paralysis or decease. For instance, the CWA sarin exhibits a median lethal dose (LD₅₀) of 1.08 mg kg⁻¹ body weight, some OFPs identified in LIBs show comparable LD₅₀ values (Figure 1).³¹ Alteration in structure and polarity of O(F)Ps changes the properties, modulate the inhibition to reversible or quasi-irreversible and

requires toxicological investigation. Besides the decomposition to volatile, non-acidic compounds, incomplete saturation of side chains ends into P-OH groups and acidic O(F)Ps.



Figure 1: Interaction of CWA sarin at the catalytic triad active side of acetylcholinesterase and homologue structures identified in LIBs. Mode of action modelled on *Dvir et al.*.³²

The formation of decomposition products correlates strongly with the applied solvents in the LIB electrolyte. Ethylene carbonate undergoes a single-electron ring opening process at the electrode surface, C₂-based alkoxy groups form side chains of OFPs with terminal groups depending on the formulation of the linear organic carbonate.^{33–35} The use of dimethyl carbonates leads entirely to methylation while ethyl methyl carbonates lead to a mixture of terminal ethyl and methyl groups, increasing the potential variety of formed OFPs drastically.³⁶ For structural investigations of O(F)Ps in LIB electrolytes *Kraft et al.* proved the comparability of the accelerated thermal aging at 80 °C to electrochemical aging experiments.²⁴

While organophosphorus compounds were considered and investigated as flame retardant additives since the 1970s, the first discovery of O(F)Ps in LIBs due to electrolyte decomposition was shown by Gachot et al. in 2011²⁷, accompanying with increased research interest via numerous analytical approaches like ion chromatography (IC), qas chromatography (GC) or nuclear magnetic resonance spectroscopy (NMR).³⁷⁻⁴⁴ Today's common technique for the investigation of non-acidic O(F)Ps and carbonate-based decomposition products is GC hyphenated to flame ionization detector or mass spectrometry (MS). However, due to the harmful properties of formed HF and high salt concentration, a sample pretreatment is mandatory.^{45,46} Furthermore, the identification of acidic O(F)Ps and ionic aging products is realized via chromatographic techniques based on capillary electrophoresis (CE) as well as one and two-dimensional IC.^{36,47} Nonetheless, the instrumental afford of these approaches is the separation of small molecules from acidic to non-acidic properties combined with a high structural variety. For a comprehensive qualitative and quantitative investigation, the application of different chromatographic instruments and detection techniques is required. This is crucial for the quantification of O(F)Ps as no analytical standards are available for this material class due to its potential harmful properties. However, plasma-based detection via phosphorus proved to be the most promising approach to overcome the lack of analytical standards, thus, offering quantification Therefore, inductively coupled plasma-mass spectrometry (ICP-MS) of O(F)Ps.³⁰ hyphenations were reported.^{38,39} Molecular mass spectrometry with fragmentation possibilities (MSⁿ) with collision cells or ion traps (IT) and high mass resolution time of flight detection (TOF) were applied for the identification.⁴⁸

High performance liquid chromatography (HPLC) is a promising separation technique due to the high variety of retention mechanisms, depending on physicochemical properties of the stationary and mobile phase. In the field of LIB electrolyte investigations, classic reversedphase (RP) chromatography has been reported.^{49–53} Nevertheless, the HPLC allows to separate non-acidic molecules with an hydrophobic stationary phases as well as acidic molecules by changing the separation mode to hydrophilic interaction liquid chromatography (HILIC)^{54,55}. HILIC enables the conversion of the chromatographic order of RP separation and allows the comprehensive investigation of O(F)Ps by using a single instrument set-up with two different stationary phases. For structure elucidation of decomposition products in

LIB electrolytes not only an effective separation is required, but also good mass accuracy by high resolution mass spectrometry and fragmentation information.⁵⁶ Thus, a hybrid ion traptime of flight-mass spectrometer (IT-TOF-MS) is the method of choice to generate high certainty in structure elucidation without analytical standards.

