

Investigation of the decomposition of organic solvent-based lithium ion battery electrolytes with liquid chromatography-mass spectrometry

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In 2015, Shimadzu introduced the lab4you student programme. This offers young scientists in Europe the opportunity to conduct their research in Shimadzu's Laboratory World in Duisburg, Germany. The scientists benefit from free lab space, unlimited instrument time and support from the product specialists. To participate in lab4you, interested and motivated students can apply at www.shimadzu.eu/lab4you.

Introduction

In the first lab4you project of Shimadzu's programme for young scientists, conventional liquid organic electrolytes from lithium ion batteries (LIBs) were investigated with liquid chromatography mass spectrometry (LC-MS).

Nowadays, LIBs are indispensable as they are used every day in many application fields. Their advantage is their low weight compared to other batteries, e.g. lead accumulators, due to their high specific energy and energy density.¹ For this reason LIBs are used mainly in portable electronic devices such as laptops, digital cameras, cell phones as well as in electromobility, for instance within electric bicycles, scooters and cars.

Figure 1 shows the functional principle of a LIB. A LIB typically contains a carbon-based anode, a lithium transition metal oxide cathode and a polyolefin-based separator that is placed between anode and cathode and soaked with the

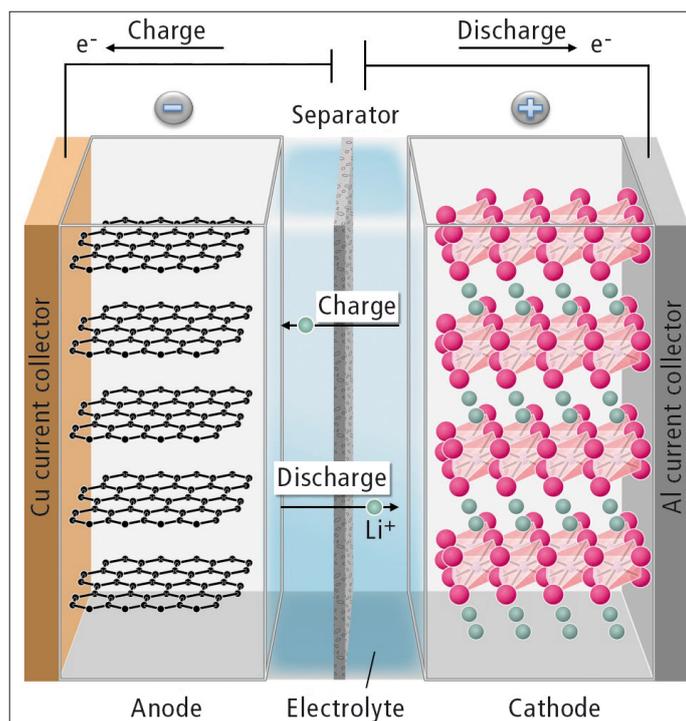


Figure 1. Schematic representation of the functional principle of a lithium ion battery.

electrolyte.^{1,2} In most cases, the electrolyte consists of an organic solvent and a lithium ion conducting salt. The solvent is usually a mixture of cyclic and linear organic carbonates, e.g. ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC). As conducting salt, 1 M lithium hexafluorophosphate (LiPF₆) is used.³

When the battery is discharged, lithium ions move through the electrolyte from the anode to the cathode. The corresponding electrons flow through an external electric circuit and usable electrical power is supplied to the connected device. The charge process is reversed, and the lithium ions are incorporated between the graphite layers of the anode.

Aging of the electrolyte

The disadvantage of LIBs is the capacity loss due to aging and the reduction of their lifetimes.^{4,5} This is due to the conducting salt which is chemically and thermally unstable. LiPF₆ is the most commonly used conducting salt in commercial LIBs today; it decomposes to LiF and PF₅. PF₅ reacts with the organic carbonates and impurities like water. Additionally, the organic carbonates are subject to transesterification reactions.^{6–8} Further, the electrolyte decomposes at the electrodes, and decomposition products are formed due to reactions at the charged anode with the electrolyte. The decomposition products build a thin layer, the solid electrolyte interphase (SEI).⁹ EC in particular supports SEI formation. All these reactions between the electrolyte and transformation reactions can lead to the formation of a variety of different aging products (for instance phosphate-based¹⁰ or carbonate-based¹¹).

To understand and counteract aging inside the electrolyte, analytical methods for identification and quantification of electrolyte components and

aging products in LIBs are essential. Mass spectrometry techniques, offering high resolution and high mass accuracy, are very beneficial by obtaining the exact masses of compounds, as well as providing structural identification including the elucidation of the fragmentation mechanisms of certain compounds. The identification of aging products facilitates the discussion of decomposition mechanisms due to the knowledge of exact reactions. Within this work, the aim was to develop a LC-MS method for identification and quantification of LIB electrolyte compounds.

