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Qualitative and quantitative investigation of organophosphates in an electrochemically and thermally treated lithium hexafluorophosphate-based lithium ion battery electrolyte by a developed liquid chromatography-tandem quadrupole mass spectrometry method†

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The presented work was focused on the development of a new liquid chromatography-tandem quadrupole mass spectrometry method (LC-MS/MS) for the identification and quantification of organophosphates in lithium hexafluorophosphate ($LiPF_6$)-based lithium ion battery electrolytes. The investigated electrolyte consists of 1 M $LiPF_6$ dissolved in ethylene carbonate/ethyl methyl carbonate (50/50, wt%) and was treated electrochemically and thermally. For the electrochemical experiments, the cut-off potential in the half cells was held at 5.5 V for 72 h. The thermal degradation experiments were performed in aluminum vials at 95 °C for a period of 13 days. In the first part of this work, an already established gas chromatography-mass spectrometry (GC-MS) method for identification of dimethyl fluorophosphates (DMFP) and diethyl fluorophosphate (DEFP) was applied. In the second part, the LC-MS/MS method including determination of characteristic transitions in a product ion scan was developed. The developed method was applied for the identification of various analytes in the decomposed electrolytes. In addition, a possible formation of ionic and non-ionic OPs based on findings of this work and our previous reports is presented. In the third and final part, a quantification study of DMFP and DEFP was performed with a newly developed LC-MS/MS method and compared with results obtained by GC-MS. In addition, trimethyl phosphate (TMP) and triethyl phosphate (TEP) were quantified. These studies included the investigation of the suppression effects caused by the sample matrix during the application of the LC-MS/MS method.

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1 Introduction

In recent years, the lithium ion battery (LIB) technology has an increasing importance for both domestic and industrial sectors.[1,2] Usually, investigations are focused on the development of new materials for electrodes and electrolytes which should further improve the cycle stability and energy density of LIBs.[3] A high energy density is summarized by a high voltage and a high capacity and it is crucial for the hybrid electric vehicle and the plug-in hybrid electric vehicle utilization.[4] One of the approaches to improve energy density is the application of high voltage cathode materials such as $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO). Although, the theoretical capacity of LNMO is moderate (147 mA h g^{-1}),[5] this cathode material can be operated at high voltages up to 4.7 V (ref. 5) making it promising for the electromobility industry. The most widely used electrolytes deployed in commercial LIBs are based on the electrolyte solution of 1 M $LiPF_6$ dissolved in a mixture of organic carbonates.[6] Their dominance on the marked is explained by excellent performance properties including ion conductivity,[7] supporting solid electrolyte interphase formation (SEI) at the anode[8] and protection of the aluminum current collector at the positive electrode.[9] The main drawback of $LiPF_6$ dissolved in organic carbonates is the chemical and thermal instability of the P–F bond.[7] $LiPF_6$ undergoes the decomposition to high reactive PF_5, which results in formation of *inter alia* POF_3, HF, alkyl fluorides and CO_2.[10,11] Furthermore, the electrochemical instability of $LiPF_6$/organic carbonates based electrolytes is well known limiting their application at high voltages.[12]

An specific class of decomposition products generated during thermal decomposition of $LiPF_6$-based electrolytes is

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represented by organophosphates (OPs), which are formed by reaction of POF_3 with organic carbonates.[10] Within the group of OPs, special attention to alkyl fluorophosphates should be paid. At least two of them, DMFP and DEFP, are very hazardous; their toxicity[13] is comparable to diisopropyl fluorophosphate.[14] These compounds are nerve agents, whose toxic effect bases on the irreversible reaction with a mammal enzyme acetylcholinesterase.[15] Furthermore, these compounds were recently found in material from a lithium ion battery recycling process using GC-MS.[16] With regard to the increasing demand on LIB working at high potentials, investigations regarding the quantification of any decomposition products should be performed.