In this work, a HPLC-IT-TOF-MS hyphenation was performed for comprehensive O(F)Ps structure elucidation by applying two different liquid chromatographic techniques. To generate the highest possible structural diversity of phosphorus-based species in LIB electrolytes, thermal decomposition was induced at 80 °C for three weeks. Acidic O(F)Ps were separated *via* HILIC for identification, non-acidic structures by changing the separation mode to a RP chromatography. 118 structures could be identified, including constitutional isomers. The knowledge of the complexity of O(F)Ps allows the progression from unknown target analysis to a target analysis in LIB electrolytes. Accompanied with the identification of main decomposition products, quantitative information enables the approximation to risk assessments for the recycling of end-of-life LIBs as well as safety assessments concerning abuse and accident cases in home storage or EVs.

2 Experimental

2.1 Instrumentation

Chromatographic method development and separation of decomposition products in LIB electrolytes were performed on a Nexera X2 UHPLC system (Shimadzu, Kyoto, Japan) hyphenated to an ion trap – time of flight (IT-TOF^M) mass spectrometer (Shimadzu, Kyoto, Japan). The flow rate and column temperature were set to 0.35 mL min⁻¹ and 40 °C, respectively. The injection volume was 1 μ L. Shimadzu LCMS solution 3.80 was used for LC-MS instrument control, data acquisition and data evaluation.

NMR measurements were conducted on an Avance[™] III HD (Bruker, Billerica, MA, USA) at 300 MHz (¹H). Proton spectra were referenced to the solvent signal of CDCl₃ at 7.26 ppm. ¹H NMR shift simulations were performed on PerkinElmer ChemBioDraw 14.0.0.117.

2.1.1 Acidic organo(fluoro)phosphates

For the separation of acidic O(F)Ps analytes the hydrophilic interaction liquid chromatography mode was used with an Hypersil GOLD™ SAX column (200×2.1 mm, 1.9 µm, Thermo Fisher Scientific Inc., Waltham, MA, USA). The mobile phase gradient consisted of a 10 mmol L⁻¹ aqueous ammonium formiate at pH 6.5 (A) and acetonitrile (B). The optimized gradient started with 95% B and decreased to 90% within 5 min. Subsequently, the mobile phase dropped to 75% within 0.1 min, decreased to 70% within 7 min and kept constant for 2 min. After a further drop to 50% the gradient was kept constant for 10 min. Finally, the column equilibrated at 95% B for 10 min. To protect the IT-TOF™ mass spectrometer from high concentrations of conducting salt LiPF₆, the flow line switched to the MS after 2.5 min. Ionization was performed in ESI(-) mode at -4.5 kV. Curved desolvation line and heat block temperature were 230°C, respectively and the nebulizer gas flow was 1.5 I min⁻¹. The ion trap operated in automatic MS² mode with an ion accumulation time of 10 msec in MS¹ and 60 msec in MS², leading to a loop time of 280 msec. The mass range was set to m/z 80-250. The collision induced dissociation energy and gas flow were set to 30%. For further structure elucidation and confirmation purposes close to the limit of detection, manual MS² and varied ion trap parameters were used.