Cell assembly and cell opening

For the study, self-assembled LIBs were investigated. The cells contained one anode and one cathode (each 3 × 3 cm). The active material from the cathode was lithium nickel manganese cobalt oxide, and from the anode, mesophase carbon microbeads. The electrodes with a polypropylene fleece separator between were arranged in a linear, layered setup. The case of the cell is made of a flexible aluminium laminated multilayer foil. This cell geometry is called the pouch-bag cell. The separator was soaked with 375 µL electrolyte (1/1 wt/wt EMC/EC and 1 M LiPF₆). Cell assembly took place in a dry room with a dew point around –65°C in order to protect the cells from moisture. The prepared cells were cycled (discharged and charged) 100 times in a climatic test chamber set to 20°C and 60°C, respectively.

After the cycling procedure, the electrolyte needed to be extracted from the pouch cells. The pouch cells were therefore opened in a dryroom. The separator was removed from the cell and transferred to a 1.5 mL Eppendorf Safe Lock Tube which was centrifuged for 15 min at 8500 rpm. With this extraction method, pure electrolyte could be removed for further LC-MS measurements.

Instrumentation

For qualitative analysis of electrolyte compounds, a hybrid ion-trap time-of-flight mass spectrometer (IT-TOF-MS) was used, and for quantitative analysis, a triple-quadrupole LC-MS/MS (LCMS-8040, Shimadzu, Kyoto, Japan). Both mass spectrometers were hyphenated to a UHPLC NexeraX2 LC-30 system (Shimadzu, Kyoto, Japan). Ionisation of the substances was performed using electrospray ionisation in the positive-ion mode.

The mobile phase consisted of water mixed with 0.1 vol% formic acid and methanol. A gradient was used with a flow rate of 0.4 mL min⁻¹; parameters used with both devices are shown in Table 1.

Results and discussion

Qualitative analysis

For structural elucidation, the electrolytes were first measured in the automatic mode to obtain retention times and *m/z* ratios of the chosen electrolyte compounds as well as first fragmentation information. Thereafter, structural elucidation was performed in the manual mode. The collision-induced dissociation (CID) energy and collision gas were adjusted for each MS stage of every compound until roughly 10% of the precursor ion intensity was observed after CID.

As an example for the structural elucidation of many aging products via MS^{*n*}, compound 7 from Table 2 is shown in Figure 2. The scheme includes the fragmentation pattern together with the CID energy for every MS^{*n*} stage and the corresponding mass spectra. The ionised molecules are mostly [M+H]⁺.

In MS¹, the signal of the ammonium adduct of compound 7 with *m/z* 386.1287 has the highest intensity. In MS², *m/z* 369.1030 is detected after an ammonia loss. In MS³, *m/z* 369.1030 is further fragmented into *m/z* 281.0907 and *m/z* 117.0523 after being trapped

Table 1. Parameters of LC-IT-TOF-MS and LC-MS/MS.

	Probe voltage (V)	Desolvation line (°C)	Heat block (°C)	Nebulising gas (Lmin ⁻¹)	Drying gas
LC-MS/MS	5	230	200	3	15Lmin ⁻¹
LC-MS-IT-TOF	4.5	200	230	1.5	100kPa

Table 2. Aging products identified using LC-IT-TOF-MS during the lab4you programme.

Compound	t_R (min)	m/z meas.	Ion	Formula	Structure
1	6.2	196.0825	$[M+NH_4]^+$	$C_6H_{10}O_6$	
2	10.3	210.0977	$[M+NH_4]^+$	$C_7H_{12}O_6$	
4	14.3	224.1131	$[M+NH_4]^+$	$C_8H_{14}O_6$	
3	11.2	267.0722	$[M+H]^+$	$C_9H_{14}O_9$	
5	14.5	298.1140	$[M+NH_4]^+$	$C_{10}H_{16}O_9$	
8	17.6	312.1303	$[M+NH_4]^+$	$C_{11}H_{18}O_9$	
6	14.5	377.0695	$[M+Na]^+$	$C_{12}H_{18}O_{12}$	
7	17.3	386.1297	$[M+NH_4]^+$	$C_{13}H_{20}O_{12}$	
9	19.7	400.1465	$[M+NH_4]^+$	$C_{14}H_{22}O_{12}$	

with the IT. The last step is the fragmentation of m/z 281.0907 in MS^4 leading to m/z 103.0408.

