

Understanding the degradation processes of the electrolyte of lithium ion batteries by chromatographic analysis

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The electrolyte of lithium ion batteries (LIBs) degrades both under normal operation – e.g. in the formation of the solid electrolyte interphase (SEI) – and in particular under conditions of extreme temperature, voltage or current flow. Degradation products of the electrolyte (typically a mixture of organic carbonates such as ethylene carbonate (EC), ethylmethyl carbonate (EMC), dimethyl carbonate (DMC) or diethyl carbonate (DEC) with a suitable conducting salt such as LiPF₆) can be volatile or permanent gases, e.g. H₂, CO, CO₂ and the low hydrocarbons (C1-C3) and are thus ideally determined by gas chromatography. GC with various detectors can be used, accounting for the vastly different detectability of the degradation products with common GC detectors like flame ionization, thermal conductivity or mass spectrometric detection. Evolved gas analysis is complemented by the direct analysis of the electrolyte which requires careful opening of the cell for post mortem analysis. In the presence of the conducting salt LiPF₆, but also in the presence of water or air, condensed or more polar degradation products are formed which are more easily separated in liquid phase by RP-HPLC or ion chromatography. These include carbonate oligomers (with varying number of ethoxy moieties resulting from the ring-opening reaction of the ethylene carbonate) and organic phosphates and monofluorophosphates, resulting from the degradation and (partial) hydrolysis of the conducting salt and its reaction with the organic solvent. Chromatographic techniques, in particular with mass spectrometric detection, are indispensable tools to characterize the wide spectrum of degradation products, and to better understand the processes leading to electrolyte degradation. This forms the basis for the improvement of lithium ion battery safety and performance.

Keywords: lithium-ion battery, electrolyte; degradation products, gas chromatography, liquid chromatography

INTRODUCTION

Lithium ion batteries (LIBs) are nowadays indispensable sources and storage devices for electric energy. They are widely used in industry, transport and telecommunication, and have become essential in many applications of our daily life such as portable computers, mobile phones, devices and instruments, and all sorts of consumer electronics [1]. LIBs are the currently preferred technology, as they are lighter than other rechargeable batteries for a given capacity; the Li-ion chemistry delivers a high open-circuit voltage; LIBs are characterized by a low self-discharge rate (about 1.5% per month) and they do not suffer from battery memory effect (i.e. loss of capacity upon repeated charging/discharging cycles) [2]. They have a large environmental impact as they are rechargeable and thus reduce toxic landfill [3]. This advantage is contrasted by a number of shortcomings. These are: poor cycle life, particularly in high current applications; rising internal resistance with cycling and age; and the need for Li-

ion batteries with even higher capacity for high-power applications [4]. Finally, but of highest relevance, are to be mentioned the safety concerns in case of overheating or overcharging or internal short circuit of the battery. A number of incidents have attracted public attention to the safety of lithium ion batteries, such as the recent recall of Samsung Galaxy Note 7 mobile phones due to potentially defective lithium ion batteries [5], three car fires involving the battery electric vehicle Tesla Model S that occurred in 2013, or the Boeing 787 Dreamliner Li-ion battery fire incidents in 2013–2014, as well as serious accidents on cargo airplanes involving Li-ion batteries in the cargo hold, that have increased the awareness of the safety risks associated with this type of battery [6].

One of the most important fields of application of LIBs is in electric vehicles (both hybrid and full electric vehicles). It is anticipated that by 2020, 12.9 million electric vehicles will exist, which would represent approx. 3% of the global car stock [7]. With both the number and the size of lithium ion battery packs increasing (the battery pack of a full

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electrical vehicle may weigh up to 250 kg), the aspect of battery safety becomes crucial. Lithium ion batteries contain by mass ca. 10-12% of an organic electrolyte [8]. This is a highly flammable solvent that has the Li salt dissolved while the Li ions cycle between cathode and anode. Electrochemical, thermal and hydrolysis reactions lead to the partial decomposition of the electrolyte and the formation of even more volatile reaction products. When these are vented upon overheating of the LIB, there is the risk of fire or explosion of the entire battery pack. As the degradation of the LIB electrolyte is a continuously proceeding process, it can be followed by monitoring the formation of volatile degradation products, as well as the composition of the electrolyte itself [9]. This provides important diagnostic information, both on the actual state (of charge, SOC, and of health, SOH) of the battery, as well as on its preceding charging history, and can thus be used to better understand electrode and electrolyte processes to eventually increase battery safety and performance. This review will therefore discuss chromatographic techniques that allow the analysis of the organic electrolyte and its reaction or degradation products (Figure 1)

Electrolytes used in lithium ion batteries must fulfill a variety of conditions: They must withstand the extreme redox environment at both cathode and anode side and the voltage range during electrochemical cycling without decomposition. Second, they should be stable at typical cell operating temperatures which may range up to 60-70°C. Third, they must be good solvents for the lithium salts dissolved at relatively high concentrations (1 M typically). Furthermore, they should have favorable physicochemical properties such as low viscosity, high flash and boiling point, and ideally be non-toxic, environmentally benign and can be produced at low cost. It is evident that none of the currently used solvents satisfies all requirements to the same extent. For this reason, solvent mixtures are used in the electrolytes of commercial LIBs: Polar aprotic solvents, such as the organic carbonates have high dielectric constant and are selected to solvate the lithium salts at the high concentrations (1 M) in which they are present.

