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ORIGINAL PAPER

Analysis of electrolyte degradation products in cylindrical automotive lithium-ion cells during thermal aging

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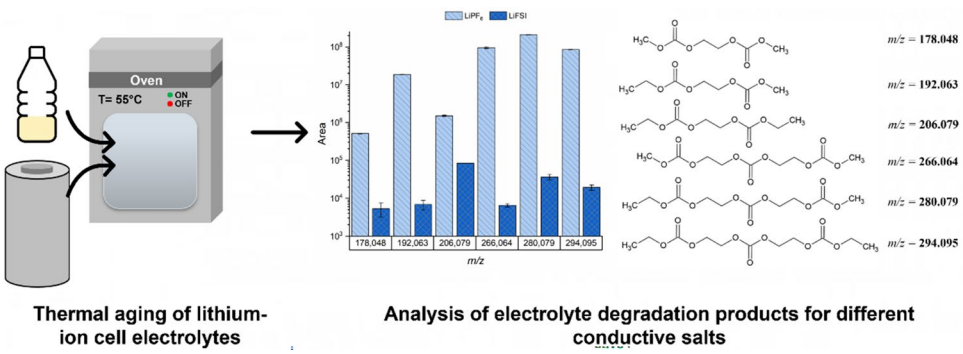
Abstract

The impact of battery electric vehicles (BEVs) using lithium-ion cells (LICs) as energy storage systems is increasing and topics as cell performance and lifetime of the cell are becoming more important. Understanding the thermal aging process of LICs is a key factor for the automotive industry aiming for the development of long-lasting, high-performance cells. The electrolyte composition can be a limiting factor for the lifetime of the cell and highly affects the performance of LICs. In this research the thermal aging process of LIC electrolytes at increased temperatures (55 °C) is investigated. For the first time the effect of thermal aging on LIC electrolytes is investigated by means of specific conductivity measurements combined with the analysis of formed degradation products. It is found that the amount of conductive salt significantly affects the conductivity decrease during thermal aging of the electrolyte. It is revealed that the selected conductive salt has a significant impact on the quantity of formed oligocarbonates. Understanding the degradation reaction of $LiPF_6$ and lithium bis(fluorosulfonyl)-imide (LiFSI) as two of the most used conductive salts is a key factor for the development of high performance electrolytes. Finally, large format cylindrical LICs containing $LiPF_6$ or LiFSI electrolytes were investigated for their electrolyte degradation products after the thermal aging process. Transferring the knowledge toward large format LICs can support industrial project to develop high performance cells.

Graphical abstract



Keywords Extraction · Green chemistry · High pressure liquid chromatography · Mass spectrometry · Material science

Introduction

The transportation sector has a significant impact on the European CO_2 emissions, and its electrification is considered as the key factor to become the first climate neutral continent [1]. Lithium-ion cells (LICs) which are used for energy storage in electric vehicles play an essential role to reach these

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goals [2, 3]. Charging and discharging of the LIC can lead toward degradation reactions in the electrolyte which are effecting the cell lifetime [4].

Electrolytes in commercial LICs consist of a conductive salt dissolved in a mixture of organic carbonates (Fig. 1) and electrolyte additives [5]. Lithium hexafluorophosphate ($LiPF_6$) is the most used conductive salt with high specific conductivity and a high dissociation constant [6]. A drawback to this conductive salt is the formation of degradation products which occur at increased temperatures (60 °C). The thermal instability of $LiPF_6$ leads toward the decomposition of the conductive salt to the highly reactive compound phosphorous pentaflouride (PF_5) which degrades to numerous further products [7, 8]. A second and often used lithium salt is lithium bis(fluorosulfonyl)imide (LiFSI). LiFSI has some advantages compared to $LiPF_6$; it is more stable against moisture, has a higher conductivity resulting in a higher cell performance. LiFSI decomposes at higher temperatures which makes the electrolyte more resistant toward increased temperatures [9]. A variety of inorganic and organic degradation products have been reported in literature on electrolytes containing $LiPF_6$ resulting in a decrease of the cell performance [10]. Thermal aging of the conductive salt leads toward the formation of hydroflouric acid (HF), alkylflourides, and organic phosphates [11]. Degradation reactions between the conductive salt and the solvent result in a variety of degradation products e.g., organofluorophosphates and oligocarbonates [12, 13].

LICs are subject to a variation of electrolyte degradation reactions affecting their cell lifetime and performance [14]. The electrolyte analysis of automotive cylindrical cells includes some challenges due to the low amount of excess electrolyte. For a quantitative electrolyte analysis, a representative sample has to be extracted from the cell materials. Therefore, the tightly wound cell materials are rewound in a specially designed extraction chamber, to increase the contact between the extraction solvent and the electrolyte [15].

The specific conductivity indicates changes in the electrolyte composition and is a measure for the entire electrolyte, which is afterward supported with further analysis methods. Many electrolytes with a variety of conductive salts and solvents have been studied in literature regarding their specific conductivity [16]. Dudley et al. [17] investigated a variety of conductive salts and Landesfeind et al. [18] studied the electrolytes at different temperatures using a two-electrode system. The analyses performed in literature have been conducted before the electrolyte was filled into a LIC. The effect of the electrolyte aging on the specific conductivity has not been studied before. It is known that the specific conductivity is related to the concentrations of the lithium salts and their decomposition products, ion chromatography-conductivity detection-mass spectrometry (IC-CD-MS) and high performance liquid chromatography-mass spectrometry (HPLC–MS) are performed to investigate the formed degradation products [19, 20].

In this study fundamental investigations of how thermal aging changes the electrolyte composition are performed and what effect these degradation reactions have on the specific conductivity of the electrolyte. In addition, the changes of electrolyte components are studied by HPLC–MS to understand the effect of the conductive salt on the aging process. Furthermore, the electrolyte degradation products are investigated in large format cylindrical automotive LICs. The LICs used in this study consist of a nickel manganese cobalt (NMC) cathode, combined with a graphite anode and a electrolyte containing 1 mol dm^{-3} $LiPF_6$ or 1 mol dm^{-3} LiFSI in EC/EMC.