With this approach, numerous aging products from this substance group were identified. Their elucidated structures are shown in Table 2. Detection of the oligocarbonates with longer chains is possible with LC-IT-TOF-MS due to its sensitivity. Additional information on the m/z ratio and the accurate masses as well as the formulae are depicted here. These aging products were also separated on a C_{18} -amide column.

The electrochemical data showed that the specific capacity of the cell cycled at 20°C was quite stable with slight fading, whereas the data from the cells cycled at 60°C was much worse. Specific capacity showed strong fading during the cycling

procedure. In this study, many different electrolyte systems and aging procedures were investigated. Here, electrochemical aging of one electrolyte system at 20°C and 60°C is chosen as an example.

The investigation focused on oligocarbonate aging products as shown in Table 2 and diethylfluorophosphate (DEFP). The cell aged at 20°C showed the generation of compounds 1, 2, 3, 4, 5, 7, 8 and 9, and DEC as aging products. In the cells that were electrochemically cycled at elevated temperatures (60°C), the same aging products were detected as well as the fluorophosphate aging product DEFP. DEFP is supposed to be toxic due to structural similarity with the nerve agent sarin.^{12,13} Investigation of these particular aging products is therefore essential in terms of safety of LIBs.

Quantitative analyses

For quantification purposes, the multiple reaction monitoring mode was used for the highest sensitivity. Only commercially available electrolyte compounds could be investigated. Several substances, main components as well as aging products, were quantified; for example EC, DMC, EMC, DEC, compound 1 and 4. Separation of these compounds was achieved with a C_{18} pentafluorophenyl phase (2.1 × 100 mm; particle size 2 μm).

Interestingly, a significant decrease of both compounds 1 and 4 in the cell cycled at 60°C was observed compared to the cell cycled at 20°C. Furthermore, in both cells, compound 4 was generated in higher amount compared to compound 1. Some of the oligocarbonates were also detected on the surface of the SEI in the

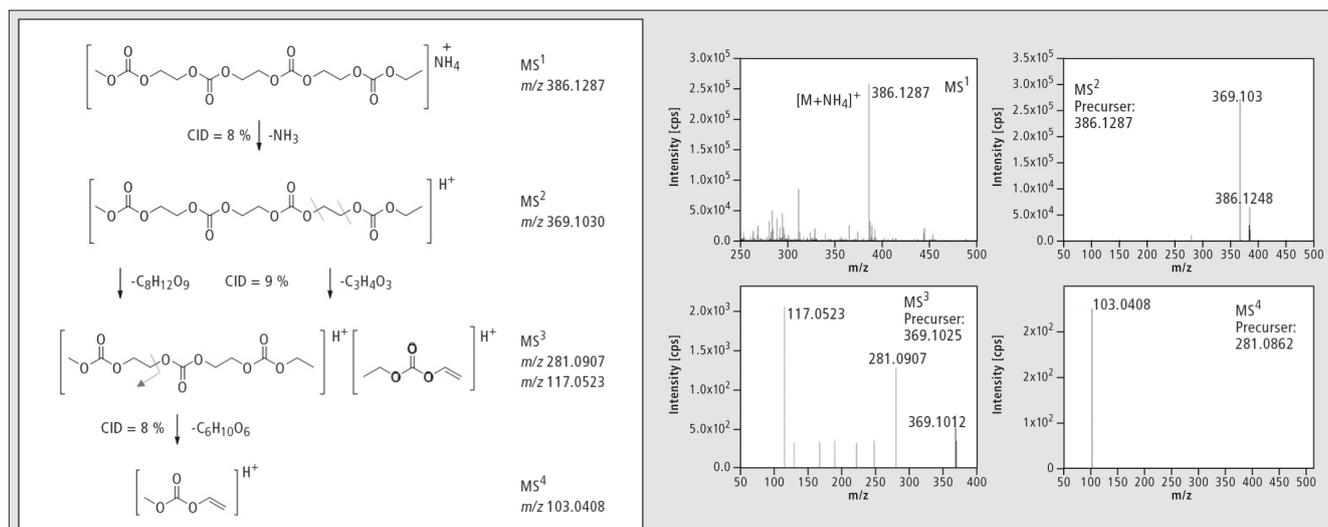


Figure 2. Fragmentation pattern of compound 7 with corresponding mass spectra.

work of Tochihara *et al.*¹⁴ It may be considered that carbonate aging products are in a certain equilibrium on the surface of the electrodes with the electrolyte.

Tochihara also found that the amount decreased in cells cycled at higher temperatures. It can be concluded here that equilibrium between electrodes and electrolyte shifted with higher temperatures. Performance of the cell was worse at higher temperatures. Additionally, in this study, the amount of DEC was also higher in the cell cycled at 60°C.

