Identification of alkylated phosphates by gas chromatography–mass spectrometric investigations with different ionization principles of a thermally aged commercial lithium ion battery electrolyte

Waldemar Weber, Vadim Kraft, Martin Grützke, Ralf Wagner, Martin Winter, Sascha Nowak *

University of Münster, MEET Battery Research Center, Institute of Physical Chemistry, Corrensstraße 46, 48149 Münster, Germany

ARTICLE INFO

ABSTRACT

The thermal aging process of a commercial LiPF$_6$ based lithium ion battery electrolyte has been investigated in view of the formation of volatile phosphorus-containing degradation products. Aging products were analyzed by GC–MS. Structure determination of the products was performed by support of chemical ionization MS in positive and negative modes. A fraction of the discovered compounds belongs to the group of fluorophosphates (phosphorofluoridates) which are in suspect of potential toxicity. This is well known for relative derivatives, e.g. diisopropyl fluorophosphate. Another fraction of the identified compounds belongs to the group of trialkyl phosphates. These compounds may provide a positive impact on the thermal and electrochemical performance of Li-based batteries as repeatedly described in the literature.

1. Introduction

LiPF$_6$ based electrolytes, using a mixture of aprotic organic carbonate solvents are preferred in lithium ion batteries (LIB) [1,2]. Currently an implementation of LiPF$_6$ based batteries in a large scale may be problematic due to potential safety and performance problems in LIB [3–5]. On the other hand, LiPF$_6$ seems to be an indispensable electrolyte component due to its beneficial effects on solid electrolyte interphase (SEI) formation and Al current collector protection [6,7]. World-wide intensive research is going on in order to understand the reactions of LiPF$_6$ based electrolytes. A well known phenomenon of LiPF$_6$/organic carbonate solvent based batteries is their pronounced thermal instability at elevated temperatures. The equilibrium of LiPF$_6$ with solid LiF and gaseous PF$_5$ is considered as mainly responsible for a variety of detrimental reactions. PF$_5$ is a strong Lewis acid and reacts with solution species/impurities such as alcohols [8], organic carbonates [9,10] and preferably with water [11] under formation of HF and POF$_3$, whereas the subsequent reactions of POF$_3$ generate a number of phosphate derivatives, organic species and HF.

To create a sufficient amount of these aging products for analysis, the majority of researchers suggest a powerful acceleration of the aging process by applying elevated temperatures to the electrolyte. As a consequence, a significant part of the available literature reports about aging of LiPF$_6$/organic carbonate describes the aging of the electrolyte only without consideration of the other cell components [12–15]. Others investigate mutual influences of the electrolyte on individual cell components such as anodes [16–19], cathodes [18,20,21] and separators [22,23]. To sum up, a complete picture of electrolyte aging inside a lithium ion cell has not been taken yet and mechanisms are by far not fully understood.

A wide range of analytical methods is available for investigations of reaction mechanisms during thermal aging of a LIB electrolyte. Online measurements by differential scanning calorimetry (DSC) [24–27], accelerating rate calorimetry (ARC) [17,28] or in situ Fourier transform infrared spectrometry (FTIR) [1,20,29] are the most commonly used techniques in studying the thermal stability of materials. However, a more detailed structural analysis of the degradation products is required to establish a meaningful analytical database. This can be accomplished by post mortem studies of electrolytes or other cell parts by nuclear magnetic resonance spectroscopy (NMR) [30–32], elemental analysis by ICP-OES [13] or mass spectrometry (MS). The last method can be also used

separately as high resolution MS (HR-MS) [31,33,34] or combined with separation techniques such as ion chromatography (IC) [13,49,50], gas chromatography (GC) [35–37,48,52,53] and liquid chromatography (LC) [51].

Herein, we report the identification of volatile organic phosphates as thermally generated degradation products of $LiPF_6$/organic carbonate electrolytes by GC–MS. The same phosphates can be observed in electrolytes after charge/discharge processes of LIBs as well. The formation of such compounds results from reactions of the formed PF_5 and POF_3 with the organic carbonate solvents and therefore represents an appropriate indicator for progressive aging processes. On the other hand, alkyl phosphates are also known to be effective flame retardants [38–41] or can be used for increasing the thermal and electrochemical performance in LIB [42].

An additional aspect is the toxicity of organophosphorus compounds, in particular of phosphorofluoridates which constitute a part of phosphorus-containing degradation products of the electrolyte. The neurotoxicity of phosphorofluoridates is well known and widely described in the literature, mostly on the example of diisopropyl phosphorofluoridate (DPF) [43–45] as deactivator of the neurotransmitter acetylcholine. The structurally similar compounds determined and quantified by our analysis, such as dimethyl phosphorofluoridate (DMPF), ethyl methyl phosphorofluoridate (EMPF) and diethyl phosphorofluoridate (DEPF) resemble the diisopropyl phosphorofluoridate very much. Their activity is based on the inhibition of human acetylcholinesterase (AChE) by irreversible phosphorylation [46,47]. This effect is comparable to significantly more potent inhibitors such as nerve agents sarin and soman. No information on hazards caused by the release of phosphorofluoridates from $LiPF_6$ based batteries is present in the current literature. Nevertheless, due to the growing interest in LIBs, an intensive research in this field is inevitable. For instance, for the application in electric vehicles (EVs) and for recycling of EV batteries, where large quantities of electrolyte are used and handled, the information about possible dangers of phosphorofluoridates is absolutely essential.