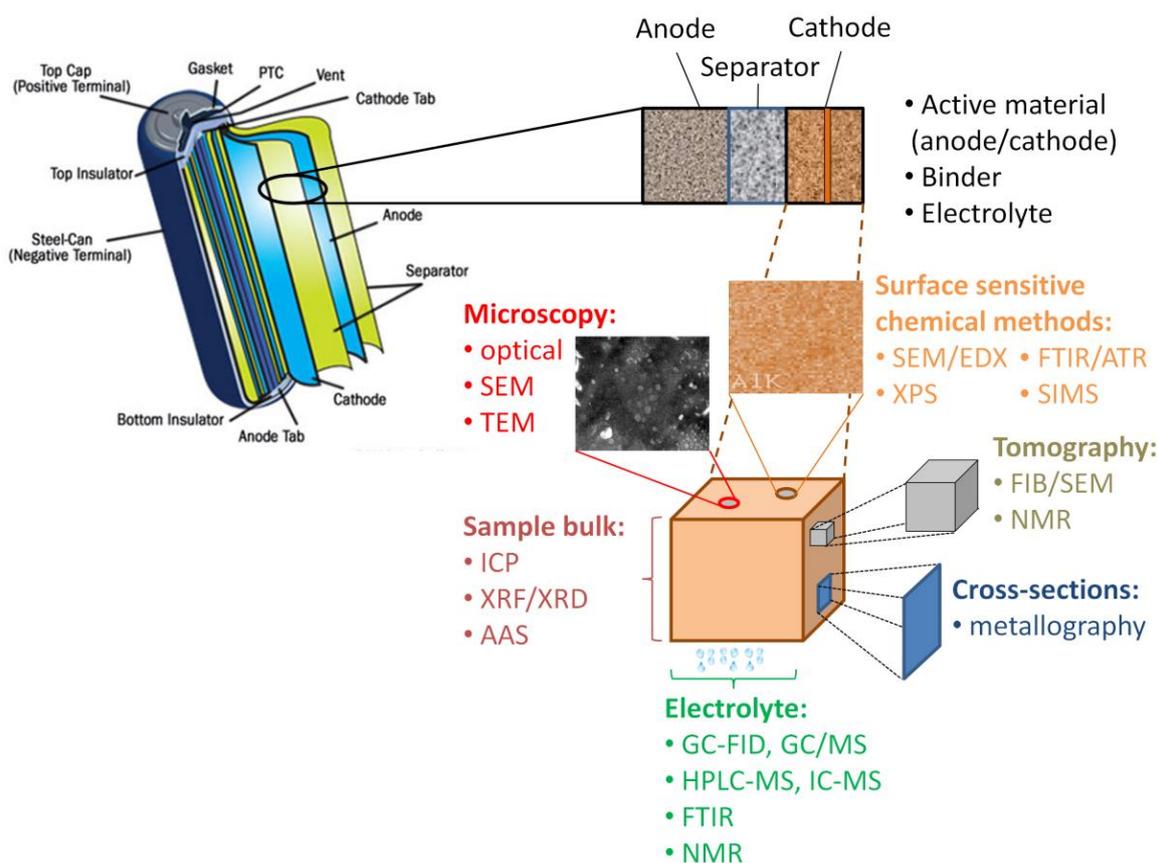


Figure 1 Overview of components inside a Li-ion battery and physico-chemical methods for their characterization after post-mortem analysis (after Waldmann *et al.* [21]).

On the contrary, solvents with low viscosity and low melting point are used to meet the requirements of high ion mobility in the temperature range considered. A variety of solvents has been investigated for this purpose, including dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), propylene carbonate (PC), ethylene carbonate (EC), diethoxyethane, dioxolane, γ -butyrolactone, and tetrahydrofuran (THF) [10]. More recently, also heteroatom-containing organic solvents have been suggested [11], as well as ionic liquids [12], however, the investigations presented in this review will concentrate on the former group of substances whose properties are presented in Table 1. A great variety of conducting salts has been investigated, including LiPF_6 , LiBF_4 , LiAsF_6 , LiClO_4 and LiCF_3SO_3 . The most characteristic properties of these conducting salts are summarized in Table 2. Only those conducting salts can be used whose anions are stable under typical operating

conditions of the LIB, avoiding the possibility of oxidation at the anode. This rules out the use of simple anions such as Cl^- , Br^- or I^- . The most commonly used conducting salt is LiPF_6 which excels in view of its safety, conductivity and the balance between conductivity and the balance between ionic mobility and the dissociation constant. The only, although significant disadvantage of LiPF_6 is its reactivity with water in the presence of which it forms the highly toxic and corrosive HF. For this reason, humidity must be minimized when handling a LiPF_4 -containing electrolyte.

Since no single solvent has all desired properties for safe and efficient LIB operation, electrolytes are typically formulated and solvents combined to produce the desired viscosity, conductivity and stability and to dissolve easily the particular Li-ion salt.

Table 1. Properties of the most important organic solvents used in LIB electrolytes. (Data compiled from Amon [13] and the PubChem database [14].)