Results and discussion

Specific conductivity during electrolyte storing at elevated temperatures

Electrolytes in lithium-ion cells (LICs) in general consist of a conductive salt as lithium hexafluorophosphate ($LiPF_6$) or lithium bis(fluorosulfonyl)imide (LiFSI) dissolved in organic solvents (Fig. 1). The amount of conductive salt highly affects the specific conductivity of the electrolyte and therefore the charging and discharging behavior of the cell [18]. The effect of increased temperatures on the specific conductivity of electrolytes with various

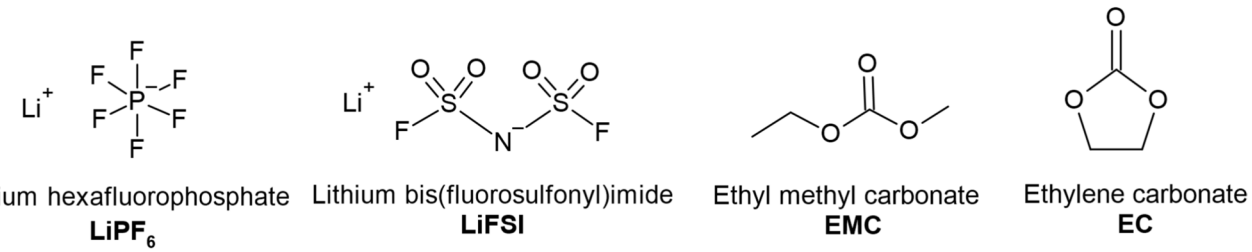

Fig. 1 Chemical structures of the electrolyte components. The two conductive salts, lithium hexafluorophosphate ($LiPF_6$) lithium bis(fluorosulfonyl)imide (LiFSI), and the carbonate solvents ethyl methyl carbonate (EMC) and ethylene carbonate (EC)

conductive salt concentrations were investigated and are displayed in Fig. 2. Therefore, the electrolytes were stored in pouch bags inside the drying oven at 55 °C for up to 42 days. For verification of the conductivity results the samples were analyzed three times and the results, including the standard deviation are listed in Tables S1–S10 of the supplementary information.

Electrolytes with the conductive salt $LiPF_6$ in EC/EMC (1:1) (Fig. 2 left) showed increasing specific conductivity up to a conductive salt concentration of 1.1 mol dm^{-3} with a maximum conductivity of 9.1 mS cm^{-1} at 25 °C and a decreasing conductivity for higher conductive salt concentrations, as reported in literature [6, 18]. At a conductive salt concentration of 1.1 mol dm^{-3} $LiPF_6$ the highest number of free ions is reached, resulting in the highest specific conductivity. By increasing the conductive salt concentration further ion pairs are formed, decreasing the ion mobility and therefore the specific conductivity of the electrolyte [21]. Storing the electrolyte at increased temperatures lead toward changes in the electrolyte composition, indicated by the reduction of the specific conductivity. In the investigated concentration range, it can be observed that low concentrations of conductive salt lead towards less conductivity loss during thermal aging. It can be concluded that the $LiPF_6$ concentration highly affects the thermal stability of the electrolyte during the aging at increased temperatures. For the identification of the formed degradation products further analysis will be performed in the following chapters.

Electrolytes based on LiFSI in EC/EMC (1:1) (Fig. 2 right) generally show higher conductivities compared to electrolytes containing $LiPF_6$ [17]. For electrolytes containing LiFSI the maximum specific conductivity of 9.7 mS cm^{-1} is achieved at a concentration of 1.1 mol dm^{-3} [17]. Electrolytes containing 0.6 mol dm^{-3} LiFSI have a low conductivity decrease of less than 0.2 mS cm^{-1}. Comparing this to conductive salt concentrations of 1.7 mol dm^{-3} a higher decrease in conductivity of 1.2 mS cm^{-1} can be observed.

By comparing the specific conductivities of the two conductive salts $LiPF_6$ and LiFSI similarities can be observed. Both conductive salts show a significant specific conductivity loss at high salt concentrations. Due to the generally higher conductivity of LiFSI the conductivity loss is less significant compared to $LiPF_6$. The degradation process of $LiPF_6$ containing electrolytes starts at lower temperatures, compared to LiFSI [5]. The significant decrease in the specific conductivity indicates that degradation reactions occur within the $LiPF_6$ containing electrolytes, changing the composition of the electrolyte.

The selected conductive salt highly affects the conductivity of the electrolyte and therefore the internal resistance of the cell. A maximum of specific conductivity leads towards a low internal resistance of the cell resulting in the optimized charging and discharging behavior for the cell. Correlations