The analysis of OPs and electrolyte degradation in LIB electrolytes was already performed with different analytical techniques including nuclear magnetic resonance spectroscopy (NMR),[10,17] GC-MS[18–20] including supercritical extraction steps,[21,22] high resolution-electrospray ionization-mass spectrometry (HR-ESI-MS)[23–25] and low temperature plasma-ambient ionization-high resolution-mass spectrometry (LTP-HR-MS).[26] In particular, both ionic and non-ionic OPs were analyzed by GC-MS[20,27] or ion chromatography hyphenated to tandem quadrupole mass spectrometry (IC-MS/MS),[28] two dimensional ion chromatography-mass spectrometry (IC-IC-MS)[29] and inductively coupled plasma-mass spectrometry-optical emission spectrometry (IC-ICP-OES).[30] Almost all studies with these methods were focused on identification of the OPs. The quantitative analysis is complicated because of the absence of commercial standards. The concentration was determined by GC-MS and only for DMFP and DEFP with limits of detection (LOD) in the low ppm range for both compounds.[16,20] The study of trialkyl phosphates, as further degradation products, was not performed due to their low contents. The LC-MS/MS technique working in a multiple reaction monitoring scan (MRM) mode is more specific as total ion current (TIC) or selective ion monitoring (SIM) modes of GC-MS. The schematic illustration of measurements obtained in the MRM mode with a triple quadrupole instrument is shown in Fig. S1.† After the separation on the chromatographic column and ionization in the ESI source, the molecular ion of a studied analyte is selected by the first quadrupole and transmitted to the second quadrupole used as a collision cell, which is filled with nitrogen as a collision gas. The collision results in formation of fragments, whose separation is performed by the third quadrupole. A fragment with highest intensity obtained by a defined value of a collision energy improves limits of detection. Compared to the MRM mode, both, TIC and SIM modes are applied with one quadrupole mass separator. The TIC mode measures the whole mass range, therefore the analytes are strongly interfered by matrix resulting in high limits of detection. In the SIM mode the molecule ions of the analytes are selected, which improves their detection. Nevertheless, measurements of the analytes and matrix compounds with the same mass results in the co-elution of the signals. The MRM mode is able to distinguish between the analyte and matrix compounds due to determination of specific fragments of the analyte, which increases in this mode, provided the characteristic fragmentation was determined. This technique was applied for the determination of trialkyl phosphates as flame retardants and plasticizers in drinking and surface waters[31–34] or air samples[35] with low instrumental LODs. In the presented work, we developed a new LC-MS/MS method for study of non-ionic organophosphates, which was then applied for the identification and quantification of OPs electrochemically and thermally generated in a $LiPF_6$/organic carbonates LIB electrolyte. The electrolyte samples were treated at elevated cathode potential or high temperature in order to generate the desired analytes in high concentrations.

2 Experimental part

2.1 Chemicals and materials

The battery grade SelectiLyte™ LP50 electrolyte (BASF, Ludwigshafen, Germany) consists of 1 M $LiPF_6$ in ethylene carbonate/ethyl methyl carbonate (EC/EMC, 50/50 wt%). Deionized water for the preparation of eluents, standard solutions and dilution of analytes was produced with a Milli-Q water system using a LC-PAK cartridge (Bedford, USA). Methanol, acetonitrile (MeOH, ACN, both HPLC gradient grade) and ethanol (EtOH, 99.8%) were ordered from VWR (Bruchsal, Germany). DMFP and DEFP (both >99.6%) were synthesized according to literature.[20] HCOOH (98–100% for analysis) was ordered from Merck (Darmstadt, Germany). Trimethyl phosphate (TMP > 99%), triethyl phosphate (TEP, 99.8%), 2-methoxyethanol (99.8%) and the electrode material for LNMO were purchased from Sigma Aldrich (Steinheim, Germany). 2-Ethoxyethanol (99%) was ordered from Alfa Aesar (Lancashire, Great Britain). Dimethyl ethyl phosphate (DMEP), diethyl methyl phosphate (DEMP), ethyl methyl fluorophosphate (EMFP) and alkoxyethyl dialkyl phosphates were synthesized according to literature.[20] The nonwoven material (FS 2226) for the separators was purchased from Freudenberg Nonwovens (Weinheim, Germany). For thermal aging experiments, 10 ml aluminum vials with butyl/polytetrafluoroethylene (PTFE) caps were used (Leicht&Appel GmbH, Bad Gandersheim, Germany).

2.2 LC-ESI-MS conditions

The liquid chromatography studies were performed on an Ultimate 3000 HPLC system, which was controlled by a Chromeleon™ 7.2 Chromatography Data System software (Thermo Scientific, Waltham, USA). The separations were carried out on an Acclaim™ 120 column (C18, 4.6 × 250 mm, Thermo Scientific) at 30 °C column oven temperature with 40% MeOH and a flow rate of 1 ml min^{-1} isocratically. The injection volume was 5 μl. The mass spectrometric measurements were performed using a triple quadrupole instrument 3200 LC/MS/MS (AB Sciex, Framingham, USA). The ESI-MS instrument was controlled with the Analyst 1.5.2 software (AB Sciex, Framingham, USA). The infusion of standard substances in a product ion scan mode was performed at a spray voltage of 4500 V; the curtain gas was set to 15 psi; the nebulizer and dry gas were set to 25 psi and 0 psi, respectively; the temperature of the turbo gas was 0 °C. The OPs were diluted (1 : 10^5, v/v) in water/ACN (1 : 1, v/v) mixture containing 0.1 vol% HCOOH. The ion spray voltage in LC-MS and LC-MS/MS experiments was set to 5500 V, the

curtain gas was set to 25 psi, the nebulizer and dry gas were set to 45 psi and temperature of the turbo gas was 550 °C. The declustering potential was set to 35 V for TMP and TEP or 30 V for other compounds, the entrance potential was 5 V, the collision cell exit potential was 4 V. The collision energy was set to 12 eV for TMP and TEP or 15 eV for other compounds. The scan time was 200 ms. For TIC measurements with LC-MS, the electrolyte samples were diluted 1 : 40 (v/v) in ACN. For quantification of DMFP and DEFP an external six-point calibration in a range of 2–100 ppmv was performed (R^2 > 0.998). The quantification of TMP and TEP was carried out with an external six-point calibration in a range of 0.01–0.5 ppmv (R^2 > 0.999). The identification and the quantification of the organophosphates with LC-MS/MS in a MRM mode and limit of detection (LOD) studies were performed by the dilution factor of 1 : 100 (v/v) in ACN. Each standard solution was measured five times; the samples were measured three times. Table S1† lists the instrumental LOD values of DMFP, DEFP, TMP and TEP obtained with LC-MS/MS and calculated according to DIN 32645.