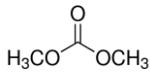
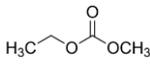
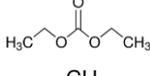
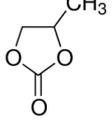
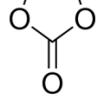
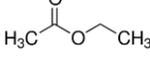
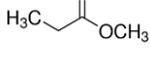
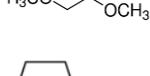
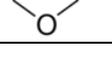
Electrolyte Components	CAS Registry No.	Structure	Melting / Boiling Point (°C)	Dielectric constant ϵ (25°C)	Viscosity η (cP, 25°C)	Vapor Pressure (torr)	Flash Point (°C)	Auto-Ignition Temperature (°C)
Dimethyl carbonate (DMC)	616-38-6		2 / 91	3.1	0.59	18 at 21°C	18	458
Ethyl methyl carbonate (EMC)	623-53-0		14 / 107	3.0	0.65	27 at 25°C	25	440
Diethyl carbonate (DEC)	105-58-8		-43 / 126	2.8	0.75	10 at 24°C	25	445
Propylene carbonate (PC)	108-32-7		-49 / 242	65	2.53	0.13 at 20°C	135	455
Ethylene carbonate (EC)	96-49-1		36 / 248	90 (at 40°C)	1.9 (at 40°C)	0.02 at 36°C	145	465
Ethyl acetate (EA)	141-78-6		-83 / 77	6.0	0.45	93 at 25°C	-4	4
Methyl propionate (MP)	554-12-1		-84 / 102	5.6	0.60	64 at 20°C	11	469
Ethyleneglycol dimethylether (DME)	110-71-4		-58 / 84	7.2	0.46	48 at 20°C	0	202
Tetrahydrofuran (THF)	109-99-9		-108 / 65...66	7.4	0.46	143 at 20°C	-17	321

Table 2. Properties of the most important conducting salts used in Li ion batteries [13, 17].

Salt	T _{Decomp.} in solvent [°C]	Al-corrosion	Conductivity (1.0 M, EC/DMC, 25°C)	Electrochemical stability until	Characteristics
LiClO ₄	>100	No	8.4 mS/cm	4.5 V vs. Li ⁺ /Li	Not sensitive to hydrolysis; no formation of HF; explosive
LiAsF ₆	>100	No. Passivates Al current collector.	11.1 mS/cm	4.5 V (cathodic) / 6.3 V anodic vs. Li ⁺ /Li	Good SEI formation. Toxic degradation products.
LiBF ₄	>100	No	4.9 mS/cm		Strong Lewis base; decomposes and forms HF
LiPF ₆	>70	Effectively suppresses Al corrosion	10.7 mS/cm	4.8 V vs. Li ⁺ /Li	Very sensitive to hydrolysis
LiCF ₃ SO ₃	>100	Yes	>10 mS/cm		
LiN(SO ₂ F) ₂	>100	Yes: Insufficient passivation of Al electrode	>10 mS/cm	4.8 V vs. Li ⁺ /Li	Not sensitive to hydrolysis, no formation of HF; expensive production

As an example, high dielectric solvents with a high viscosity are typically mixed with solvents of low viscosity to produce an electrolyte that is sufficiently conductive and liquid in the temperature window of operation. Some commonly used electrolytes are 1 M LiPF₆ in 50:50 w/w mixtures of EC with DMC, DMC or EMC (known under trade names LP30, LP40 and LP50 electrolytes, respectively). EC can stabilize Li⁺ ions more effectively than DEC or DMC [15]. The resulting electrolyte offers a reasonable stability over a wide potential range. In order to improve the formation of a stable solid-electrolyte interphase (SEI) which is of crucial importance for cell stability, various additives such as vinylene carbonate (VC) are added to the electrolyte [16, 17].

In addition to liquid electrolytes [18], other forms of electrolytes exist such as polymer [19], gel and ceramic electrolytes [20]; however, these will not be discussed in this context

METHODS FOR THE ANALYSIS OF LITHIUM ION BATTERY ELECTROLYTES

When studying LIB electrolyte decomposition only as an effect of temperature, humidity or oxidation, simulation experiments can be performed under laboratory conditions with the isolated electrolyte, without the need of using a commercial

electrochemical cell or a laboratory cell set-up. As soon as electrochemical reactions are to be considered as well, it is inevitable to have either a commercial battery or a laboratory-type electrochemical cell to be able to go through various charging / discharging cycles, or to subject the electrochemical cell to defined stress conditions. For fundamental studies, laboratory-made electrochemical cells are often favorable, as the fraction of electrolyte relative to the other cell components is typically larger, and also can easier be extracted. Commercial cells require a very careful disassembly (under inert atmosphere), the separation into its components, and the partially tedious extraction of the electrolyte prior to analysis (Figure 2). A very comprehensive description of cell disassembly procedures has been given by Waldmann *et al.* [21]. It shall be noted that chromatographic analysis not necessarily has to take place *ex situ* and *post mortem*. *In situ* chromatographic analysis is also possible and meaningful when targeting the volatile products of LIB electrolyte degradation: Since most of the LIBs have a gas vent valve in order to avoid pressure build-up due to the formation of gaseous degradation products, they would release volatiles to the environment during operation which can be analyzed by gas chromatography.