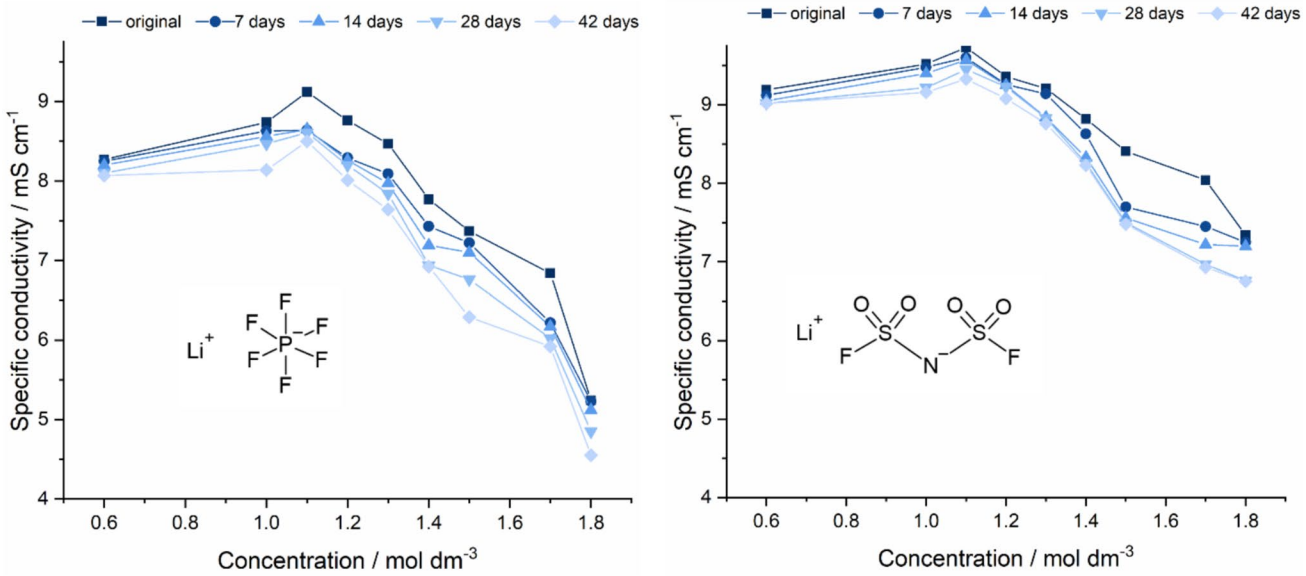

Fig. 2 Specific conductivities of the electrolytes for different concentrations after storage at 55 °C for 0, 7, 14, 28, and 42 days in sealed pouch bags. Specific conductivity measurements were performed at 25 °C in a microcell with a platinum beaker and a glassy carbon electrode. Each measurement was performed three times, the values and deviations are listed in Table S1–S10 in the supplementary information. Left: Electrolytes containing the conductive salt $LiPF_6$ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:1). Right: Electrolytes containing the conductive salt LiFSI in EC and EMC (1:1)

between the conductive salt concentration and the degradation process of the electrolyte at elevated temperatures could be observed. To investigate the origin of the conductivity decrease at high conductive salt concentrations further analysis have to be performed in the following chapters.

The effect of thermal aging on the conductive salt concentration

In the next step, the impact of the thermal aging process on the conductive salt concentration is investigated. To analyze changes in the conductive salts during the aging period of 42 days (Fig. 3) two replicates of each electrolyte were analyzed by means of IC-CD-MS.

The conductive salt quantification of $LiPF_6$ electrolytes (Fig. 3 left) shows that the aging process at 55 °C over the period of 42 days has no significant impact on the conductive salt concentration of the entire electrolyte. Degradation products such as difluorophosphate ($PO_2F_2^-$), dimethylphosphate ($PO_4C_2H_6^-$), and methyl fluorophosphate ($PO_3FCH_3^-$) identified in previous studies could be detected in the aged electrolytes containing $LiPF_6$ [13, 20]. It can be concluded that the concentration range of the degradation products is at least an order of magnitude lower than the amount of conductive salt used in the electrolyte. The specific conductivity measurements (Fig. 2) clearly show a decrease in conductivity during the aging period, outlining the high impact of the degradation products on the electrolyte performance despite their low concentration.

Quantification of LiFSI containing electrolytes (Fig. 3 right) displays, similar to $LiPF_6$, no significant changes in the conductive salt during the investigated aging period. Furthermore, it can be observed that electrolytes with low and high conductive salt concentrations show similar aging behavior during the 42 days at 55 °C.

It can be concluded that the thermal aging of the electrolyte does not significantly change the overall conductive salt concentration of the investigated electrolytes. Despite no visible decrease in the conductive salt concentration many ionic degradation products of $LiPF_6$ containing electrolytes could be observed in the thermally aged samples, which have been reported in literature [13, 20]. The analyzed degradation products occur in a different concentration range compared to the conductive salt. Even though only traces of the degradation products could be determined in the aged electrolytes the specific conductivity decreases during the aging process.

Effect of conductive salt on the formation of oligocarbonates

In this chapter the impact of the selected conductive salt for the electrolyte and its effect on the formed degradation products is investigated. The specific conductivity measurements (Fig. 2) display that degradation reactions occur at increased conductive salt concentrations, indicating that degradation products are formed.

Oligocarbonates represent one of the main electrolyte degradation products in commercially used LIC electrolytes and have been reported in previous studies [22]. Spotte-Smith et al. [23] and Shi et al. [24] proposed reaction

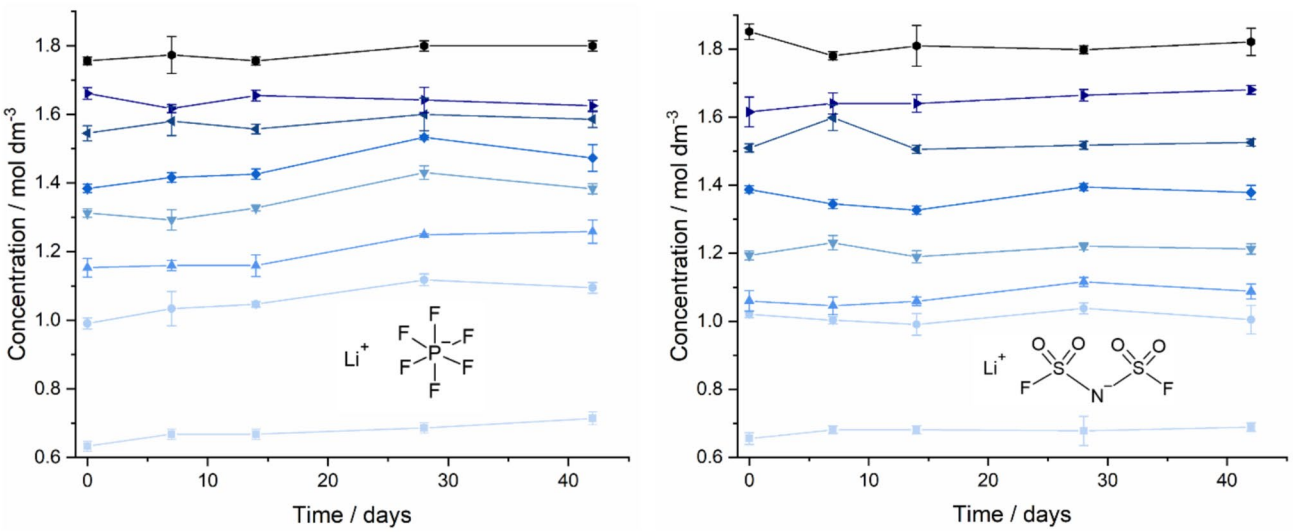

Fig. 3 IC-CD-MS electrolyte analysis for different conductive salt concentrations after storage at 55 °C for 0, 7, 14, 28, and 42 days in sealed pouch bags. For each measurement two identically prepared electrolytes were analyzed and the mean value including the deviations are displayed. Left: Electrolytes containing the conductive salt $LiPF_6$ in EC/EMC. Right: Electrolytes containing the conductive salt LiFSI in EC/EMC

