



Comprehensive gas and electrolyte analysis in aged automotive lithium-ion cells cycled in various voltage windows

Sabrina Schönemeier^{a,b,*}, Christoph Stinner^b, Michael Rampfl^b, Verena Peters^b, Fabian Horsthemke^b, Frank-Michael Matysik^{a,**}

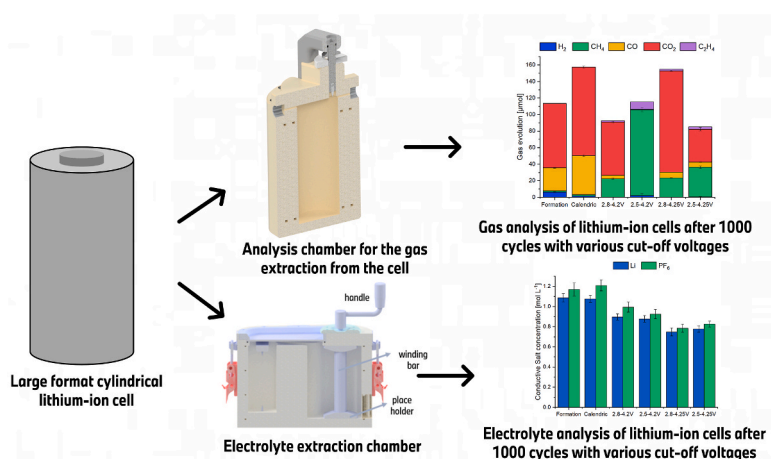
^a University of Regensburg, Institute of Analytical Chemistry, Universitätsstrasse 31, Regensburg, 93053, Germany

^b BMW AG, Battery Cell Competence Center, Lemgostrasse 7, Munich, 80935, Germany

HIGHLIGHTS

- First method for comprehensive electrolyte characterization by analyzing gas and liquid phase in large format cylindrical lithium-ion cells.
- Application variety of the developed tools is illustrated by investigating cells after formation and after 1000 cycles.
- Electrolyte analysis including gas composition and gas amount after long term cycling applying different cut-off voltages.

GRAPHICAL ABSTRACT



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1. ABSTRACT

Background: Increasing the range of battery electric vehicles is of significant interest in the automotive industry. Enhancing the voltage window in which the lithium-ion cell is operating directly affects the driving range of the vehicle but can reduce the cell lifetime. The electrolyte and associated degradation reactions have a significant impact on this parameter. To understand lithium-ion cell aging mechanisms comprehensive electrolyte analysis methods are required.

Results: A new approach for the gas analysis in industrially produced cells is presented, allowing the identification of the gas amount within the cell and the quantification of the gas composition. By applying this method a comprehensive gas and liquid phase analysis of the electrolyte in large-format automotive cells can be performed to gain insights in the electrolyte degradation process. In a next step the method is applied to perform an electrolyte analysis of lithium-ion cells after long-term cycling. Different cut-off voltages are analyzed to

* Corresponding author. University of Regensburg, Institute of Analytical Chemistry, Universitätsstrasse 31, 93053 Regensburg, Germany.

** Corresponding author.

E-mail addresses: Sabrina.Schoenemeier@bmw.de (S. Schönemeier), Frank-Michael.Matysik@chemie.uni-regensburg.de (F.-M. Matysik).

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investigate the effect of the voltage window on long-term cycling stability of the electrolyte and identify degradation reactions leading towards capacity loss of the cell.

Significance: A comprehensive analysis of the gas and liquid phase can be performed to gain further understanding in the electrolyte degradation process. Identifying the suitable voltage window for cycling lithium-ion cells is essential for the development of long lasting battery packs for vehicles with a wide electrical range.

1. Introduction

Lithium-ion cells (LICs) are a key factor in replacing fossil fuels in the transportation sector by rechargeable energy storage systems [1,2]. The charging infrastructure and the electric range of the vehicle are important characteristics for the customer to switch to a battery electric vehicle (BEV) [3,4]. Optimizing the voltage window in which the cell is cycled can affect the lifetime and the performance of the cell [5]. By increasing the voltage window, the electric range of the vehicle can be extended but this can lead towards degradation reactions on the electrodes and in the electrolyte [6].