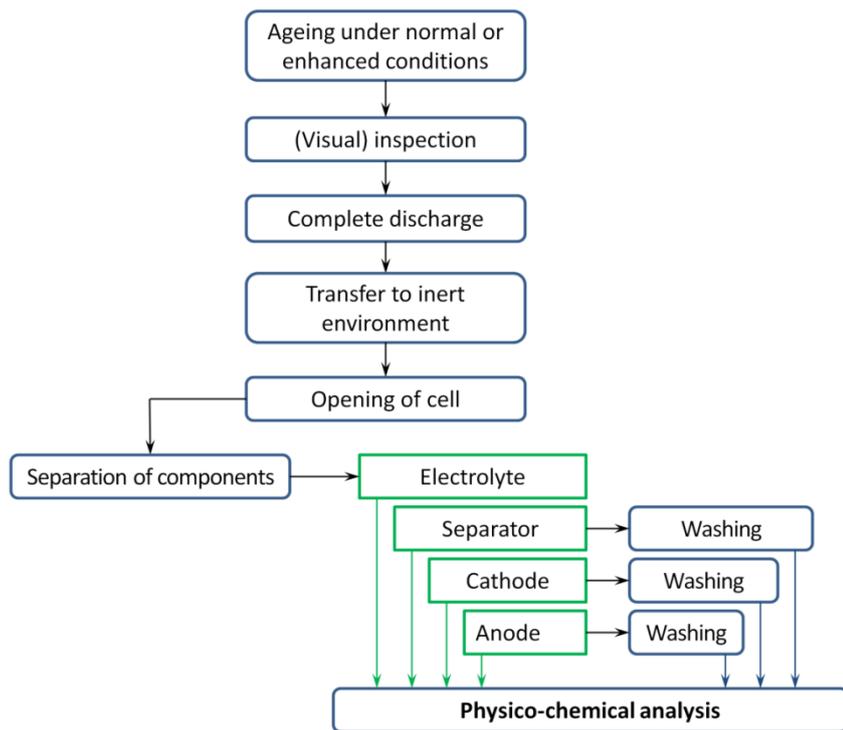


Figure 2 Flow chart for the disassembly of Li-ion batteries prior to the analysis of individual cell components (after Waldmann et al. [21])

Analysis of the LIB electrolyte provides information on the degradation products and allows modeling of the (electrochemical, thermal, oxidative or hydrolytic) reaction mechanisms leading to these products. Spectroscopic methods (particularly UV/Vis [22], FTIR [23, 24, 36], NMR [25] and mass spectrometry [26]) are widely used and are at advantage when measuring electrolyte composition and degradation *in situ* in laboratory set-ups, as they offer high time resolution and they do not necessarily require sampling. Chromatographic methods, on the contrary, do require sampling, but at the same time provide more information as they are capable of resolving and quantifying even more complex mixtures.

For the analysis of the electrolyte mixture, both liquid and gas chromatographic techniques can be used: Gas chromatography offers high separation power, positive identification capabilities (when mass spectrometric (MS) detection is used), good quantification and a high dynamic range, making it possible to detect even minor constituents in the mixture, such as electrolyte additives or degradation products. Liquid chromatography is used to investigate the less or non-volatile constituents of the electrolyte and particularly its polar degradation compounds; the technique often results in a less efficient separation than GC, and identification is more difficult even with mass spectrometric

detection due to the lack of spectral libraries. Confirmation of tentative structures is therefore either based on high-resolution MS measurements which allow the calculation of the elemental composition of the particular analyte, or the use of MS/MS detection, in which a selected precursor ion is fragmented and the fragments are detected, thereby providing increased structural information.

Gas chromatographic analysis

Gas chromatography with flame-ionization detection (GC-FID) and thermal conductivity detection (GC-TCD) was used for the analysis of volatile products generated during long cycling of a LIB [27]. The use of two GC setups is necessary due to the fact that the FID does not respond to fixed gases and oxidized compounds, such as N₂, O₂, or CO₂ which have to be determined by TCD, although with lower sensitivity. The authors developed a device in which they could quantitatively collect the volatiles formed in the degradation of the electrolyte and establish a mass balance. It was found that during normal cycling, the volume of gaseous products formed is between 1 and 2 ml for a standard 18,650 (Boston Power) cell, and that the low hydrocarbons (CH₄, C₂H₆, C₃H₈ and C₃H₆) represent the largest fraction of this. Under overcharging conditions, the gas volume formed is drastically increased (to ca. 10 cm³) of which CO₂ forms the by

far largest fraction with about 75%, whereas overdischarge conditions will lead to the formation of an even larger gas volume (of about 40 cm³), with the appearance of CO as a major product and the virtual disappearance of the lowest alkanes (Table 3).

Analyzing the neat electrolyte by GC/FID or GC/MS is straightforward: Medium polarity columns (such as DB-17 ((50%-phenyl)-methylpolysiloxane), DB-1701 ((14%-Cyanopropyl-phenyl)-methylpolysiloxane) or DB-200 ((35% Trifluoropropyl)-methyl-polysiloxane) and equivalent) of dimensions 30 m x 0.25 mm ID can

be used with relatively large film thickness (up to 1 μm) in order to provide sufficient capacity to avoid column overload by the main constituents of the electrolyte. Direct liquid injections of the undiluted electrolyte or after dilution in a suitable solvent (e.g. methanol or acetonitrile) are performed with a suitable high split ratio (e.g. 100:1). Under these conditions, the main volatile constituents of a commercial LIB electrolyte can be determined and identified on the base of their mass spectra as well as the additives present at the low and sub-percent level [28, 29] (Figure 3).

Table 3. Composition of gases generated in the nominal operating voltage range 4.2 V–2.5 V, and during overcharging and overdischarging (relates to a standard 18650 Li ion cell with 1 Ah capacity). (Reprinted from [26], with permission of Elsevier)