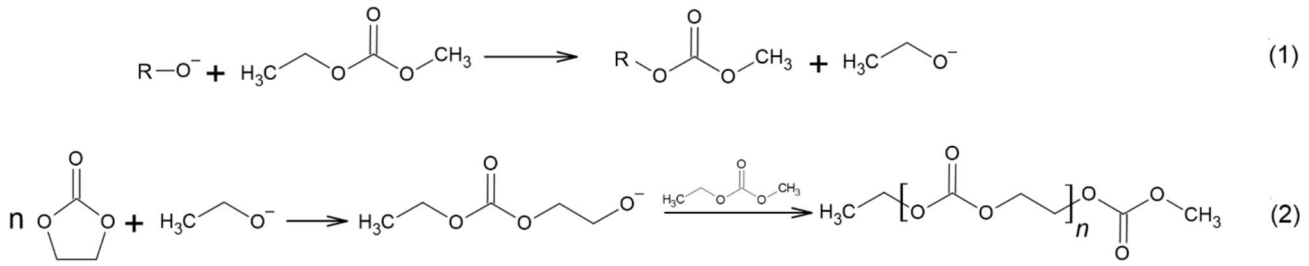

Fig. 4 Possible chemical mechanism of the oligocarbonate formation suggested by Spotte-Smith and Shi [23, 24]. During the thermal and electrochemical aging of the electrolyte the solvent ethylene carbonate (EC) and ethyl methyl carbonate (EMC) can react forming oligocarbonates

mechanisms for linear and cyclic carbonates in lithium-ion cell electrolyte to degrade towards oligocarbonates (Fig. 4).

In this reaction a nucleophilic species reacts with a linear carbonate to form an ethoxy anion (1). The ethoxy anion triggers the decomposition of the cyclic carbonates and by further reaction with a linear carbonate the oligocarbonates can be formed (2). The end groups of the linear carbonate determine the end groups of the oligocarbonate [22].

For the identification of various oligocarbonates high performance liquid chromatography-mass spectrometry (HPLC–MS) measurements of the electrolyte containing 1.5 mol dm^{-3} $LiPF_6$ or 1.5 mol dm^{-3} LiFSI were performed. Figure 5 shows the chemical structures of the investigated oligocarbonates and the correlation to the conductive salt. For most of the identified oligocarbonates no standards were commercially available. Therefore, instead of quantifying the oligocarbonates the identified analytes were compared by the detected area in the HPLC–MS. For validation of the presented results two identical sample preparations of the electrolyte were performed and analyzed.

The HPLC–MS measurements show that electrolytes containing $LiPF_6$ have higher concentrations of the oligocarbonates compared to electrolytes containing LiFSI (Fig. 5), indicating that $LiPF_6$ electrolytes accelerate the reaction of EC and EMC towards the oligocarbonates. The HPLC–MS measurements show that the choice of conductive salt has an effect on the degradation products formed at increased temperatures.

The formation of oligocarbonates is triggered by a nucleophilic species reacting with the linear carbonates of the electrolyte, as shown in the mechanism in Fig. 4. Degradation products of electrolytes containing $LiPF_6$ have been studied in literature and a frequently reported analyte is the difluorophosphoric anion [13]. The difluorophosphoric

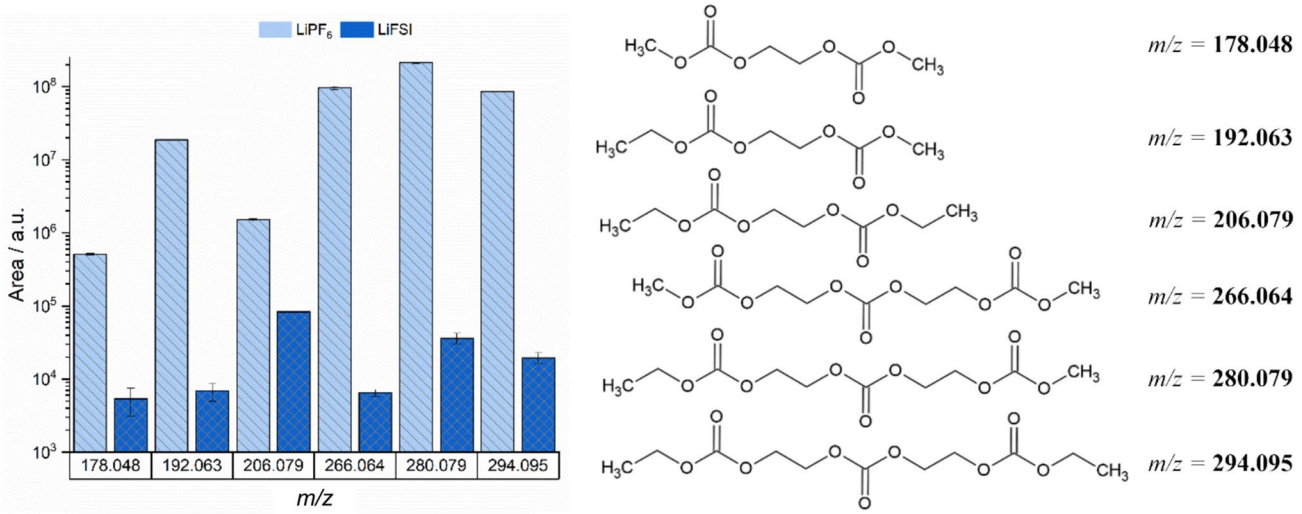

Fig. 5 left: HPLC–MS results of aged electrolyte at 55 °C for 42 days stored in pouch bags. The electrolytes contain 1.5 mol dm^{-3} $LiPF_6$ in EC/EMC (1:1) or 1.5 mol dm^{-3} LiFSI in EC/EMC (1:1). For each measurement two identically prepared electrolytes were analyzed and the mean value including the deviations are displayed. Right: Chemical structures of the identified oligocarbonates (from top to bottom) dimethyl-2,5-dioxahexane dicarboxylate ($m/z = 178.048$), ethyl methyl-2,5-dioxahexane dicarboxylate ($m/z = 192.063$), diethyl-2,5-dioxahexane dicarboxylate ($m/z = 206.079$), oligocarbonate 1 ($m/z = 266.064$), oligocarbonate 2 ($m/z = 280.079$) and oligocarbonate 3 ($m/z = 294.095$)

anion is formed during the decomposition of $LiPF_6$ [11]. The formation of difluorophosphoric anion is analyzed by means of IC-CD-MS in the thermally aged electrolytes with conductive salt concentrations from 0.6 to 1.8 mol dm^{-3} (Fig. 6).