An increase in the voltage window of the lithium-ion cell enhances the accessible energy but can also lead towards electrolyte degradation reactions. In this study increasing the upper cut-off voltage (4.2 V $\rightarrow$ 4.25 V) and decreasing the lower cut-off voltage (2.8 V $\rightarrow$ 2.5 V) in a lithium-ion cell is investigated and the effect on the gas and liquid electrolyte composition is highlighted. The cells are composed of a Nickel-Manganese-Cobalt (NMC811) cathode material coated on an aluminum current collector; shown on the left side of Fig. 1. The anode consists of a silicon graphite material on a copper current collector (right side Fig. 1). The electrodes are separated by the separator and the electrolyte consisting of the conductive salt and carbonate solvents. Fig. 1 displays possible electrolyte degradation reactions in the cell, which result in the formation of permanent gas products.

The conductive salt LiPF₆ will form degradation products such as LiF, POF₃ and HF when it comes in contact with protic species and water ①

[7,8]. In a subsequent reaction these conductive salt degradation products can lead towards transition metal dissolution from the cathode material ② [9,10]. A secondary degradation reaction occurring on the Nickel-Manganese-Cobalt (NMC) material is the oxidation of a lithium carbonate layer at increased voltages (at 3.8 V Li/Li⁺) towards CO, CO₂. At high voltages the electrolyte oxidation of ethylene can start at the cathode material ③ [11,18]. Trace water from different cell materials will get reduced to H₂ on the anode materials (at 2 V Li/Li⁺) during the first cycles ④ [12,18]. The cyclic carbonate reduction of EC on the graphite material towards CO and C₂H₄ is taking place at low voltages (at 0.8 V Li/Li⁺) ⑤ [13,14,18]. To prevent this degradation the SEI formation additive FEC is added to the electrolyte. FEC is also reduced on the graphite material to produce CO₂, compared to EC the degradation of FEC starts at higher voltages (at 1.2 V Li/Li⁺) and resulting in a decrease of cyclic carbonate reduction of EC ⑥ [15,16,18]. Linear carbonates can be reduced towards CO₂ and CH₄ at low voltages ⑦ [17]. Investigating these degradation reactions can be a key factor in producing long lasting lithium-ion cells.

For a comprehensive electrolyte analysis, the investigation of the gas and liquid phase is required. Therefore, the gas products formed during the aging period need to be extracted from the automotive cell, several approaches have been reported in literature. Scharf et al. [14] customized a prismatic automotive cell during the production by adding a sample port, so the gas can be analyzed during the formation by means of online electrochemical mass spectrometry (OEMS). In 2020, Matthiesen et al. [19] performed OEMS analysis of a commercially built