Test no.	Test conditions		Cycle number	Capacity at end cycle (Ah)	Composition of detected gases (%)							Total volume (ml)	
	Charge current	Discharge current			O ₂	N ₂	CO ₂	CO	CH ₄	C ₂ H ₆	C ₃ H ₈		C ₃ H ₆
R1	Before cycle test				5.3	42.5	1.7		40	4.2	0.4		0.95
R2		100 mA	2043	0.6	2.7	8.5	2.2		72	6.7	7.2	0.4	2.23
R3	200 mA	125 mA	2397	0.6	1.7	5.9	4.1		73	7.0	7.9	0.4	2.42
R4		200 mA	2331	0.5	1.5	6.5	7.2		61	7.6	15.6	0.8	2.63
R5		500 mA	2301	0.5	2.3	11.0	4.0		62	9.2	10.4	0.6	1.73
R6	125 mA		1915	0.6	2.1	7.7	1.3		75	7.8	6.2	0.2	2.01
R7	200 mA	125 mA	2570	0.5	3.2	6.6	3.2		72	8.3	7.2	0.4	2.78
R8	500 mA		3111	0.6	6.1	25.4	2.5		51	6.2	8.5	0.4	1.75
R9	200/200 mA, overcharge		880	0.6	1.3	5.3	75.6		12	2.6	2.7		10.57
R10	200/200 mA, over-discharge		880	0.0	0.3	1.5	71.2	0.6	21	3.2	0.8	1.0	40.21

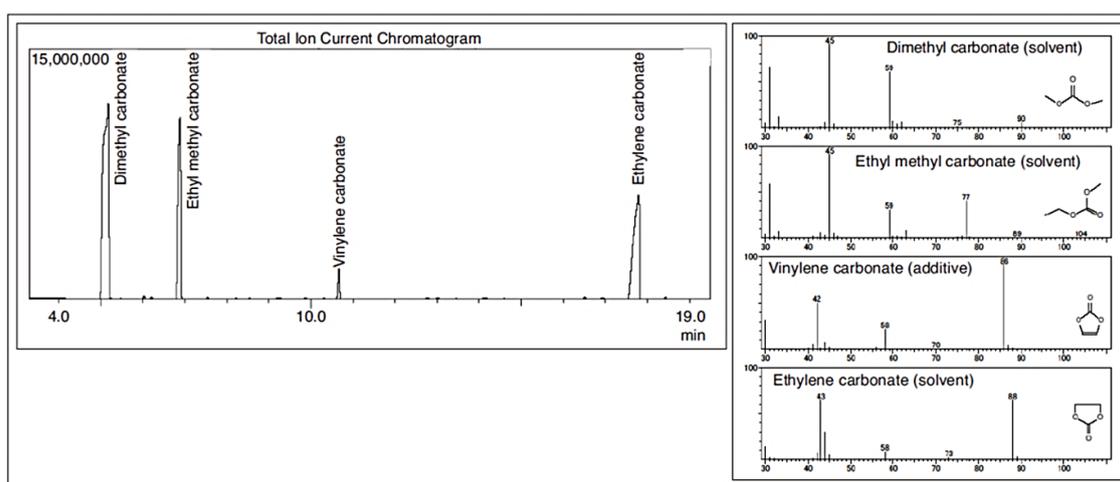


Figure 3: GC/MS chromatogram of a mixture of common electrolyte compounds (DMC, EMC and EC) and an electrolyte additive (VC) and mass spectra of the individual constituents [29].

In a study of the thermal stability of the organic electrolyte, various electrolyte mixtures were exposed to elevated temperature in the presence and absence of oxygen [30]. Even in the presence of oxygen and humidity, the carbonate solvents are

remarkably stable up to a temperature of ca. 70°C which is often considered a normal operating temperature for LIBs. When this temperature is exceeded, then the electrolyte rapidly starts decomposing, leading to the formation of a large

number of aliphatic and cyclic degradation products (Figure 4). A similar study was performed by Nowak and co-workers [31] who have thermally aged commercial LP50 electrolyte for 21 days at 80°C. The formation of the organic phosphates diethyl- (DEFP), dimethyl- (DMFP), and methyl-ethylfluorophosphate (MEFP) as well as triethyl- (TEP) and trimethylphosphite (TEP) was detected by GC/MS [32], and also confirmed by ion chromatography with electrospray-MS detection (IC-ESI-MS). In a further extension of this work, the same group of authors used GC/MS with chemical ionization to elucidate the structure of LP50 thermal degradation products [33]. The authors were able to confirm the formation of various cyclic and (dominantly) aliphatic (poly)ethers and carbonate esters as illustrated in Table 4.

The most interesting finding of these authors was that, when the electrolyte was kept at elevated temperature (90°C) for a longer period of time (21 days), degradation commenced to a larger extent only after an induction period of ca 5-10 days. After this period of time, the formation of linear polyethylene glycol ethers increased continuously, while the concentration of carbonate esters with a monoethylene glycolether moiety appeared to reach equilibrium, and the formation of carbonate esters with di- and presumably also triethyleneglycol ether moieties further increased. This appears plausible, as this would explain some of the reaction mechanisms observed within the commercial Li electrolytes.