It can be observed that traces of the difluorophosphoric anion can be identified in electrolytes containing $LiPF_6$ after the thermal aging process. In the thermally aged LiFSI electrolytes the difluorophosphoric anion could not be identified. The IC-CD-MS analysis showed that electrolytes with higher $LiPF_6$ concentrations show larger amounts of the decomposition product after the aging process compared to lower salt concentrations. The formation of the difluorophosphoric anion and other anionic degradation products in electrolytes containing $LiPF_6$ could initiate the reaction mechanism towards the oligocarbonates (Fig. 4). Anionic degradation products after the decomposition of the conductive salt could be identified by means of IC-CD-MS for electrolytes containing $LiPF_6$ and not in LiFSI electrolytes. The formation of oligocarbonates due to anionic degradation products could explain the increased concentrations of oligocarbonates for electrolytes containing $LiPF_6$.

The formation of oligocarbonates could be confirmed by HPLC–MS (Fig. 5) and these analysis results underline the specific conductivity measurements. A significant difference in the oligocarbonates formation could be determined by variation of the conductive salt. $LiPF_6$ showed higher concentrations for all investigated oligocarbonates. The formation of the degradation product difluorophosphoric anion was confirmed in electrolytes containing $LiPF_6$. Anionic decomposition products can induce the formation of oligocarbonates, resulting in increased oligocarbonates concentrations for $LiPF_6$ electrolytes.

The effect of the conductive salt concentration on the formation of oligocarbonates

The effect of the selected conductive salt on the formed oligocarbonates at elevated temperatures was shown. Electrolytes with $LiPF_6$ display an increased amount of oligocarbonates and electrolytes with a higher conductive salt concentration generally have a lower specific conductivity after the aging process at elevated temperatures. In this chapter the effect of the $LiPF_6$ concentration on the amount of formed oligocarbonates is investigated. Therefore, the electrolytes with a concentration variation of the conductive salt $LiPF_6$ from 0.6 to 1.8 mol dm^{-3} were stored in the drying oven for 42 days and analyzed my means of HPLC–MS (Fig. 7).

Figure 7 displays the formation of the oligocarbonate for several different conductive salt concentrations. It can be observed that higher salt concentrations of $LiPF_6$ show increased amounts of oligocarbonates, underlining the specific conductivity results (Fig. 2). Furthermore, the HPLC–MS results in Fig. 7 align with the IC-CD-MS results of the previous chapter. For increasing conductive salt concentrations higher amounts of anionic degradation products can be identified after the aging at elevated temperatures.

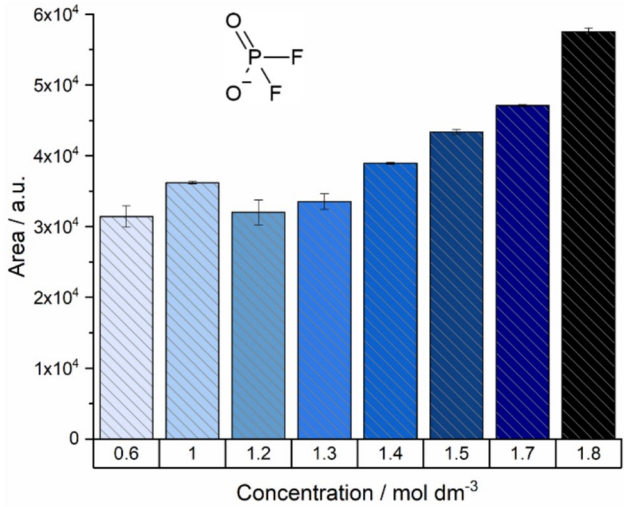

Fig. 6 IC-CD-MS studies of the formed difluorophosphoric anion $m/z = 101.07$ after the electrolyte was stored at 55 °C for 42 days in sealed pouch bags in the drying oven. The electrolytes contained different conductive salt concentrations in the range of 0.6–1.8 mol dm^{-3} $LiPF_6$. For each measurement two identically prepared electrolytes were analyzed and the mean value including the deviations are displayed

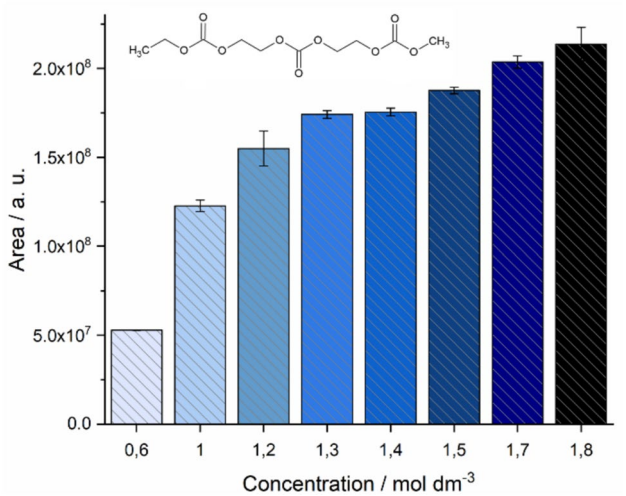

Fig. 7 HPLC–MS studies of the formed oligocarbonates $m/z = 280.079$ after the electrolyte was stored at 55 °C for 42 days in sealed pouch bags in the drying oven. The electrolytes contained different conductive salt concentrations in the range of 0.6–1.8 mol dm^{-3} $LiPF_6$. For each measurement two identically prepared electrolytes were analyzed and the mean value including the deviations are displayed

The anionic decomposition products can induce the reaction of the carbonate solvents to oligocarbonates, resulting in higher oligocarbonate concentrations at higher salt concentrations.