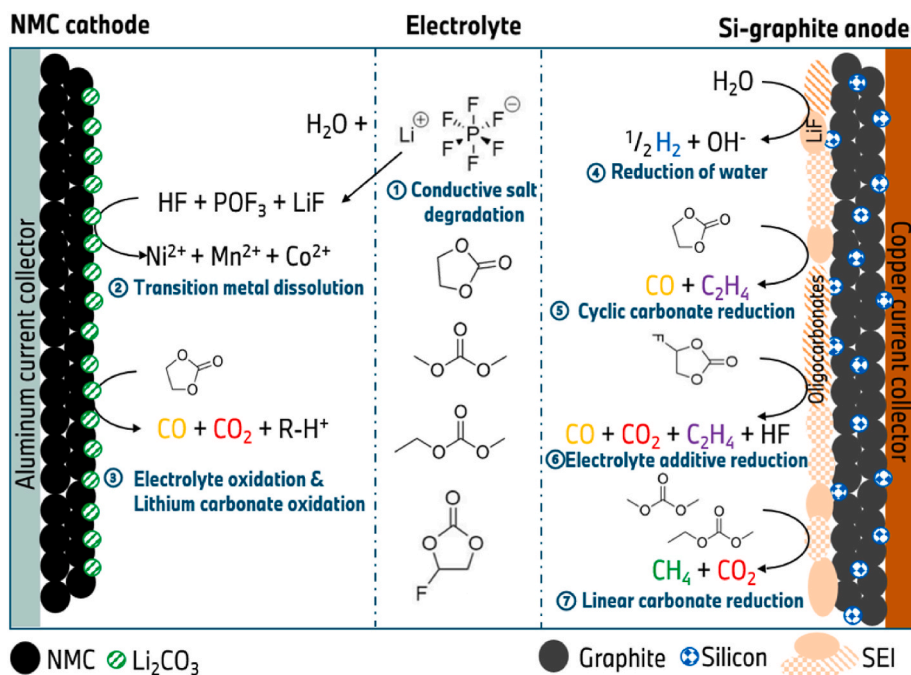


Fig. 1. Schematic drawing of a lithium-ion cell and possible degradation reactions in the electrolyte resulting in the formation of gas production. The left side shows the cathode material composed of Nickel-Manganese-Cobalt (NMC) with lithium carbonate and the reactions occurring on the interface, resulting in gas production. The right side illustrates the silicon graphite anode material, including the formed solid electrolyte interface (SEI) and the degradation reaction taking place. The electrodes are separated by the electrolyte, consisting of the conductive salt lithium hexafluorophosphate (LiPF₆) and the solvents dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC), with the additive fluoroethylene carbonate (FEC). Adapted from the following sources [7–17]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

18650 cell by making a small incision into the steel can. The puncturing of the cell before the analysis could potentially lead towards contamination or loss of gases. S. Kunihiro et al. [19] described a system analyzing the gas composition of lithium-ion cells inside a case by puncturing the cell, afterwards the extracted gas gets transferred to an analyzer. Patent publication presented the first method to perform analysis of the gas composition on commercially produced and tested cells. In this research the concept by is adapted and optimized by having the opportunity of two analyzers. A gas pressure analyzer is used in combination with a μ -GC analysis to identify the formed gas amount in combination with the gas composition.

In the present research, we introduce a novel method for the gas analysis of industrially produced automotive cells which combines the analysis of the gas composition and the liquid electrolyte composition. In a next step, the developed method is applied to investigate the difference in capacity loss in LICs after long-term cycling with various cut-off voltages in reference to calendaric aging and a cell after the formation process. Therefore, gas and liquid phase of the electrolyte are analyzed side by side to identify degradation reactions and the root cause for the performance differences of the cells within different cut-off voltages.

2. Experimental part

2.1. Chemicals

For the quantification of the following carbonates the listed chemicals were obtained from Thermo Scientific (Dreieich, Germany): Dimethyl carbonate (99.0%), ethyl methyl carbonate (98.0%), ethylene carbonate (99.0%), diethyl carbonate (99.0%) and ethyl propionate (99.0%). 2-butoxyethyl acetate (99.0%) and fluoroethylene carbonate (98.0%) were obtained from Merck (Darmstadt, Germany). For LC-MS analysis acetonitrile by Merck (Darmstadt, Germany) were combined with formic acid (99.0%) by Avantor (Radnor, USA). Water was purified using a Millipore Milli-Q IQ7000 from Merck (Darmstadt, Germany).