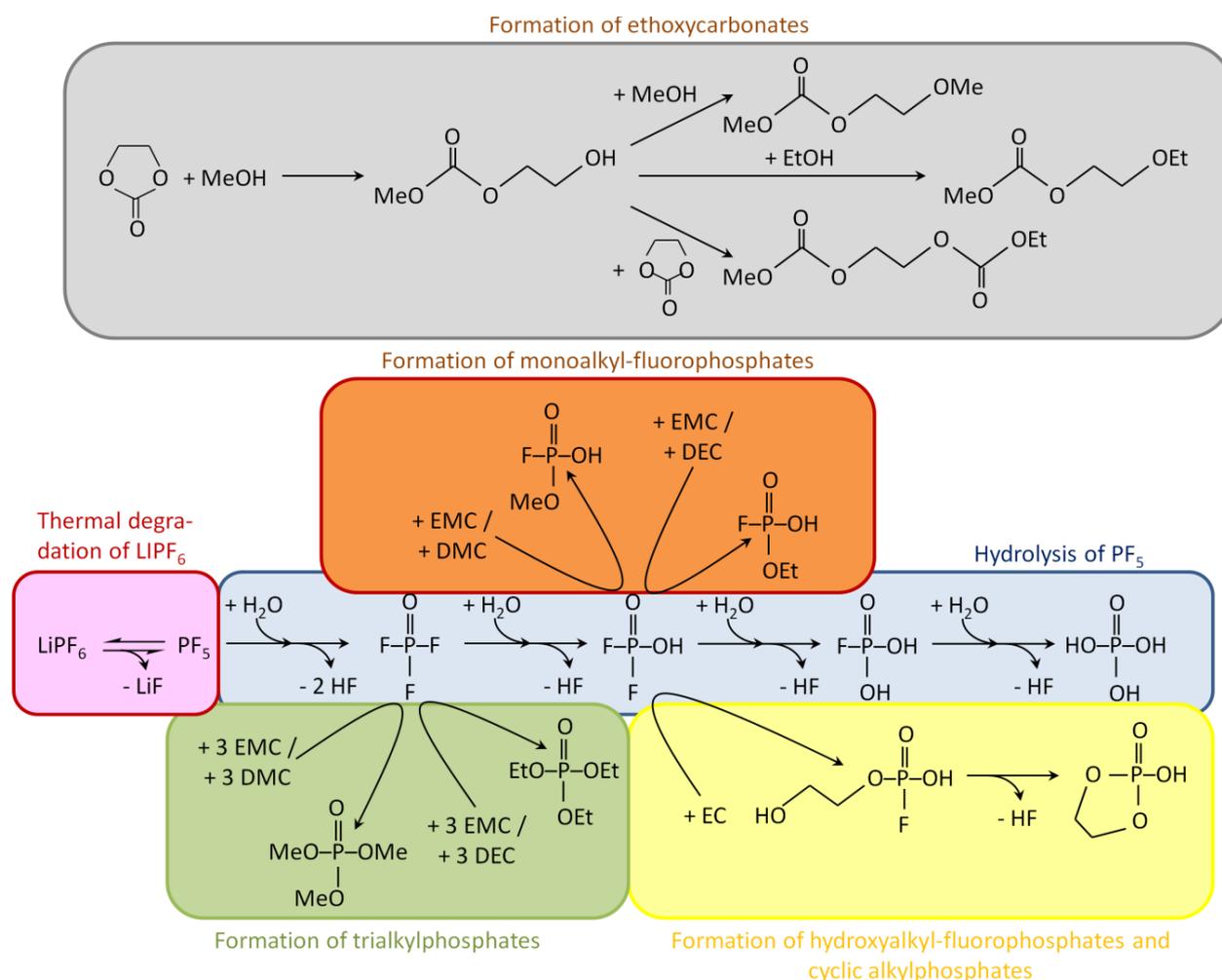
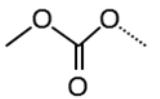
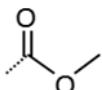
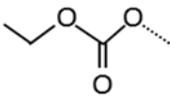
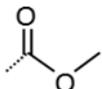
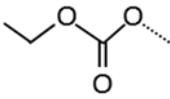
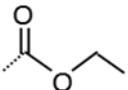
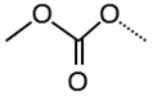
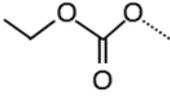
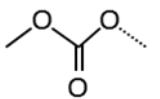
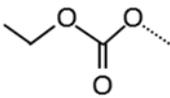


Figure 4. Reaction schemes proposed for the degradation of commercial electrolytes containing EC, EMC, DEC or DMC and LiPF₆ as conductive salt. After Grützkke *et al.* [32].

Table 4. Thermal degradation products of LP50 electrolyte identified by GC-MS with gas- and liquid chromatographic methods [9, 32].

$R^1 \left(\text{---} \left[\text{---} \text{CH}_2 \text{---} \text{CH}_2 \text{---} \text{O} \right]_n \text{---} R^2 \right)$	R^1	R^2	n	Sum Formula	Molecular mass
Series 1			1	C ₆ H ₁₀ O ₆	178.047740
			2	C ₈ H ₁₄ O ₇	222.073955
Series 2			1	C ₇ H ₁₂ O ₆	192.063390
			2	C ₉ H ₁₆ O ₇	236.089605
Series 3			1	C ₈ H ₁₄ O ₆	206.079040
			2	C ₁₀ H ₁₈ O ₇	250.105255
Series 4		CH ₃	1	C ₅ H ₁₀ O ₄	134.057910
			2	C ₇ H ₁₄ O ₅	178.084125
Series 5		CH ₃	1	C ₆ H ₁₂ O ₄	148.073560
			2	C ₈ H ₁₆ O ₅	192.099775
Series 6	CH ₃ O	CH ₃	1	C ₄ H ₁₀ O ₂	90.068080
			2	C ₆ H ₁₄ O ₃	134.094295
Series 7		H	1	C ₄ H ₈ O ₄	120.042260
			2	C ₆ H ₁₂ O ₅	164.068475
Series 8		H	1	C ₅ H ₁₀ O ₄	134.057910
			2	C ₇ H ₁₄ O ₅	178.084125
Series 9	HO	CH ₃	1	C ₃ H ₈ O ₂	76.052430
			2	C ₅ H ₁₂ O ₃	120.078645
Series 10	HO	H	1	C ₂ H ₆ O ₂	62.036780
			2	C ₄ H ₁₀ O ₃	106.062995

It was already observed earlier that the degradation of the LIB electrolyte is dependent on the water content and also the container material [34]. The authors speculated that in glass containers the reaction of hydrofluoric acid with the silicon oxide from the glass leads to the formation of SiF₄ and H₂O which itself can induce further electrolyte decomposition.