The specific conductivity measurements in Fig. 2 show a decreasing conductivity in the thermally aged electrolytes. The HPLC–MS results confirm an increasing amount of degradation products at elevated temperatures with high conductive salt concentrations. The HPLC–MS measurements (Fig. 7) of various conductive salt concentrations confirm that the degradation products increase with higher conductive salt concentrations. These findings support the suggested mechanism by Spotter-Smith and Shi which suggests that the reaction is accelerated by high conductive salt concentrations [23, 24].

Electrolyte degradation analysis of large format cylindrical LICs

The performance and lifetime in large format LICs are highly important topics in the automotive industry. In the following chapter the electrolytes of automotive cells are analyzed and the effects of formed degradation products after the aging at 55 °C are investigated. The cylindrical cells were filled with different electrolytes to investigate the effect of the conductive salt after the thermal aging of the cell. Cells were filled with 1 mol dm^{-3} $LiPF_6$ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:1) or 1 mol dm^{-3} LiFSI in EC/EMC (1:1). The formation protocol described in the experimental section, was applied and the cells were stored at 55 °C for 42 days at 2.8 V. For authentication of the results the electrolyte was extracted from two identical large format LICs.

A computer tomography (CT) image was conducted after the electrolyte was filled into the cell (Fig. 8 left) and the excess electrolyte was highlighted in blue by gray level analysis. A second CT image was taken after the formation and the aging process at elevated temperatures was performed (Fig. 8 right). The CT image shows no excess electrolyte in the cell, indicating that during the formation and aging process of the cell the electrolyte was soaked into the electrode materials. For the electrolyte analysis of the large format automotive LICs an electrolyte extraction from the cell materials is necessary. The cells were extracted using a previously developed method [15]. Here, the electrodes are extracted using dimethyl carbonate and rewinding them in a specially designed extraction chamber to increase the contact between the extraction solvent and the cell materials.

After the electrolyte extraction the conductive salt concentration was analyzed by means of IC-CD-MS. The electrolyte was analyzed before filling it into the cell, after the formation process and after the aging period of 42 days (Fig. 9). For the electrolytes extracted from the formed and aged cells the recovery rate for the lithium concentration of the previous developed extraction method was included [15]. The quantification of the conductive salts $LiPF_6$ and LiFSI over the investigated aging period shows similar results for

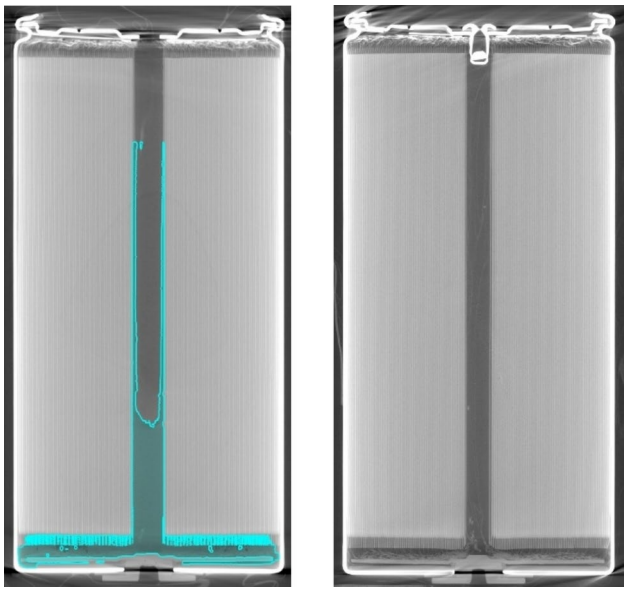

Fig. 8 Computer tomography (CT) images of large format cylindrical automotive cells. The excess electrolyte, which is not soaked into the electrodes is highlighted in light blue by gray-level analysis. Left: CT image after the electrolyte is filled into the cell. Right: CT image after the formation of the cell and the aging at 55 °C for 42 days

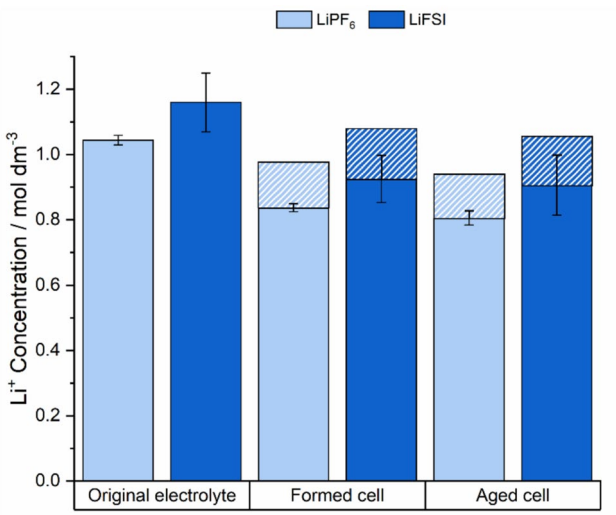

Fig. 9 IC-CD-MS measurements of the original electrolyte before the cell filling process and the extracted electrolyte form the cell after the formation and after the aging process. By extracting the electrolyte from the cylindrical cell, the recovery rate of the extraction method (shaded area) is included [15]. For each measurement two identical cells were evaluated and the mean value including the deviations are displayed

both salts. It can be observed that a conductive salt reduction occurs after the formation process which is mainly associated with the formation of the solid electrolyte interface building a protective layer on the anode material [5]. The measurements also show that no conductive salt reduction occurs over the aging period of 42 days at 55 °C, confirming the results from Fig. 3.

In a next step the extracted electrolyte samples were analyzed by means of HPLC–MS. The effect of the cell formation and the thermal aging process of the cells on the formed oligocarbonates in the electrolytes using $LiPF_6$ or LiFSI as the conductive salt (Fig. 10) was investigated.

The HPLC–MS measurements show an increased concentration of oligocarbonates in the electrolytes using $LiPF_6$ conductive salt compared to LiFSI. This confirms the results from the electrolyte storage experiments indicating that the oligocarbonates are formed intensively by electrolytes containing $LiPF_6$. It can be observed that the oligocarbonate concentration of the extracted electrolytes is significantly higher after the formation of the cells for both conductive salts compared to the thermally aged electrolytes. Indicating that the formation of the oligocarbonates can be ignited chemically and electrochemically. Electrolytes containing the conductive salt $LiPF_6$ show a higher amount of chemically induced reactions towards the selected oligocarbonates compared to electrolytes containing only LiFSI. The amount of electrochemically induced reactions during the formation process of the cell towards the oligocarbonates are similar for both conductive salts.