2.2. Cell assembly

The automotive lithium-ion cells and the electrodes used in this research project were produced in the prototype production at the BMW AG Munich, Germany. The large-format cylindrical cells had a diameter of 46 mm and a height of 95 mm. The cell chemistry used in this study consisted of a $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ cathode and a Si-Graphite anode material, with a silicon content of less than 10 wt%. The cell consists of a double-sided cathode with a specific mass loading of $m_{\text{NMC}} = 185 \pm 5 \text{ g m}^{-2}$ and a double-sided anode with a specific mass loading of $m_{\text{Si-Gr}} = 100 \pm 5 \text{ g m}^{-2}$ and an N/P ratio of ~ 1.05 . A state-of-the-art polyethylene separator was used within this research project. A state-of-the-art electrolyte was used in the cells, consisting of 1.2 mol L^{-1} LiPF_6 dissolved in a mixture of dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and ethylene carbonate (EC), fluoroethylene carbonate (FEC) was used as an additive. The cells were filled with at least 1.3 g Ah^{-1} of electrolyte. Literature describes a state-of-the-art lithium-ion cell with NMC811/Si-Graphite electrodes can reach capacities of up to 33 Ah [20].

2.3. Cell formation and aging

The formation was performed in a battery cycler by Keysight Technologies (Santa Rosa, CA; USA) located in the dry room. During the pre-charge the cell was not sealed to release the formed gas during the first charging. Therefore, the cells were charged to $\approx 3.3 \text{ V}$ with 0.1 C (C, battery capacity) using constant current (CC). Afterwards, the cells were sealed and charged to 4.2 V using a two-step charging process applying constant current followed by constant voltage (CC-CV). In a next step, the cells were discharged using 0.1 C and CC to 2.8 V .

Battery cycling was performed in a battery cycler by Keysight Technologies (Santa Rosa, CA; USA). Eight cells were cycled at 25°C with a charging and discharging rate of 0.5 C (C, battery capacity) using CC-CV charging profile and a CC discharging profile. Four different voltage windows (Table 1) were investigated for 1000 cycles, always using two cells for each voltage window.

2.4. Cell disassembly and electrolyte extraction

The cylindrical cells were disassembled in an argon-filled glovebox with H_2O and O_2 values below 1 ppm. During the disassembly the bottom cap of the cell was removed and the jelly roll was separated from the steel can. The isolation tapes were removed, the copper and aluminum discs were disconnected from the jelly roll. For the electrolyte extraction the current collector taps were removed from the jelly roll. Recovery rates of $83.3 \pm 1.7\%$ for the lithium cation and $82.5 \pm 3.6\%$ for hexafluorophosphate could be achieved. Furthermore, $89.4 \pm 1.7\%$ for ethylene carbonate and $87.7 \pm 2.7\%$ could be achieved for the carbonate solvents. Further information on the electrolyte extraction principle of large-format automotive LICs was described in detail in a previous study [21].

2.5. Gas analysis chamber

Fig. 2 shows the novel gas analysis chamber developed at BMW AG and built at Alpha Modellbau GmbH. Here, a cylindrical lithium-ion cell was punctured to extract the formed gas during cycling. The gas analysis chamber was composed of the electrolyte resistant material polyetheretherketone (PEEK) and the thorn consists of stainless steel.

Before the analysis the chamber was dried in a vacuum oven at 60°C to reduce the amount of trace water on the material which can come in contact with the extracted gas. The cylindrical cell was discharged to 2.8 V and stored for at least 24 h before the analysis afterwards the cell was transferred into the gas analysis chamber with the vent to the top. The chamber was equipped with a PXM409 pressure sensor by Omega (Deckenpfronn, Germany). In the next step, a pressure differential controller F620 by ATEQ (Rammingen, Germany) using 5 bar argon for carrier gas was used to measure the excess volume in the chamber. The chamber was flushed with argon for 3 min to generate an inert atmosphere. Afterwards the gas analysis chamber was closed and the screw was inserted into the vent of the cell to release the gases formed during cell cycling. The pressure sensor was recording the difference in pressure before and after the cell was punctured. Finally, the gas analysis chamber is connected to the micro – gas chromatography (μ -GC) to analyze the extracted gas composition.