Very similar results were obtained when the electrolyte and gaseous emissions from commercial cells were investigated: Looking at the volatile emissions, Dahn and co-workers remarked that the emission of gaseous components takes place in two distinguishable steps, namely at 3.7 and 4.3 V charging voltage [35], the first step being attributable to reactions mainly at the cathode, while

the second step was attributed to the anodic reaction, distinguished by a stronger formation of CO₂ and a decreased production of the low hydrocarbons (C₂H₆, C₂H₄ and C₃H₈) compared to the first gas evolution step.

More recently, three further hyphenated GC techniques were used to identify volatile emissions from degraded LIB electrolytes. In the first study, Laruelle and co-workers used gas chromatography with Fourier-transform infrared spectrometric detection (GC/FTIR) to complement GC/MS analyses, thereby confirming the presence of degradation products such as acetaldehyde whose chromatographic peak coincides with that of ethylene oxide [36]. Schug and co-workers [37] used GC with vacuum UV detection (GC-VUV) for the

determination of degradation products in the off-gassing from three different lithium-ion battery samples. Gas samples collected from LiCoO₂, LiMn_{0.33}Ni_{0.33}Co_{0.33}O₂, and LiMnNi 18,650 cells (LCO, NMC, and MN cells, respectively) showed similar qualitative and somewhat diverging quantitative patterns with the confirmation of the production of acetaldehyde and traces of propionaldehyde. Kanakaki *et al.* [30] have used gas chromatography with a dielectric barrier-discharge ionization detector (GC-BID) for the analysis of volatile degradation products. The particular advantage of this plasma ionization detector is that it responds to virtually all compounds, including the permanent gases (N₂, O₂) and highly or fully oxidized compounds (as CO, CO₂ and HCHO) which give a very poor or no FID response at all. While most of the studies so far have been of qualitative nature, aiming to identify the volatile degradation products from the decomposition of the electrolyte under thermal aging or overcharge conditions, few authors only reported quantitative results. Among these are Ohsaki and co-workers who report the formation of volatile compounds from the degradation of an EC/EMC electrolyte in a 633,048 type prismatic cell [38]. Dahn *et al.* [35] have investigated initial gas formation in Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O₂ (NMC442) pouch cells with three different electrolytes: 3:7 ethylene carbonate : ethyl methyl carbonate (EC:EMC) with 1 M LiPF₆ as the control, control + 2% prop-1-ene-1,3-sulfone (PES) and control + 2% vinylene carbonate (VC). *In situ* volume measurements revealed three main features of gas evolution, namely an initial gas step, gas absorption, and a second gas step at higher voltage. In addition to identification by GC/MS, the authors also determined the gas volumes formed. These results compare well with the findings of Kumai and co-workers [27] who have determined quantitatively the gases evolving during charging cycles of Li_xC₆/Li_{1-x}CoO₂ cells using electrolytes such as 1 M LiPF₆ in propylene carbonate (PC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC). A further study also reported quantitative results for the gases liberated in the thermal abuse of high-power lithium cells [39]. The commercial cell used in this study (a high-power 18,650 cell) contained an electrolyte consisting of ethylene carbonate/ethyl methyl carbonate (EC:EMC, 3:7 by wt.) solvent with 1.2M LiPF₆ as conducting salt. Most interesting was the observation that the profile of volatile emissions (mainly H₂, CO, CO₂ and C1-C3 hydrocarbons) from the cell for which thermal runaway was induced by heating to a temperature of >84°C

differed, depending on whether the cell housing was punctuated to vent the evolved gases or not.

Liquid chromatographic analysis

Somewhat less frequent than GC methods, liquid chromatography has been used for the analysis of degradation products. LC separation addresses the less volatile degradation products, including the analysis of the conducting salt and its degradation/reaction products with the organic solvents. For the latter task, ion chromatography is preferably used, as ions show little retention on reversed phase stationary columns. The probably first use of chromatographic techniques to identify LIB degradation products was reported by Yoshida *et al.* [40] who used hyphenated HPLC-FTIR to elucidate the degradation mechanism of electrolytes in a lithium-ion cell with LiCoO₂ and graphite electrodes during initial charging. The solvents used in this work were EC, DMC, EMC and DEC with LiPF₆ as conducting salt. In addition to transesterification products, diethyleneglycol dicarbonate methyl- and ethyl esters were further products identified in the electrolyte. In their seminal work [36], Laruelle and co-workers used electrospray-high resolution-MS (ESI-HR-MS) to elucidate the structure of degradation products. They concluded that at least six series of degradation products of varying ethoxylate chain length and different end groups (H-, methyl- and methyl carbonate-terminated) are formed. Subsequent work from the group of Nowak used ion chromatography to detect monofluorophosphate and organic substituted phosphates in the aged commercial LP50 electrolyte in LMNO/Li half cells after performing about 50 electrochemical cycles [41]. In a follow-up work of the same group [42], a larger number of organic phosphates (including organic monofluorophosphates) was detected by IC-ES-MS in the electrolyte under thermal ageing conditions. The study was slightly extended to report the influence of the electrolyte volume and the temperature on the formation of organophosphates, and the influence of the separator materials and the storage container materials on the thermal ageing, as well as to provide quantitative results on the degradation products [31]. Earlier obtained results were repeatedly reported by the group in other papers using ESI-MS/MS and ESI-time of flight (TOF)-MS [43, 44] as well as HPLC-DAD and HPLC with ESI- and APCI-MS detection (Figure 5) [45]. Osaka and co-workers [46] used HPLC-Q-TOF-MS which would allow elucidation of the deterioration mechanism. The analysis results showed that the degradation products contain multiple components, including polymers of

carbonate compounds and – detected for the first time –also (polymeric) phosphate esters, which are formed via electrochemical and chemical reactions, resulting in remarkably reduced capacity. Altogether, this demonstrates the versatility that HPLC has – particularly with MS detection – as a complementary analytical tool to GC/MS, providing information on the polar, ionic and oligomeric compounds that are not amenable to GC analysis.