2.1.2 Non-acidic organo(fluoro)phosphates

Reversed-phase chromatography of non-acidic O(F)P analytes were performed on an Hypersil GOLDTM C18 column (150×2.1 mm, 3 µm, Thermo Fisher Scientific Inc., Waltham, MA, USA). The mobile phase gradient consisted of a 0.1% aqueous formic acid (A) and acetonitrile (B). The optimized gradient started with 3% B from 0 to 5 min and increased to 70% within 11 min. Subsequently, the mobile phase kept constant at 70% for 4 min. Finally, the column equilibrated at 3% B for 10 min. To protect the IT-TOFTM mass spectrometer from high concentrations of conducting salt LiPF₆, the flow line switched to the MS after 5 min. Ionization was performed in ESI(+) mode at 4.5 kV. Curved desolvation line and heat block temperature were 230°C, respectively and the nebulizer gas flow was 1.5 l min⁻¹. The ion trap operated in automatic MS² mode with an ion accumulation time of 10 msec in MS¹ and 60 msec in MS², leading to a loop time of 280 msec. The mass range was set to m/z 100-300. The collision induced dissociation energy and gas flow were set to 30%. For further structure elucidation and confirmation purposes close to the limit of detection, manual MS² and varied ion trap parameters were used.

2.2 Chemicals and materials

Four different battery grade SelectiLyte[™] electrolytes (BASF, Ludwigshafen am Rhein, Germany) were investigated. All electrolytes contained 1 mol L⁻¹ LiPF₆ and vary in the composition of linear and cyclic organic carbonates. LP30 consists of ethylene carbonate (EC) and dimethyl carbonate (DMC) (50/50 wt%), LP40 of ethylene carbonate (EC) and diethyl carbonate (DEC) (50/50 wt%), LP50 of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (50/50 wt%) and LP572 of ethylene carbonate (EC), ethyl methyl carbonate (EMC) and vinylene carbonate (30/70/+2 wt%). Acetonitrile (VWR International GmbH, Darmstadt, Germany, LC-MS grade), ammonium formiate (MS grade, >99.0%), formic acid (Sigma Aldrich Chemie GmbH, Steinheim, Germany, LC-MS grade), isopropanol (Merck, Darmstadt, Germany, EMSURE[©], 99.9% purity, for analysis) and deionized water (Millipore, Molsheim, France, 18.2 MΩ cm⁻¹) were used for the preparation of eluents. For thermal experiments 10 mL gas-tight aluminum vials with butyl/polytetrafluoroethylene (PTFE) caps were used (Leicht & Appel GmbH, Bad Gandersheim, Germany). All chemicals were used as received.

2.3 Sample preparation

Gas-tight 10 mL aluminum vials were cleaned with isopropanol/MilliQ and dried in a vacuum drying oven at 60 °C for 2 hours. 500 µL battery grade SelectiLyte[™] were stored at 80 °C for 3 weeks. Samples were diluted 1/20 with acetonitrile for measurements.

2.4 Standard material synthesis

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in oven-dried glassware. The solvents used were purified by distillation over standard drying agents and were stored over molecular sieves and transferred under argon. Except where stated, the starting materials 1,2,4-triazole (Alfa Aesar, Karlsruhe, Germany), KOt-Bu (TCI, Eschborn, Germany) phenyl phosphorodichloridate (Fluorochem, Hadfield, UK), triethylamine (Acros Organics, Geel, Belgium) POCl₃ and diethylene glycol (Sigma Aldrich, Steinheim, Germany) were commercially available and used as received. Reaction temperatures are reported as the temperature of the oil bath or metal block surrounding the vessel, respectively.

2.4.1 2-hydroxy-1,3,6,2-trioxaphosphocane 2-oxide

The acidic standard was prepared following a literature procedure.^{57,58} To a solution of 1,2,4-triazole (207 mg, 3.00 mmol, 3.00 equiv.) and triethylamine (416 µL, 3.00 mmol, 3.00 equiv.) in 1,4-dioxane (5.0 mL) was added POCl₃ (91.1 µL, 1.00 mmol, 1.00 equiv.) dropwise at 0 °C. The mixture was allowed to warm to room temperature and stirred for 15 min. In a separate flask, diethylenglycole (85.3 µL, 0.90 mmol, 0.90 equiv.) was dissolved in pyridine (8.0 mL). Then, the crude tri(triazolyl)phosphine oxide solution was added dropwise to the diethylene glycol solution at room temperature. The mixture was stirred for 10 minutes, quenched with H₂O (0.2 mL) and concentrated *in vacuo*. The residue was dissolved in H₂O (1.0 mL) and passed through a Dowex 50W×8/H⁺/resin (1 mL) with MeOH and the filtrate was concentrated *in vacuo*. The residue was triturated with CH₂Cl₂ and concentrated *in vacuo* to afford a colorless oil (54.1 mg) that was analyzed with HILIC-IT-TOF-MS without further purification.