Conclusion

This study presents the development of two powerful LC-MS methods (qualitative and quantitative) to conduct a comprehensive structural LIB electrolyte analysis. Method development for the identification, separation and quantification of electrolyte components as well as their aging products was successful.

For both methods, the organic carbonates as main components of electrolytes as well as phosphate- and carbonate-based aging products were baseline separated. Within the qualitative method, structural elucidation of numerous aging products was performed with MSⁿ measurements using LC-IT-TOF-MS. Different groups of aging products including carbonate and fluorophosphate aging products were identified.

Electrochemical aging of LIBs at 20°C showed the generation of several oligo-carbonate aging products with different

chain lengths. Electrochemical aging at 60°C showed less formation of carbonate aging products but the additional generation of DEFP. In general, this method can contribute to understanding of LIB electrolyte aging.

Acknowledgement

The authors thank the lab4you Team from Shimadzu in Duisburg, Germany, for their support and the possibility to work with the Shimadzu Laboratory World devices.

References

1. M. Winter and J.O. Besenhard, "Wiederaufladbare Batterien", *Chem. Unserer Zeit* **33(6)**, 320–332 (1999). doi: <http://dx.doi.org/10.1002/ciuz.19990330603>
2. K.M. Abraham, "Directions in secondary lithium battery research and development", *Electrochim. Acta* **38**, 1233–1248 (1993). doi: [http://dx.doi.org/10.1016/0013-4686\(93\)80054-4](http://dx.doi.org/10.1016/0013-4686(93)80054-4)
3. M. Wakihara and O. Yamamoto, *Lithium Ion Batteries: Fundamentals and Performance*, Wiley-VCH, Weinheim (1998). doi: <http://dx.doi.org/10.1002/9783527612000>
4. J. Vetter *et al.*, "Ageing mechanisms in lithium-ion batteries", *J. Power Sources* **147**, 269–281 (2005). doi: <http://dx.doi.org/10.1016/j.jpowsour.2005.01.006>
5. C.K. Dyer *et al.*, *Encyclopedia of Electrochemical Power Sources*. Elsevier Science (2013).
6. L. Terborg *et al.*, "Development of gas chromatographic methods for the analyses of organic carbonate-based electrolytes", *J. Power Sources* **245**, 836–840 (2014). doi: <http://dx.doi.org/10.1016/j.jpowsour.2013.07.030>
7. L. Terborg *et al.*, "Ion chromatographic determination of hydrolysis products of hexafluorophosphate salts in aqueous solution",

Anal. Chim. Acta **714**, 121–126 (2012). doi: <http://dx.doi.org/10.1016/j.aca.2011.11.056>

8. S. Wilken *et al.*, "Initial stages of thermal decomposition of LiPF₆-based lithium ion battery electrolytes by detailed Raman and NMR spectroscopy", *RSC Advances* **3**, 16359–16364 (2013). doi: <http://dx.doi.org/10.1039/c3ra42611d>
9. M. Winter, "The solid electrolyte interphase—the most important and the least understood solid electrolyte in rechargeable Li batteries", in *Z. Physikal. Chem.* **223**, 1395–1406 (2009). doi: <http://dx.doi.org/10.1524/zpch.2009.6086>
10. V. Kraft *et al.*, "Two-dimensional ion chromatography for the separation of ionic organophosphates generated in thermally decomposed lithium hexafluorophosphate-based lithium ion battery electrolytes", *J. Chromatogr. A* **1409**, 201–209 (2015). doi: <http://dx.doi.org/10.1016/j.chroma.2015.07.054>
11. C. Schultz *et al.*, "Separation and quantification of organic electrolyte components in lithium-ion batteries via a developed HPLC method", *J. Electrochem. Soc.* **162**, A629–A634 (2015). doi: <http://dx.doi.org/10.1149/2.0401504jes>
12. V. Kraft *et al.*, "Study of decomposition products by gas chromatography-mass spectrometry and ion chromatography-electrospray ionization-mass spectrometry in thermally decomposed lithium hexafluorophosphate-based lithium ion battery electrolytes", *RSC Advances* **5**, 80150–80157 (2015). doi: <http://dx.doi.org/10.1039/C5RA16679A>
13. R. Gotor *et al.*, "A molecular probe for the highly selective chromogenic detection of DFP, a mimic of sarin and soman nerve agents", *Chem.—Eur. J.* **17**, 11994–11997 (2011). doi: <http://dx.doi.org/10.1002/chem.201102241>
14. M. Tochihara *et al.*, "Liquid chromatography-quadrupole time of flight mass spectrometry analysis of products in degraded lithium-ion batteries", *J. Electrochem. Soc.* **162**, A2008–A2015 (2015). doi: <http://dx.doi.org/10.1149/2.0231510jes>