2.3 GC-MS conditions

The GC-MS measurements were performed on a GCMS-QP2010 Ultra GC-MS equipped with an AOC-5000 Plus autosampler and an OPTIC-4 injection system (Shimadzu, Duisburg, Germany). The analytes were separated on a Supelco SLB-5 ms column (30 m, 0.25 mm × 0.25 μm) from Sigma-Aldrich (Seelze, Germany). As carrier gas helium (6.0) with a column flow of 1 ml min^{-1} and a split of 1 : 10 were used. The GCMS Solution software (GCMS Real Time Analysis and GCMS Postrun Analysis) was used for instrument control and data analysis (Shimadzu, Duisburg, Germany). 1 μl of the diluted samples (1 : 100 vol%, ACN) was injected at an injection temperature of 230 °C. The measurements were performed with following column oven program: starting with 40 °C for 1 min, the temperature was increased with a rate of 3 °C min^{-1} to 60 °C, then with 30 °C min^{-1} to 210 °C and held finally for 1 min. Electron impact (EI) ionization was used at an ion source temperature of 200 °C, a filament voltage of 70 V and a GC-MS interface temperature of 250 °C. The quantification of DMFP and DEFP an external six-point calibration in a range of 2–100 ppmv was carried out in a SIM mode (R^2 > 0.996). Following mass fragments were used: *m*/*z* 98 for DMFP, *m*/*z* 113 for DEPF, *m*/*z* 110 for TMP and *m*/*z* 155 for TEP. The LOD values calculated according to DIN 32645 are presented in Table S1.†

2.4 Electrochemical and thermal aging experiments

The used LMNO electrodes were composed of 85 wt% LMNO, 7 wt% polyvinylidene difluoride (PVdF, Kynar® 761) and 8 wt% carbon black SuperC65 (Imerys). The preparation procedure is described by Kasnatscheew *et al.*[36] The active mass loading of the electrodes was around 14 mg cm^{-1}. The measurements were carried out in 2032 coin cells. As counter electrode, Li-metal was used. Polyolefin separators FS 2226 (6 fold) were soaked with 120 μl electrolyte. The potentiostatic experiments were carried out on a battery tester (Series 4000 from MACCOR) at 20 °C. The LNMO/Li half cells were charged/delithiated to the upper cut-off potential of 5.5 V *vs.* Li/Li^+. After reaching the desired cut-off potential, the potential was held for 72 h. The cells were disassembled in the discharged state (3.0 V *vs.* Li/Li^+) in an argon filled glove box. After the electrochemical experiments, the separators were placed into plastic vials (Eppendorf Hamburg, Germany) and centrifuged at 8500 rpm for 5 min. The thermal decomposition of samples was achieved by heating 1 ml of the electrolyte in 10 ml aluminum vials with butyl/PTFE caps at 95 °C for 13 days.

2.5 Evaluation of suppression effects caused by matrix

The evaluation of suppression effects caused by the matrix was performed according to work of Chen *et al.*[37] 50 μl of the diluted solution (1 : 50, v/v in ACN for DMFP and DEFP and 1 : 150, v/v in ACN for TMP and TEP) of the decomposed electrolytes were mixed with 50 μl of 10 ppmv DMFP/DEFP standard or 2 ppmv TMP/TEP standard (sample A_i). Sample B_i contained 50 μl of the diluted sample (1 : 50, v/v in ACN for DMFP and DEFP and 1 : 150, v/v in ACN for TMP and TEP), which was dissolved in 50 μl of ACN. The third sample, C_i, was obtained by mixing of 50 μl of 10 ppmv DMFP/DEFP standard or 2 ppmv TMP/TEP standard with 50 μl of ACN. The matrix effects (ME, %) were calculated as followed:

$$ME\ [\%] = 100 \times (A_i - B_i)/C_i$$

3 Results and discussion

3.1 Determination of organophosphates by GC-MS

Based on the work of Weber *et al.*,[20] dialkyl fluorophosphates were determined in thermally and electrochemically aged LP50 electrolytes. Fig. 1 displays the mass traces of analytes in the range of 3.8 and 8.4 min, which were generated in an electrochemical aged sample. All three compounds, DMFP (*m*/*z* 98), DEFP (*m*/*z* 113) and EMFP (*m*/*z* 98), are clearly separated and could be detected with high intensity in both, the electrochemically and thermally degraded electrolytes. The identification of DMFP and DEFP is additionally supported by mass spectra and the retention time obtained with synthesized