2.4.2 2-phenoxy-1,3,6,2-trioxaphosphocane 2-oxide

The intermediate for the synthesis of methyl and ethyl 8-membered rings (cf. chapter 2.4.3/2.4.4) was prepared following a literature procedure.⁵⁹ To a solution of diethylene glycol (521 μ L, 5.50 mmol, 1.10 equiv.) in pyridine (3.0 mL) was added phenyl phosphorodichloridate (748 μ L, 5.00 mmol, 1.00 equiv.) dropwise at 0 °C. The mixture was stirred at room temperature overnight. The solids were removed by filtration and washed with benzene. The filtrate was concentrated *in vacuo* and then dissolved in benzene. The organics were washed with H₂O, sat. NaHCO₃ (aq.), dried over MgSO₄ and concentrated *in vacuo* to afford a colorless oil (246 mg) that used without further purification.

2.4.3 2-methoxy-1,3,6,2-trioxaphosphocane 2-oxide

The first non-acidic standard was prepared following a literature procedure.⁶⁰ Under air, to a solution of crude 2-phenoxy-1,3,6,2-trioxaphosphocane 2-oxide (244 mg, 1.00 mmol, 1.00 equiv.) in MeOH (10.0 mL) was added KOt-Bu (112 mg, 1.00 mmol, 1.00 equiv.) at room temperature. The mixture was stirred overnight at room temperature, quenched with H_2O , extracted with CH_2CI_2 . The organics were dried over MgSO₄ and concentrated *in vacuo* to afford a colorless oil that was analyzed with RP-LC-IT-TOF-MS without further purification.

2.4.4 2-ethoxy-1,3,6,2-trioxaphosphocane 2-oxide

The second non-acidic standard was prepared following a literature procedure.⁶⁰ Under air, to a solution of crude 2-phenoxy-1,3,6,2-trioxaphosphocane 2-oxide (52 mg, 0.21 mmol, 1.00 equiv.) in EtOH (10.0 mL) was added KO*t*-Bu (112 mg, 1.00 mmol, 4.76 equiv.) at room temperature. The mixture was stirred overnight at room temperature, quenched with H₂O, extracted with CH_2CI_2 . The organics were dried over MgSO₄ and concentrated *in vacuo* to afford a colorless oil that was analyzed with RP-LC-IT-TOF-MS without further purification.



Figure 2: Structures of synthesized standards 2-hydroxy-1,3,6,2-trioxaphosphocane 2-oxide (a) and its phenyl (b), methyl (c) and ethyl ester (d).

3 Results and discussion

Structure elucidation of formed decomposition products required a separation of the analytes. Due to their structural analogy the fragmentation pattern of O(F)Ps can be very similar. Hence, the suggested structures were evaluated based on the (i) mass accuracy of the precursor ions, and subsequent MS^{2/3} fragments, (ii) fragment intensity distribution in the mass spectra as well as (iii) retention times in HILIC and RP separation. Furthermore, the suggested structures were confirmed *via* the formation or absence in either exclusively methyl groups containing LIB electrolyte (SelectiLyte™ LP30) or ethyl groups containing electrolyte (SelectiLyte™ LP40). Separation of acidic species, containing a free P-OH bond, was performed by HILIC on a strong anion exchange (SAX) stationary phase, whereas separation of non-acidic species was obtained by reversed-phase chromatography with a C18-based stationary phase.