2.6. Micro – gas chromatography (μ -GC)

The gas phase of the lithium-ion cell was analyzed by means of a 990 micro-gas chromatography (μ -GC) from Agilent Technologies controlled by Open Lab CDS Chem Station VL. The μ -GC was equipped with a two-channel system for the separation of the following analytes: H_2 , O_2 , N_2 , CH_4 , CO (channel 1) and CO_2 , C_2H_2 , C_2H_4 , C_2H_6 , $\text{C}_3\text{H}_8/\text{C}_3\text{H}_6$ (channel 2). The separation of the analytes on the first channel was achieved by the MGC MS5A molecular sieve column using argon as the carrier gas.

Table 1
Applied voltage windows for cell cycling.

Cell Aging	Voltage Window (V)
Begin of life (BOL)	Formation
Calendar Aging	Formation & storage 20°C
Cycling	2.8 – 4.2
Cycling	2.5 – 4.2
Cycling	2.8 – 4.25
Cycling	2.5 – 4.25

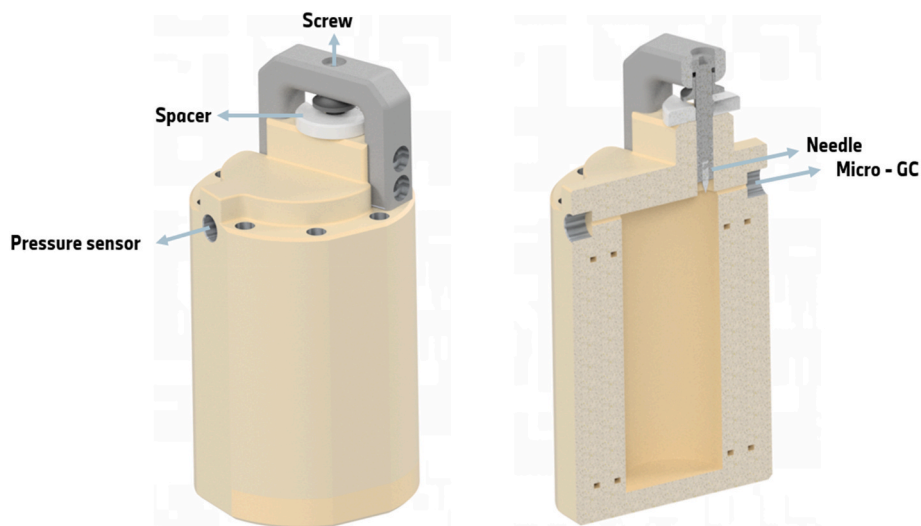


Fig. 2. Schematic representation of the gas analysis chamber for the pressure analysis and permanent gas analysis of large-format cylindrical cells. The cell is transferred into the chamber with the vent facing upwards. The needle is screwed into the cell vent using the spacer to prevent the needle from going too deep into the cell. Two capillaries can be connected to the chamber for the pressure sensor and the micro gas chromatography.

The separation of the on the second channel was performed by the CP-PoraPLOT U column (10 m $\times$ 0.32 mm, 10 μ m fused silica) using helium as the carrier gas. The signal was detected by a micromachined thermal conductivity detector. A Teckso low volume device for μ -GC controlled the vacuum pump and the sampling of the gas.

For the injection of the gas sample the chamber was connected to the μ -GC by a capillary which was evacuated to 20 mbar. By opening a valve 600 mbar of the gas sample is transferred into the μ -GC. Afterwards the capillary was evacuated to 20 mbar and flushed with argon, this procedure was repeated three times.

2.7. Ion chromatography – conductivity detection – mass spectrometry (IC-CD-MS)

Quantification of the conductive salt was performed on a Thermo Scientific™ Dionex ICS-6000 high performance ion chromatography (HPIC) connected to a Thermo Scientific™ Orbitrap Exploris™ 120. The IC-CD system was composed of a Dionex™ ICS-6000 DP dual pump system, a Dionex™ ICS-6000 EG dual eluent generator, a Dionex™ AS-AP autosampler, a Dionex™ ICS-6000 DC dual column compartment, a Dionex™ ADRS-600 dynamic regenerated suppressor (anionic flow), a Dionex™ CDRS-600 dynamic regenerated suppressor (cationic flow), a Dionex™ ICS-6000 conductivity detector, a Dionex™ ICS-6000 auxiliary pump and Dionex™ ICS-6000 regeneration pump. The IC-CD was connected to an Orbitrap Exploris™ 120 to investigate the anionic flow the following instrument settings were applied: Heated electrospray ionization (H-ESI) with 2 kV, low mass range m/z 40 – 200, high mass range m/z 150 – 1500 and a collision energy of 15%. Chromeleon 7.2 was used to control the IC-CD-MS system and perform data evaluation by Thermo Scientific™.