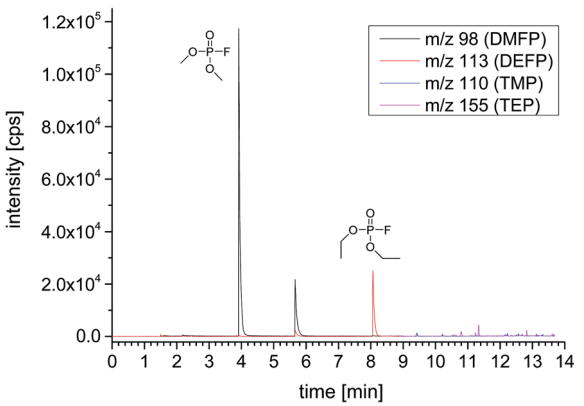


Fig. 1 SIM gas chromatograms of the investigated OPs generated in an electrochemically decomposed LP50 electrolyte. The peak at 5.9 min with *m*/*z* 113 can be assigned to the presence of EMFP.

standards. Furthermore, the mass traces of TMP (m/z 110) and TEP (m/z 155) as possible products of dialkyl fluorophosphates were monitored. Their commercially available standards have higher retention times compared to dialkyl fluorophosphates: TMP ($t_R = 9.4$ min), TEP ($t_R = 11.2$ min). The determination of the trialkyl phosphates in aged electrolytes is not reliable, since the occurrence of co-eluting signals of the studied m/z values is accompanied by very low intensity for the retention times measured with standards. In addition, these compounds constitute only minor products of $LiPF_6$ degradation, which further complicates their study by GC-MS.[20]

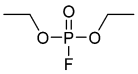
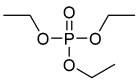
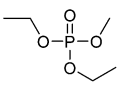
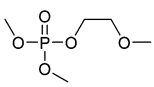
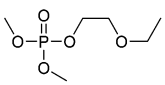
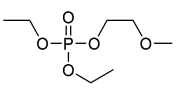
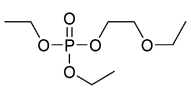
3.2 ESI-MS/MS experiments

Preliminary tests with TIC mode measurements of both thermally and electrochemically aged electrolytes reveal a very complex matrix. The mass chromatograms contain many signals, where assignment could not be achieved. The interpretation is additionally complicated by the presence of both Na^+ and NH_4^+ adducts. By searching for the molecule peaks ($M + H^+$) of OPs found by GC-MS (see 3.1) in a SIM mode, several co-eluted signals are detectable, which inhibits the identification. A MRM mode, as a characteristic LC-MS/MS mode, is more specific and sensitive compared to TIC or SIM, but it requires detailed knowledge about the fragmentation of the analytes. In Table 1, the chemical structures, monitored $[M + H]^+$, abbreviations and resulting fragments obtained by infusion of the standards of commercially available or synthesized OPs in a product ion scan mode are presented. The signal characteristic is strongly dependent from the presence of a proton donating compound. The addition of 20 mM formic acid significantly increases the signal stability.

Furthermore, DMFP, DEFP and several alkoxyethyl dialkyl phosphates (see Table 1), which are commercially not available were synthesized to support the further identification process. The products are contaminated with different OPs, which were detected by LC-ESI-MS in the TIC mode. These OPs are the result of the trans-esterification process. Since the purity of the substances was not sufficient enough for quantitative measurements, they were only used for identification purposes.

In general, highly resolved fragmentation patterns are accessible for all analytes, which is demonstrated on an example of six OPs in Fig. 2. The fragments of other OPs are

Table 1 Chemical structures, monitored $[M + H]^+$, abbreviations and fragments obtained with the product ion scans of the investigated compounds

Compound	Chemical structure	Monitored $[M + H]^+$ (m/z)	Abbreviation	Fragments (m/z)
Dimethyl fluorophosphate		129	DMFP	113, 109, 97, 95
Diethyl fluorophosphate		157	DEFP	129, 101
Trimethyl phosphate		141	TMP	127, 109, 95, 79, 47
Triethyl phosphate		183	TEP	155, 127, 99
Dimethyl ethyl phosphate		155	DMEP	127, 109, 99, 95
Diethyl methyl phosphate		169	DEMP	141, 113, 95
Methoxyethyl dimethyl phosphate		185	MEDMP	141, 127, 109, 59
Ethoxyethyl dimethyl phosphate		199	EEDMP	127, 73, 45
Methoxyethyl diethyl phosphate		213	MEDEP	185, 155, 127, 99, 59
Ethoxyethyl diethyl phosphate		227	EEDEP	155, 127, 99, 73, 45