Despite the small number of reactants in LIB electrolytes the structural variety of decomposition products concerning solvent-originated molecules led to many isobaric interferences in extracted ion chromatograms (EICs) of possible O(F)Ps (Figure 3). This emphasized the importance of high resolution mass spectrometry combined with fragmentation information to obtain reliable results and avoid false positive results. Nevertheless, at higher m/z ratios the high resolution reached its limit due to a more difficult attribution of fragments while a partial-fragmentation of side chains occurred. Furthermore, the structural variety increased up to 9 constitutional isomers (cf. m/z 273.110) and the structure prediction software revealed several possible sum formula. Besides, signal intensities decreased for higher mass-to-charge ratios, which diminished the MS³ fragmentation opportunity.

The following work is divided into three parts to classify phosphorus based decomposition products of the hexafluorophosphate anion regarding their different structures with the same head group and to keep track of the high variety.



Figure 3: Isobaric interferences of the extracted ion chromatogram of m/z 245.095 (ESI(+)) and two theoretical suitable OFP structures for this m/z ratio are depicted. MS² showed no phosphorus- or fluorine-based fragments whereas carbonate-originated characteristic fragmentation occurred.

3.1 Structure elucidation of organophosphates

The separation on C18-based stationary phases relies on the hydrophobic interaction of alkyl chains with the analytes. Accordingly, retention of non-acidic OPs depended on the hydrophobicity of molecules regarding the shielding of the polar phosphate head group due to the three side chains and their length. Therefore, the retention times in Figure 4 increased strongly from trimethyl phosphate (m/z 141.031, 6.6 min), to ethyl dimethyl phosphate (m/z 155.047, 14.0 min), to diethyl methyl phosphate (m/z 169.063, 20.4 min) and to triethyl phosphate (m/z 183.078, 23.6 min). The elongation of side chains by ethoxy groups originating from EC led only to slightly increased retention times on the C18 stationary phase, therefore, tris(2-ethoxyethyl) phosphate (m/z 315.157) eluted already after 26.2 min. The integration of ethoxy groups into side chains enhanced the hydrophobicity only slightly, whereas terminal hydroxyl groups at the side chains had a strong abridging influence on retention times (see Table S1 m/z 185.058). Additionally, RP chromatography was capable of separating several acidic species. These structures were not taken into account and are discussed in HILIC results. A characteristic charge transfer to the side chain fragments in positive ionization mode could have simplified the identification of acidic compounds with RP retention but for the omnipresence of organic carbonate-based polymerization products in LIB electrolytes isobaric interferences aggravated the identification especially for higher masses.



Figure 4: EICs from IT-TOF-MS in ESI(+) mode of non-acidic OPs in LP50 electrolyte separated by RP chromatography.

MS² fragmentation was performed to obtain further information about OP structures and, in combination with the retention time in chromatography, was an important tool to distinguish constitutional isomers. The prevalent fragmentation behavior of OPs was the loss of a single or multiple side chains (see Figure 5). Therefore, the phosphate fragment was an indicator for OPs with stable leaving groups like ethyl groups (loss of ethylene) or longer side chains. Hence, methyl groups revealed to be bad leaving groups in the fragmentation process and no phosphate fragments were detected. Structures with a single methyl group showed the cleavage of the P-O bond and the release of methanol whereas two or three methyl groups containing OPs exhibited the unlikely methane loss (Table S1 m/z 141.031, 185.058 and 215.068). Therefore, the absence of fragments indicated a structural feature as well as the fragment intensity distribution, which was used to recognize homologous side chains. Furthermore, the generation of characteristic fragments and short scan times of the IT-TOF-MS in MS² mode enabled the resolution of co-eluting constitutional isomers (see Figure 6). Fragmentation within side chains occurred only with very low probability leading to low intensities in MS² spectra but increased with longer side chains and

complicated clear attribution of signals to a specific isomer. With increasing m/z ratios, MS spectra exhibited less characteristic fragments and MS3 experiments were in some cases impossible due to insufficient signal intensities. This effect complicates the investigation of high mass OPs and leads to the exclusion of possible OP signals.