The analysis of phosphorus-based products can be carried out by different analytical methods. For non-volatile compounds, e.g. di- and monofluorophosphates, the separation by ion chromatography (IC) and detection by conductivity or electrospray ionization-MS (ESI-MS) has been successfully carried out [13,49,50]. A number of the volatile phosphates could be detected by high resolution electron ionization (HR-EI-MS) but without an assignment of the fragment ions to specific molecules [33,36]. Independent of their volatility the phosphates could be successfully determined by NMR using ^{31}P, ^{19}F NMR [8,9,32] or proton decoupled $^{13}C-^{1}H$ NMR [30]. Though, due to the high limit of detection of NMR techniques, only major compounds could be detected. In several publications the determination of organophosphates by gas chromatographic techniques (GC–MS or GC-FID) is described, mostly for gaseous compounds such as $(MeO)F_2PO$ and $(EtO)F_2PO$ [30]. A comprehensive study of the formation, consecutive reactions and composition of the organophosphates does currently not exist. In this paper, a detailed identification of the formed phosphorofluoridates (e.g. DMPF, EMPF and DEPF) and their consecutive reaction products is described, including the identification of compounds by CI- and NCI-MS which have not been described in the literature, yet. Finally, a quantification of DMPF and DEPF using an external calibration on GC–MS was successfully performed.

The overall goal of this and our other related analytical studies is to show that quantitative analysis of specific electrolyte decomposition products allows a judgment about the aging degree of the battery electrolyte. In consequence, this electrolyte "fingerprint" may give an approximate assessment about the "age" of a battery cell.

2. Experimental

2.1. Materials

LP50 electrolyte (1 mol L^{-1} $LiPF_6$, ethylene carbonate – EC/ethyl methyl carbonate – EMC, 50/50 wt%, battery grade) were purchased from BASF. 2-fluorethanol (95% purity) and ethylene glycol (99%) were obtained from Sigma Aldrich (Steinheim, Germany). Dichlormethane (>99%) was obtained from Sigma Aldrich (Steinheim, Germany). The GC-equipment was run with helium (purity 6.0) as carrier gas and NH_3 (purity 3.8) for chemical ionization (CI). These gases were purchased from Westfalen Gas (Germany).

2.2. Instrumental analysis

A Perkin Elmer GC–MS Clarus 600 with a Restek Rxi-5 ms column (30 m × 0.25 mm × 0.25 μm), with TurboMass 5.4.2 software was used. 1 μL of solution was injected at an injection temperature of 210 °C. The system was run with helium as carrier gas with a column flow of 1 mL min^{-1}, a split of 1:10 and the following column oven program were used: starting with 40 °C for 1 min, the temperature was increased with a rate of 3 °C min^{-1} to 60 °C and then with 30 °C min^{-1} to 210 °C, held for 1.0 min. An electron impact (EI) ionization mode was used with a filament voltage of 70 V and a detector voltage of 1.5 kV. GC–MS experiments with chemical ionization (CI) and negative chemical ionization (NCI) were done with NH_3 (introduced with 3 bar) on a Shimadzu GC–MS-QP2010 Ultra equipped with an AOC-5000 Plus autosampler, an OPTIC-4 injection system and a Restek Rxi-5 ms column (30 m × 0.25 mm × 0.25 μm). Identical conditions were used as described for the Perkin Elmer GC–MS. The water content in the electrolyte was determined with an 851 Titrando Karl Fisher Coulometer (Metrohm, Herisau, Switzerland).

2.3. Sample preparation

Volumes of 2 mL of electrolyte were sealed in 10 mL aluminum vials with butyl/PTFE caps and tempered at 95 °C for a defined time period. 25 μL of sample were exactly weighed in a 2 mL polypropylene Safe-Lock tube, diluted with 1 mL dichloromethane and centrifuged for 5 min at 8500 rpm to remove the solid $LiPF_6$. The centrifuged solution was transferred into a 2 mL GC glass vial and measured by GC–MS.

2.4. Quantification of DMPF and DEPF

For quantification of dimethyl phosphorofluoridate (DMPF) and diethyl phosphorofluoridate (DEPF) an external six-point calibration ($R^2 > 0.999$) with synthesized standards (purity > 99%) in a range of 1.4–63 ppm has been used. Each standard solution and sample was measured five times. Mass fragment $m/z = 98$ was used for calibration of DMPF and $m/z = 113$ for DEPF. Limits of detection (LOD) and limits of quantification (LOQ) were calculated according to DIN 32645: DMPF (1.2 ppm, 4.5 ppm), DEPF (0.9 ppm, 3 ppm) respectively.

2.5. List of identified phosphates

Table 1 shows the identified trialkyl phosphates and phosphorofluoridates according to their retention time and their characteristic EI-MS fragments.

2.6. Synthesis of reference standards

The synthesis for phosphate **7** was performed by stirring DMPF with 2-fluorethanol (50:50 wt%) for 1 h at room temperature.