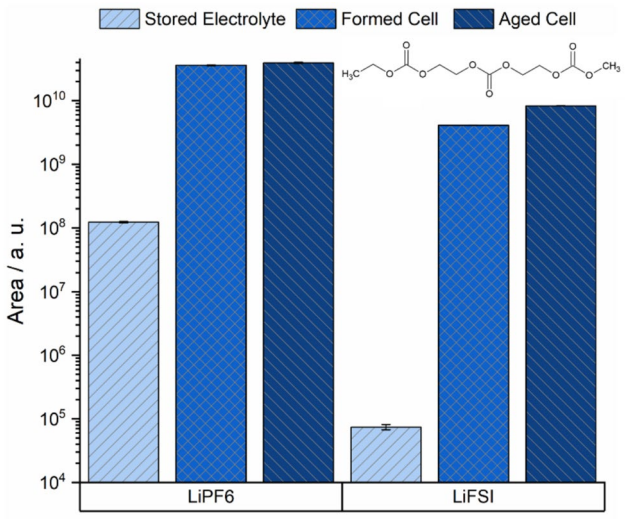

Fig. 10 HPLC–MS studies of the formed oligocarbonate $m/z = 280.079$ for electrolytes containing the conductive salt $LiPF_6$ or LiFSI. The electrolyte was analyzed after storage at 55 °C and extracted from large format cylindrical LICs after the formation and after the cell was aged for 42 days at 55 °C. For each measurement two identical cells were evaluated and the mean value including the deviations are displayed

The results achieved in the electrolyte storage experiments could be confirmed on large format cylindrical LICs. Furthermore, it could be shown that the degradation from carbonates towards oligocarbonates can be chemically and electrochemically ignited. Understanding and improving electrolyte degradation reactions in LICs towards longer lifetime and higher performance can have a significant impact on the automotive industry.

Conclusion

In this research the thermal aging of electrolytes and its effect on changes in the composition were investigated. The impact of the conductive salt variation between $LiPF_6$ and LiFSI on the formed degradation products were studied. For the first time the effect of thermal aging on LIC electrolytes was investigated by means of a combination of specific conductivity measurements, and characterization of the formation of oligocarbonates and degradation products of lithium salts. It was found that thermal aging of electrolytes with higher conductive salt concentrations showed a significant decrease in specific conductivity. The conductive salt highly affects the formation of degradation products like oligocarbonates. Electrolytes containing $LiPF_6$ led to significantly higher concentrations of the formed oligocarbonates compared to electrolytes with LiFSI. Furthermore, by increasing the $LiPF_6$ concentration in the electrolyte the amount of formed oligocarbonates was increasing.

Understanding the degradation reactions of $LiPF_6$ and LiFSI, as representatives of the most used conductive salts, paves the way to the development of new high performing electrolytes. The electrolyte affects the aging process of LICs and by improving the electrolyte performance regarding cell lifetime a significant impact on large format automotive cells can be achieved.

Experimental

The conductive salts lithium hexafluorophosphate ($LiPF_6$) and lithium bis(fluorosulfonyl)imide (LiFSI), and the solvents ethylene carbonate (EC) and ethyl methyl carbonate (EMC) were obtained in battery grade. The standard solution potassium chloride (1413 µS cm^{-1}) from Hanna Instruments (Vöhringen, Germany) was used for conductivity measurements. Deionized water was produced by Millipore Milli-Q IQ7000 from Merck (Darmstadt, Germany). Deionized water and LC–MS grade acetonitrile from Merck (Darmstadt, Germany, 99.9%) were used with formic acid (Avantor, Radnor, USA, 99.0%) for HPLC–MS measurements. The chemicals ethylene carbonate (99.0%), ethyl methyl carbonate (98.0%), diethyl carbonate (99.0%) and dimethyl

carbonate (99.0%) were obtained from Thermo Scientific (Dreieich, Germany) for HPLC–MS standard solutions. Samples were diluted in anhydrous acetonitrile (Merck, Darmstadt, Germany, 99.0%). The following chemicals were obtained from Merck (Darmstadt, Germany) for IC-CD-MS measurements: sodium carbonate (99.9%), LC grade acetone (99.0%), sulfuric acid (97.0%), and nitric acid (65.0%).

Electrolyte mixing and aging at elevated temperatures

The electrolytes were mixed in an argon-filled glovebox ($H_2O < 1$ ppm; $O_2 < 1$ ppm). The produced concentrations can be identified in the supplementary information Tables S11 and S12. Ion chromatography-conductivity detection-mass spectrometry (IC-CD-MS) was performed to verify the conductive salt concentration of the produced electrolytes. Inside the dry room with a dew point lower then −60 °C 4 cm^3 of the sample was transferred into pouch bags (10 × 2 cm) for LICs from Showa Denko with an inner polypropylene foil and vacuum sealed. The electrolytes were stored in a Thermo Scientific HeraTherm oven at 55 °C for 7, 14, 28, and 42 days.

Cell assembly

In this study large format cylindrical LICs with a diameter of 46 mm and height of 95 mm were produced in the pilot plant at the BMW AG Munich, Germany. The cell is comprised of a nickel manganese cobalt (NMC) cathode material in an 8:1:1 ratio and a silicon-graphite anode material. The electrodes have a specific mass loading, defining the active material amount on the electrodes. The cathode has a specific mass loading of $m_{NMC} = 195 \pm 5$ g m^{-2} and the anode of $m_{Si\text{-}Gr} = 100 \pm 5$ g m^{-2}. The principle of the electrolyte filling process for cylindrical automotive cells was recently published [15]. The LICs were filled with 42 ± 5 g 1 mol dm^{-3} $LiPF_6$ or 1 mol dm^{-3} LiFSI in EC/EMC (1:1).