Figure 5: MS^2 fragmentation pattern of three OPs in ESI(+) mode (a, b, c). Bond cleavages and resulting fragments are indicted with different colors. Two MS^3 spectra are depicted for m/z 301.141 (d, e) showing side chain cleavage and fragmentation to the phosphate head group.

The elongation of side chains with ethoxy groups and termination with methyl or ethyl groups led to a high variety in structures, even at the same molecular mass by different conjunction possibilities at three side chains. The retention behavior and formation of OP decomposition products in thermally aged electrolytes were investigated until PO_4 -($C_{12}H_{27}O_3$). Despite this limitation, over 60 structures were theoretically possible and 46 were identified by RP-IT-TOF-MS, the majority not described in literature, yet. The number of identified structures in LP30 and LP40 was significantly lower with 8 and 11 OPs, respectively. Only structures with appropriate retention behavior, mass accuracy and MS² fragmentation pattern were considered and depicted in Table S1.

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Figure 6: EIC of the precursor 213.089 in ESI(+) mode and corresponding MS² fragments. Bond cleavage and resulting fragments are indicated with different colors. Different signal maxima of fragment EICs indicate the co-elution of two constitutional isomers.

Acidic OP structures showed only poor retention on RP chromatography. Therefore, the separation was performed in HILIC mode on a SAX column with negative electrospray ionization for increased sensitivity. As a result of the negative ionization mode no non-acidic OPs and only a few carbonate-based analytes were ionized, and the total ion current was less complex. The retention mechanism changed completely from hydrophobicity and side chain dependency to a characteristic anionic head group based separation with only minor influence by side chains or their attached terminal hydroxyl groups. Nevertheless, enhanced hydrophobicity led to slightly decreased retention times, thus, 26 acidic OP structures eluted in a period from 9-12 minutes. A second group of acidic OPs with an additional hydroxyl group at the phosphate showed high retention and peak broadening due to strong interaction with anion exchange functional groups of the stationary phase. The elution time of this group of signals ranged from 17-22 minutes (see Figure 7).

Remarkably, the PF_6 anion showed very low retention in RP as well as in HILIC mode. This retention behavior was beneficial to cut off the signal within the first 2.5 minutes of the chromatography by a switching valve.



Figure 7: EICs from IT-TOF-MS in ESI(-) mode of acidic OP in LP50 electrolyte separated by HILIC.

Fragmentation in negative ionization mode revealed to be analogous to the fragmentation in positive ionization mode with the preferential cleavage of side chains and stable leaving groups. Furthermore, better sensitivities for methanol loss at methylated OPs were shown. The formation of PO_3H fragments appeared to be common as well as fragments from possible initial ring closure reactions with loss of a water molecule at terminal ethoxy groups

(*m*/*z* 185.022) or from ethoxy groups formed after side chain cleavage accompanied with a release of a stable leaving group (C_2H_4 or higher). 5-membered ring fragments (*m*/*z* 122.985) showed comparably high intensities and therefore have a good stability. The setup of HILIC-IT-TOF-MS revealed a total of 36 acidic OP in thermally aged LP50 electrolyte, for LP30 14 and LP40 11 species, respectively (see Table S2).

3.2 Structure elucidation of organofluorophosphates

The separation of non-acidic OFPs with RP chromatography showed only the formation of mono fluorinated OFPs which indicates a low stability of difluoroalkyl phosphate intermediates. Formation of fluoroalkyl side chains was not observed. This structural change shifted the retention time to slightly lower values due to the higher polarity of fluorine atoms, but overall the retention behavior was similar to non-acidic OPs (see Figure 8). The remaining P-F bond reduced the number of side chains to two and therefore decreased the amount of possible structures and constitutional isomers. Hence, the number of non-acidic OFPs was 15 in the LP50 electrolyte, 3 in the LP40 and 4 in the LP30, respectively, and are depicted in Table S3.