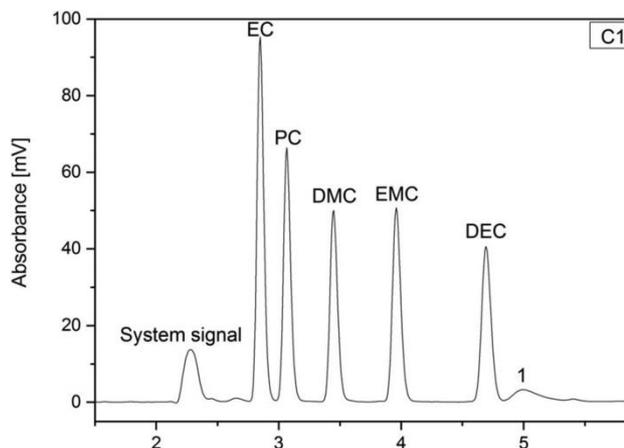


Figure 5. Separation of the electrolyte components EC, PC, DMC, EMC and DEC by HPLC-UV/VIS using a C18 column (Thermo Fisher Scientific Acclaim 120 C18, 250 mm x 4.6 mm ID, 5 μ m particle size). Reproduced from [44] with permission.

SUMMARY AND CONCLUSION

Chromatographic methods have been shown to be valuable tools to gain insight into the thermal, electrochemical, hydrolytic and oxidative processes leading to the formation of degradation products. GC/MS is the method of choice to identify and quantify volatile degradation products ranging from permanent gases (e.g. H₂, CO, CO₂ and the low hydrocarbons) to higher and oxygenated hydrocarbons (linear and cyclic ethers, esters and ethylene glycol derivatives). The amount and relative fractions in the evolved gas are indicative for the dominant degradation reaction. The polar, ionic and polymeric degradation products are more advantageously detected by HPLC, particularly with MS detection. Since the soft ionization mechanisms in LC/MS with single-quadrupole MS detection provide only simple mass spectra with hardly any structural information, more sophisticated mass spectrometers, such as MS/MS, TOF-MS or Q-TOF-MS instruments are required to increase the structural information by providing either high mass accuracy (and thus the ability to calculate elemental formulae), or fragmentation. In this way both the degradation products of the conducting salt (most often LiPF₆), as well as its numerous reaction products with the organic solvent of the electrolyte

can be identified. The identification of degradation products of LIB electrolytes is an important step in understanding the degradation mechanisms of LIB electrolytes, and in being able to improve battery safety and performance.

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ИЗЯСНЯВАНЕ ПРОЦЕСА НА РАЗПАД НА ЕЛЕКТРОЛИТА ОТ ЛИТИЕВО-ЙОННИ БАТЕРИИ ЧРЕЗ ХРОМАТОГРАФСКИ АНАЛИЗИ

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(Резюме)

Електролитът от литиево-йонните батерии се разпада както при нормални експлоатационни условия - например формиране на твърда междинна електролитна фаза, така и при екстремни условия, като висока температура, напрежение, електрически ток. Продуктите на разпад на електролита (обикновено смес от органични карбонати, като етиленкарбонат, етилметил карбонат, диметилкарбонат или диетилкарбонат с различни електропроводими соли като LiPF_6) могат да бъдат летливи или постоянни газове като H_2 , CO , CO_2 , или късоверижни въглеводороди (C1-C3), които са подходящи за определяне чрез газова хроматография GC.

Предвид многообразието на продуктите на разпад, могат да бъдат подбирани газови хроматографи с различни детектори, които да регистрират продуктите чрез пламъчно-йонизационни детектори, детектори по топлопроводност (катарометъри), мас спектрометри. Като допълнение на предложените GC анализи, могат да се приложат директни анализи на електролита, след внимателно разрязване на батерията за *post mortem* анализ.

В присъствието на електропроводимата сол LiPF_6 , както и в присъствието на вода или въздух, се образуват кондензирани или силно полярни продукти, които могат да бъдат по-лесно определени в течна фаза чрез високо ефективна течна хроматография с обърнати фази RP-HPLC, или чрез йонна хроматография IC. Това включва карбонатни олигомери (с различен брой на етоксигрупите, получени след разкъсване на етилен карбонатния пръстен) и органофосфати и монофлуорофосфати, които са продукти на реакциите на разпад и (частична) хидролиза на електропроводимата сол и нейното взаимодействие с органичния разтворител.

Хроматографските техники, особено тези с масспектрометрична детекция са незаменимо средство за охарактеризиране на широкия спектър от разпадни продукти, и за изясняването на процесите, водещи до деградация на електролита. Това формира основата за подобряване на безопасността и ефективността на литиево-йонните батерии.

Ключови думи: литиево-йонни батерии, електролит; разпадни продукти, газова хроматография, течна хроматография