Cell formation and aging at elevated temperatures

The formation was performed in a climate chamber (Li plus GmbH) at 25 °C using a Maccor series 4000. Starting with the PreCharge the cylindrical automotive cells were charged with constant current (CC) and 0.1 C (battery capacity) to 3.3 V. After the PreCharge the cells were sealed in the dry room. During the formation the cells were charged to 4.2 V using constant current-constant voltage (CC–CV) with 0.1 C. The cell was hold at 4.2 V with constant voltage for 1 h and discharged with 0.1 C to 2.8 V. The cells were stored at 30% state of charge (2.8 V) in the climate chambers for 42 days at 55 °C.

Cell disassembly and electrolyte extraction

The automotive cell was disassembled in an argon-filled glovebox. The cell can and isolation tapes were removed. The cell material was disconnected from the disks and the current collectors were removed. The electrolyte extraction of the entire cylindrical automotive cell was performed in the glovebox. The principle of the developed electrolyte extraction method was described previously [15]. For the extraction the cell material, the cell was transferred into the designed extraction chamber and completely rewound after the addition of the extraction solvent DMC. A homogeneous mixture of the electrolyte in the cell materials and the added solvent was achieved by an extraction period of 48 h while shaking at 10 osc min^{-1}. An aliquot of the electrolyte extract was taken for analysis.

Conductivity measurements

The conductivity studies were performed using an Autolab AUTM101.S from Metrohm (Filderstadt, Germany) controlled by NOVA 2.1.6. A TSC microcell 1600 closed GC (rhd instruments, Darmstadt, Germany) with a platinum beaker electrode and glassy carbon electrode was used for the conductivity measurements. The microcell was connected to the temperature controlled microcell HC basic package from rhd instruments (Darmstadt, Germany).

Impedance measurements were performed outside of the glovebox in a frequency range of 200–0.1 kHz with an amplitude of 10 mV. A calibration was performed using the potassium chloride (KCl) standard solution. The standard KCl solution was measured at various temperatures (0, 10, 20, 25, and 30 °C) and compared to the reference values. Furthermore, a cell constant of 1.27 ± 0.03 cm^{-1} was determined. Afterward the microcell was cleaned using a water isopropanol mixture and dried in the vacuum chamber at 60 °C. The microcell was transferred into a glovebox and injected with 900 mm^3 of electrolyte sample and sealed airtight. Electrolytes with a different conductive salt concentration were analyzed at 25 °C. The specific conductivity values were measured three times for each electrolyte sample. The results, including the standard deviation are listed in Tables S1–S10 in the supplementary information.

High performance liquid chromatography—mass spectrometry (HPLC–MS)

The samples were separated by means of a Vanquish™ HPLC (Thermo Scientific, Dreieich, Germany) consisting of a Vanquish™ binary pump, an Vanquish™ autosampler, a Vanquish™ column compartment with a Vaquish™ diode array detector. The HPLC was connected to a Orbitrap Exploris 120™ (Thermo Scientific, Dreieich, Germany)

using a heated electrospray ionization (H-ESI) at 2.0 kV for the ionization. Samples were analyzed in positive and negative mode in a mass range from *m/z* 40–1000. Data evaluation was performed with Trace Finder™ 5.1 General Quan (Thermo Scientific, Dreieich, Germany) and Compound Discoverer™ 3.3 SP2 (Thermo Scientific, Dreieich, Germany).

Separation of the samples was performed by a pentafluorophenyl column (150 × 2.1 mm) with a pore diameter of 2.7 µm from Raptor™ (Restek, Bellefonte, USA) at 45 °C. A gradient system of formic acid (0.02%) and acetonitrile (2%) in water (solvent A) and formic acid (0.02%) and water (5%) in acetonitrile (solvent B) was used at a flow rate of 0.4 cm^3 min^{-1}. The gradient system started with solvent A (100%) for 1 min. From 1—10 min solvent B was increased to 100% and hold for 1 min. Afterwards, solvent B was decreased to 0% and hold at solvent A (100%) for 4 min. The thermally aged electrolyte samples were diluted 1:50 and extracted electrolyte samples were diluted 1:5 in anhydrous ACN inside the glovebox and sealed airtight. An aliquot of 1 mm^3 was directly injected into the HPLC–MS system and a double determination was performed. The HPLC–MS method was developed in a previous study Schönemeier et al. [15].

Ion chromatography—conductivity detection—mass spectrometry (IC-CD-MS)

IC-CD-MS data was acquired using a Professional IC AnCat MSM-HC MCS by Metrohm (Filderstadt, Germany) connected to a 6130 single quadrupole MS from Agilent Technologies (Santa Clara, USA). The anionic species were analyzed in the mass spectrometer. Negative electrospray ionization mode (ESI) with 3 kV was performed in a mass range of *m/z* 50–300.

The cationic species were separated using a Metrosep C4 100/4.0 column connected to a Metrosep C4 Guard 4.0 column. Separation of the anionic species was achieved on a Metrosep A Supp 5–250/4.0 column coupled to a Metrosep A Supp Guard 4.0 column. Cationic eluation was achieved by 2 mM HNO_3 in water with a flow rate of 0.9 cm^3 min^{-1}. Anionic eluation was performed using a 10 mM $NaHCO_3$ and acetone (30%) in water with a flow rate of 0.7 cm^3 min^{-1}. Electrolyte solutions of $LiPF_6$ (2 mol dm^{-3}) and LiFSI (2 mol dm^{-3}) in DMC were prepared and diluted in water. Quantification was performed in the range of 0.1–2.0 mol dm^{-3} using an external six-point calibration. The thermally aged electrolyte samples were diluted 1:1000 and extracted electrolytes 1:100 in purified water and an aliquot of 10 mm^3 (cation) and 20 mm^3 (anion) was injected into the IC-CD-MS. The IC-CD-MS method was developed in-house and were described in a previous study Schönemeier et al. [15].

Computer tomography (CT)

CT scans were conducted on a FF35 CT X-ray system using a FXT 225.48 fine focus directional tube and a 4343CT digital flat image detector with CsI scintillator. A current of 200 µA and a voltage of 220 kV with a performance of 44 W was used to scan the automotive LICs. Data visualization was performed using VGStudio Max 3.5 by Volume Graphics and electrolyte illustration was conducted by gray-level analysis.

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Data availability Data will be made available on request.

Declarations

Conflict of interest The authors declare that they have no known competing interest or personal relationships that could have appeared to influence the work reported in this paper.

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