Figure 8: EICs from IT-TOF-MS in ESI(+) mode of non-acidic OFPs in LP50 electrolyte separated by RP chromatography.

The retention and fragmentation behaviors of non-acidic OFPs in positive ionization mode were similar to those of OPs due to the structural homology (Table S3). Stabilization by ring formation was not observed for non-acidic OFPs in positive mode whereas terminal ethoxy groups led to 5- and 8-membered ring fragments for acidic structures due to HF loss and the cleavage of fluorine which was detected for methyl fluorophosphates (m/z 112.981). Characteristic fragmentation pattern of OFPs with terminal methyl or ethyl groups are depicted in Figure 9.



Figure 9: Fragmentation patterns of different OFPs in ESI(-) (a, b) and ESI(+) modes (c, d). Characteristic bond cleavages and resulting fragments are indicated with different colors.

In agreement to the results of non-acidic OFPs, acidic fluoroalkylation products were not detected. The structure of the acidic head group, especially number of fluorine present, showed a remarkable influence on the retention on the SAX stationary phase. Thus, the retention times raised from 1.4 min (hexafluorophosphate), to 3.1 min (difluorophosphate) and to 7.9 min for mono-fluorinated structures (Figure 10). The effect of side chain composition was negligible. Nevertheless, several co-eluting mono-fluorinated structures were identified by their fragmentation pattern and due to the low structural variability with 3 of 4 fixed conjunctions at the phosphorus atom constitutional isomers could be excluded.



Figure 10: EICs from IT-TOF-MS in ESI(-) mode of acidic OFPs in LP50 electrolyte separated by HILIC.

12 acidic OFP structures were identified in LP50, 7 in LP30 and 4 in LP40, respectively (Table S4). The mitigated formation of high molecular ethyl-based OFPs could indicate a higher stability of DEC-based electrolytes. Nonetheless, predictions regarding the stability of

different electrolyte formulations were difficult since the pristine water content is the crucial parameter for promoted electrolyte degradation in relation to the used linear organic carbonate. Overall, the lower structural variability is reflected by the number of formed acidic and non-acidic O(F)Ps in thermally aged LIB electrolytes due to more fixed side groups. The formation of compounds with elongated side chains is theoretically less likely. This is in good agreement since detected signals were close to the limit of detection of the instrument.

3.3 Structure elucidation of cyclic organo(fluoro)phosphates

Heterocyclic 5-membered or 8-membered rings suffer from high ring strain. Therefore, cyclic O(F)Ps represent an unexpected group of decomposition products in LIB electrolytes. In contrast to 8-membered rings, 5-membered rings have been reported in literature.⁴¹ Thus, assignments of 8-membered rings were confirmed by synthesized standards and a possible formation scheme based on literature is shown in Figure 11.^{27,61,62} Ethylene oxide polymers generated under EC addition and subsequent decarboxylation are substrate for the ring organophosphate compounds, presumably.



Figure 11: Decomposition of LiPF₆ and ethylene carbonate leading to 8-membered ring organophosphates. Pristine electrolyte composition is indicated in blue, features from degraded electrolyte in red. Scheme adapted and expanded from *Lee et al.*, *Sloop et al. and Gachot et al.*^{27,61,62}

Several ring structures were identified in thermally aged LIB electrolytes with side chains having terminal methyl or ethyl but no hydroxyl groups (cf. Table 5). The increase in chain length led to higher retention times in RP chromatography with a small abridging effect after extension with an oxygen atom and higher retention times for 8-membered compared to 5-membered ring isomers (Figure 12).



Figure 12: EICs from IT-TOF-MS in ESI(+) mode of cyclic OPs in an LP50 electrolyte separated by RP chromatography.