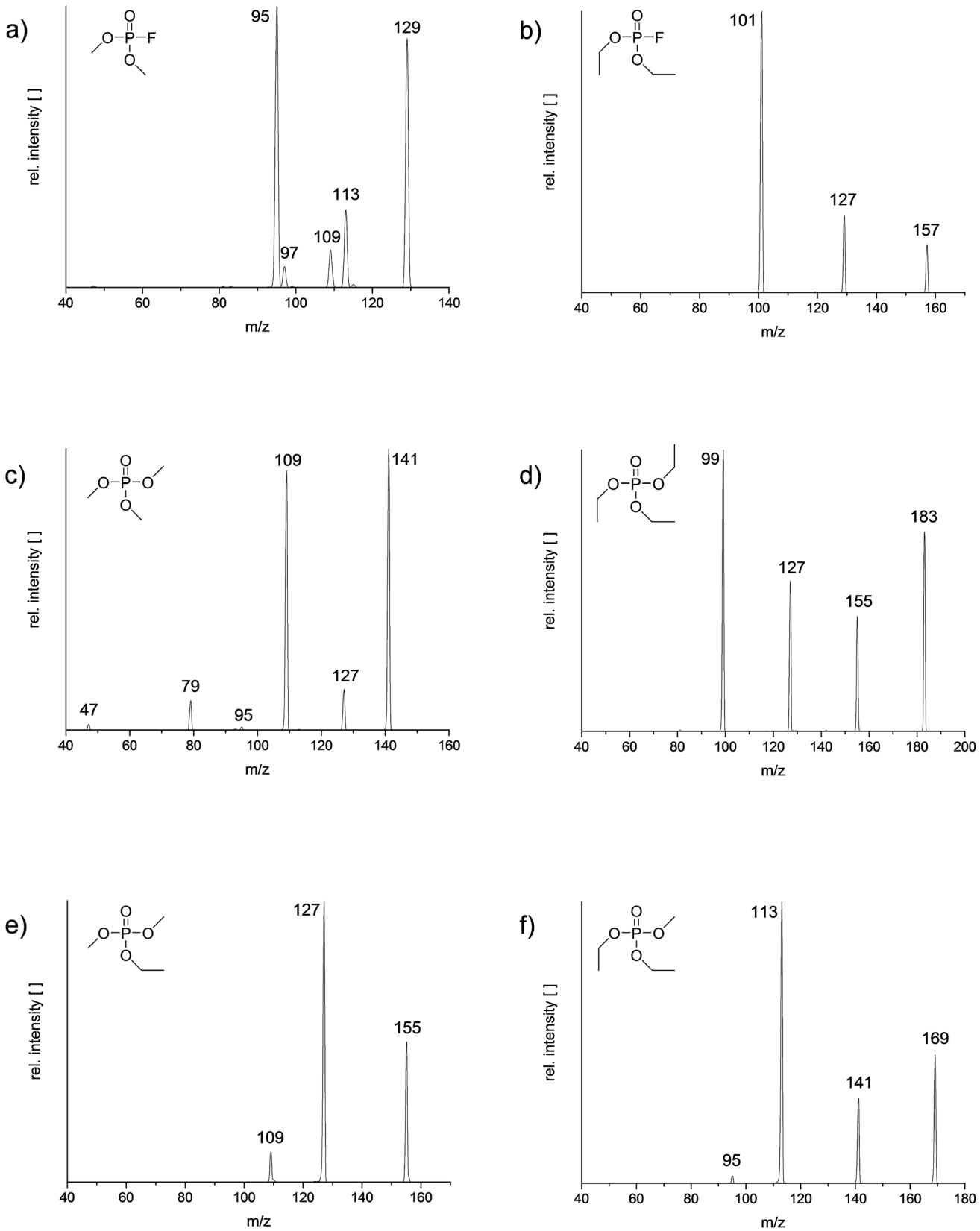


Fig. 2 Fragmentation patterns of DMFP (a), DEFP (b), TMP (c), TEP (d), DMEP (e) and DEMP (f) obtained in a product ion scan mode.

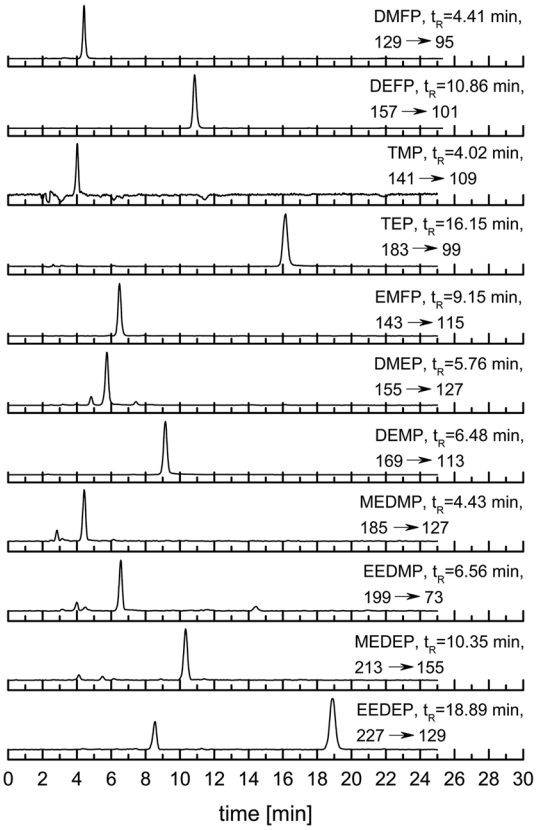


Fig. 3 MRM chromatograms of the investigated OPs generated in an electrochemically decomposed LP50 electrolyte. The *y*-axis (intensity in cps) are not shown.

shown in Table 1. The mass spectra of TMP and TEP investigated by LC-MS/MS are known in literature[31–33,35] and are in agreement with the presented results. Furthermore, the interpretation of the mass spectra is highly facilitated with fragmentation rules for non-ionic OPs, which were systematized by Weissberg *et al.*[38] and Schwarzenberg *et al.*[39] A neutral loss of ethene (*m*/*z* 28) was observed by DEFP, TEP, DMEP, DEMP, MEDEP and EEDEP. Furthermore, diethylated or triethylated compounds such as DEFP, TEP and DEMP have a multiple loss of ethene in agreement to the rules. Similar fragmentation was observed by MEDMP and MEDEP or EEDMP and EEDEP with the neutral loss of methyl vinyl ether (*m*/*z* 58) and ethyl vinyl ether (*m*/*z* 72), respectively. In addition, fragments with *m*/*z* 59 or *m*/*z* 73 were detected in mass spectra of these compounds, which indicates protonated methyl vinyl ether or ethyl vinyl ether, respectively. A characteristic cleavage by TMP and DMFP is the loss of −*m*/*z* 32 as methanol followed by addition of water. The water addition as a possible reaction was discussed in literature.[39]

3.3 Development of LC-MS/MS methods

The addition of organic solvents to an aqueous eluent increases the ionization yield because of the decrease of the surface tension and consequently a more effective de-solvation of the analytes.[40] Fig. 3 shows the MRM chromatograms of the studied OPs in the electrochemically decomposed electrolyte. The chromatographic measurements were performed with 40% MeOH on a reversed phase. The addition of 20 mM HCOOH as a proton donor source for the ionization is necessary in order to suppress the secondary ionization effect with NH_4^+ and Na^+, which were present as contaminants in the ESI source. The peak shapes measured with a 40% MeOH eluent besides slightly tailed TMP are in general symmetric. The elution sequence of the analytes depends on the number of alkyl groups and their chain length of the analyte and it bases on the hydrophobic interaction with stationary phase of C18 column. According to this finding, among the alkyl fluorophosphates and trialkyl phosphates, the highest retention time is observed with TEP. The ethylene glycol group of MEDMP, EEDMP, MEDEP and EEDEP decreases the adsorption of these analytes on the stationary phase, which results in high distribution degree in the mobile phase leading to shorter retention times. The analysis time with applied parameters is about 25 min, which is also sufficient for the complete elution of all unknown compounds observed in the TIC mode. The applied MRM transitions are specific in regard to the studied OPs (see Fig. 3). In the last chromatogram of EEDEP, an additional peak with the MRM transition 227 → 129 at 8.5 min is observable. It should be noticed, that a standard for EMFP was not available. Nevertheless, the MRM transition 143 → 115 (loss of ethene) indicates a peak at $t_R = 4.41$ min. The retention time for this compound is between the values for DMFP ($t_R = 9.15$ min) and DEFP ($t_R = 10.86$ min), which additionally confirms EMFP.

In Fig. 4, a global scheme for the decomposition mechanism of $LiPF_6$/linear organic carbonates electrolyte with focus on the formation of inorganic and organic phosphates identified in this work is illustrated. The reaction of a cyclic carbonate, EC, with POF_3 is similar.[10,20] Furthermore, the scheme summarizes the so far applied techniques for the separation and detection of the analytes. POF_3 is sequently alkylated to produce non-ionic compounds, which are detectable by GC-MS[20] and/or LC-MS/MS. Other products of the reaction are CO_2 and alkyl fluorides, whose identification by GS-MS was performed by Gachot *et al.*[11] The fluorinated phosphates are hydrolyzed in parallel reaction. The separation and identification of hydrolyzed products was performed in our previous works by IC-MS[27,30] and IC-MS/MS.[27,30,41] The phosphorus containing compounds POF_3 and alkyl difluorophosphate were not investigated in this work. But their formation in degraded electrolytes detected by GC-MS was discussed in literature.[10,20,27]

3.4 Quantification of organophosphates

A typical method for quantifications of analytes by LC-MS/MS is the external calibration using analytical standards. The disadvantage of this method constitutes the dependence on matrix effects leading to suppression or enhancement of the signal intensity of target analytes. The possibility to determine this effect is described by Chen *et al.*[37] The investigation of the suppression effects were performed for two independent electrochemically aged cells and two thermal aged electrolytes. The methods applied for the determination of OPs, M1 and M2, were used for quantification experiments. The results obtained