Fragmentation of cyclic O(F)Ps showed primary the afore mentioned chain cleavage as well as a ring opening reaction in 8-membered rings with a presumably subsequent re-forming of a 5-membered ring. Thus, the decomposition of LIB electrolytes to 8-membered rings is confirmed by the fragmentation pattern of synthesized standards as well as the retention behavior of the analytes. Additionally, this disproved both the formation of terminal vinyl groups or interferences with in-source fragmentations, which might cause the same m/z ratio. Retention times of one acidic and two non-acidic synthesized standards were in accordance to samples (Figure 13). The cleavage of an ethyl group from m/z 197.058 with a stable neutral loss of ethane indicated that an 8-membered ring exists (Figure 14). Furthermore, the fragmentation pattern of the 8-membered methylated ring and the 8-membered free acid ring were identical to the analytes in the sample. The ring opening reaction is probably induced by a C-O cleavage, leading to a nucleophilic attack and ring closure at the phosphorus atom and the subsequent release of ethanol. Additionally, NMR data showed no evidence of a vinyl group in the estimated region of 5.0 - 5.5 ppm in the non-acidic methylated standard (cf. Figure S1).



Figure 13: HILIC (ESI(-) *m*/*z* 167.012) and RP (ESI(+) *m*/*z* 183.042, 197.057) chromatograms of three 8-membered rings formed in LIB electrolyte LP50 in comparison to synthesized standards.



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Figure 14: Fragmentation pattern of different cyclic O(F)Ps (a, b, c) and synthesized standard (d) in ESI(+) mode. Characteristic bond cleavages and resulting fragments are indicted with different colors.

Overall, 14 different cyclic O(F)P structures were identified in LP50, 6 in LP30 and 4 in LP40, respectively. This unexpected group revealed the possible presence of several further kinds of decomposition products in LIB electrolytes. These findings emphasized the importance of qualitative and quantitative consideration of phosphorus-based aging products for the evaluation of safety concerns as well as performance impacts.

4 Conclusion

This study reveals the high structural variety of phosphorus-based decompositions products in thermally aged lithium ion battery electrolytes by the hyphenation of liquid chromatography to IT-TOF-MS. Additionally, it reports the applicability of HILIC with a strong anion exchange column for the separation of acidic O(F)Ps as well as a successful reversed phase chromatography of non-acidic O(F)Ps. This allows a comprehensive, qualitative investigation with a single instrument setup. Besides the formation of longer side chains with higher variation and structural isomers, organophosphates with 8-membered ring structure are identified for the first time and confirmed with synthesized standards. For standard-less identification high mass resolution, fragmentation pattern and intensity distribution, achieved with IT-TOF-MS, are considered, combined with the retention behavior on two orthogonal separation techniques as well as different electrolyte formulations. In thermally aged ethyl methyl carbonate containing battery electrolyte (LP50) 82 OPs, 27 OFPs and 13 cyclic O(F)Ps are identified. For the only ethyl groups containing solvent in LP40 the number declines expectably to 22, 7 and 4, respectively. In LP30, dimethyl carbonate solvent, the amount is also lower with 22, 11 and 6, respectively.

The results illustrate the complex decomposition possibilities of the conductive salt LiPF_6 and the range of O(F)P-based structures with potentially tremendous toxicity. These contribute to the significance of toxicological investigations for risk assessments of LIB electrolytes. The specific toxicity may change accompanied with structural variety, and therefore consideration of qualitative and quantitative information is important. This study gives an overview on 121 phosphorus-based decomposition products in LIB electrolytes and enables a target analysis for quantitative speciation approaches with ICP-MS techniques which are necessary for a significant safety assessment.

5 Conflict of interest

There are no conflicts to declare.

6 Acknowledgements

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7 Supporting information

The reader is kindly referred to the supporting information to obtain following information: Tables S1-S5: Structure suggestions with underlying MS identification data Figure S1: ¹H-NMR of synthesized standard 2-methoxy-1,3,6,2-trioxaphosphocane 2-oxide

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