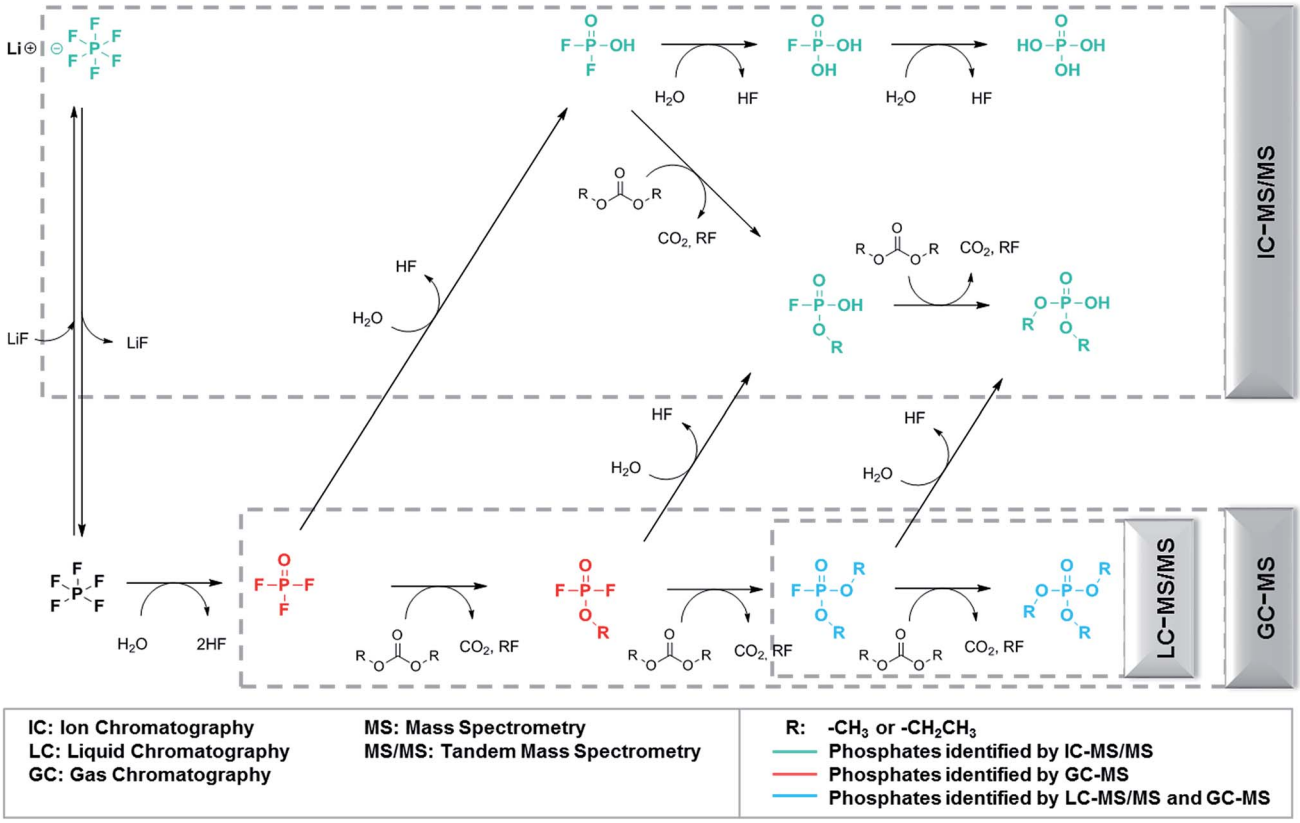


Fig. 4 A global scheme for the thermal or electrochemical decomposition mechanism of $LiPF_6$/linear organic carbonate mixture based electrolyte with a focus on the formation of inorganic and organic phosphates resulting from IC-MS/MS, GC-MS and LC-MS/MS analysis.

Table 2 Matrix effects (%) of the investigated organophosphates (E_i: electrochemically decomposed electrolyte; T_i: thermally decomposed electrolyte). The dilution factor for DMFP and DEFP studies is 1 : 100 in ACN. TMP and TEP were investigated by a 1 : 300 dilution. RSD values are showed in brackets

Sample	DMFP	DEFP	TMP	TEP
E_1	92.6 (21.0)	99.8 (2.9)	75.4 (5.9)	175.5 (8.5)
E_2	109.2 (5.8)	118.4 (7.2)	63.2 (5.5)	91.1 (0.1)
T_1	95.5 (4.0)	93.1 (9.5)	90.2 (6.2)	77.4 (4.2)
T_2	99.0 (1.0)	99.8 (6.8)	84.6 (8.5)	81.5 (10.0)

for DMFP, DEFP, TMP and TEP are collected in Table 2. In the ideal case, the percentage values should be 100%, resulting in no matrix effects. The most results for DMFP and DEFP are close to the ideal values. The differences can be explained by errors of sample preparation and detection, but the errors are in an acceptable range. It can be concluded, that both fluorophosphates are not significantly suppressed by the matrix at the applied dilution of 1 : 100 of the measured samples. The quantification of DMFP and DEFP with the developed LC-MS/MS method was carried out (see Table 3). In addition, GC-MS was applied to validate the results of the developed LC-MS/MS method. The correlation coefficients (R^2) are >0.992 for both analytes and ensure an accurate determination. The results for both dialkyl fluorophosphates measured with LC-MS/MS and GC-MS correlate well. The concentration of DMFP and DEFP in both sample types with 0.05–0.2 wt% is quite high and indicates strong decomposition of the electrolyte.

In contrary to the dialkyl fluorophosphates, the quantification of TMP and TEP is strongly dependent on matrix effects due to their low content in samples, which results in high

Table 3 Concentration of DMFP and DEFP (ppm) in the investigated electrolyte samples measured with LC-MS/MS or GC-MS (E_i: electrochemically decomposed electrolyte; T_i: thermally decomposed electrolyte). The RSD is stated in brackets

	DMFP			DEFP		
Sample	LC-MS/MS	GC-MS	Deviation [%]	LC-MS/MS	GC-MS	Deviation [%]
E_1	1504.8 (2.8)	1446.8 (4.6)	4.0	590.7 (3.0)	632.0 (4.1)	6.5
E_2	989.6 (1.3)	920.6 (8.0)	7.5	693.5 (0.1)	789.8 (2.2)	12.2
T_1	168.9 (3.4)	168.5 (2.7)	0.3	1673.3 (2.0)	1608.6 (3.6)	4.0
T_2	161.2 (1.0)	163.2 (0.5)	1.2	1533.4 (1.6)	1478.7 (3.2)	3.7

Table 4 Concentration of TMP and TEP [ppm] in the investigated electrolyte samples measured with LC-MS/MS (E_i: electrochemically decomposed electrolyte; T_i: thermally decomposed electrolyte). The RSD is stated in brackets

Sample	TMP	TEP
E_1	15.9 (3.6)	60.3 (2.1)
E_2	4.0 (0.8)	8.7 (3.1)
T_1	3.5 (1.8)	22.4 (2.9)
T_2	4.0 (2.9)	21.3 (3.6)

suppression effects. In preliminary tests, a suppression of approximately 50% accompanied by bad reproducibility was observed for TMP and TEP upon dilution by a factor of 1 to 100. As it was discussed by Stuber *et al.*, sample dilution can reduce matrix effects. Nevertheless, the decrease of sensitivity resulting from the dilution is compensated by a low LOD of trialkyl phosphates.[42] The instrumental LODs for TMP and TEP are much lower compared to GC-MS as it is shown in Table S1.† The dilution factor of 1 to 300 minimizes the suppression from the range of 27–9% (see Table 2). Furthermore, an increase of the ionization is observed in E_1 sample for TEP. Despite the observed suppression effects, the concentration for trialkyl phosphates could be determined. It is up to two magnitudes lower compared to DMFP and DEFP and indicates a low decomposition degree of dialkyl fluorophosphates in the studied electrolytes in according to the proposed degradation mechanism (see Fig. 4) (Table 4).

4 Conclusions

This paper reports the first reversed phase LC tandem MS method for identification and quantification of organophosphates in an electrochemically and thermally decomposed $LiPF_6$-based lithium ion battery electrolyte. This method relies on the separation of compounds on the reversed phase and the detection of the analytes in a multiple reaction monitoring mode, which avoids the non-specificity of the total ion current and the selective ion monitoring modes. In total, the commercially available or synthesized standards of eleven organophosphates were baseline separated and investigated with a product ion scan. The measurement with determined MRM transitions allow the quantification of the analytes including the study of suppression effects caused by a matrix, which was demonstrated selectively on DMFP, DEFP; TMP and TEP. The content of highly hazardous DMFP and DEFP measured in an at 95 °C thermally decomposed and at 5.5 V electrochemically treated electrolytes is very high; it was determined in the range from 0.02 to 0.16 wt%. The concentration of these compounds could be determined by a dilution of 1 : 100, since the suppression effects were negligible at the studied decomposition stage of the electrolytes. Furthermore, the determined concentration could be validated by GC-MS.

The quantification of the much lower concentrated TMP and TEP (up to two orders of magnitude) were performed with a higher dilution degree. The dilution of samples 1 : 300 showed moderate suppression (27–9%). Hence, the higher dilution minimized the matrix effects, but also decreased the sensitivity. However, this circumstance was compensated by the low limits of detection (140–150 ppb) of the LC-MS/MS method for the studied trialkyl phosphates. Alternatively, a standard addition as a matrix independent quantification method instead of the external calibration could be an alternative. The validation by GC-MS was not performed due to uncertainties during the determination by this technique in contrast to the developed method.

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