Dionex™ EGC 500 potassium hydroxide KOH (anionic) and Dionex™ EGC 500 methane sulfuric acid MSA (cationic) cartridges were used for the eluent generation. For the separation of the cationic analytes the following gradient system was used: 0 – 3 min, 3 mM MSA; 3 – 3.6 min, continuous increase to 6 mM MSA; 3.6 – 6 min, continuous increase to 22 mM MSA; 6 – 15 min, continuous increase to 25 mM MSA; 15 – 22 min, continuous decrease to 3 mM MSA; 22 – 25 min, 3 mM MSA. The separation of the anionic analytes was achieved by applying the gradient system described below: 0 – 10 min, 15 mM KOH; 10 – 15 min, continuous increase to 100 mM KOH; 15 – 50 min, 100 mM KOH; 50 – 50.1 min decrease to 15 mM KOH; 50.1 – 55 min, 15 mM KOH. The separation of the cationic analytes was achieved by using a

Dionex IonPac™ CS21-Fast-4 μ m analytical column (2 $\times$ 150 mm) equipped with a Dionex IonPac™ CG21-Fast-4 μ m guard column (2 $\times$ 30 mm). The separation of the anionic analytes was achieved with a Dionex IonPac™ AS20 analytical column (2 $\times$ 250 mm) equipped with a Dionex IonPac™ AG20 guard column (2 $\times$ 50 mm). Both columns are heated to 30 °C using a flow rate for anionic flow of 0.35 mL min⁻¹ and a flow rate for cationic flow of 0.3 mL min⁻¹. 5 μ L of each sample is injected onto the columns. The determination coefficient (R^2) for the quantification of the conductive salt LiPF₆ (Li: R^2 > 0.995 PF₆: R^2 > 0.998) was identified using an external calibration in the range of 1 mmol – 0.1 mol. A stock solution of lithium hexafluorophosphate was prepared in purified water and sequentially diluted 1 + 1. The electrolyte samples were stored inside a glovebox and for sample preparation the electrolyte extracts were diluted 1:100 in purified water.

2.8. Head space - gas chromatography – flame ionization detector (HS-GC-FID)

Headspace gas chromatography-flame ionization detector (GC-FID) measurements were performed on a Thermo Scientific™ TRACE 1610 GC equipped with a TRI PLUS 500 Headspace (Thermo Fisher Scientific™, Dreieich, Germany) equipped with a Restek Rtx-200MS column (30 m $\times$ 0.25 mm $\times$ 0.25 μ m). Chromeleon 7.2 was used to control the GC-FID system and perform quantification of the analytes.

10 μ L of the sample was analyzed in a 20 mL head space vial. A vial incubation temperature of 120 °C for 10 min was applied and the sample path temperature was set to 140 °C. Helium was used as the carrier gas with a split flow of 680 cm s⁻¹ and constant linear velocity of 30 cm s⁻¹ as column flow. The column oven program started with 40 °C for 2 min and increased 3 °C min⁻¹ to 60 °C and was afterwards further increased by 10 °C min⁻¹ to 260 °C. The determination coefficient (R^2) for the quantification of the following carbonates was identified: DMC (R^2 > 0.998), EMC (R^2 > 0.997), DEC, (R^2 > 0.994), EC (R^2 > 0.998) and FEC (R^2 > 0.994). A calibration using 2-butoxyethyl acetate and ethyl propionate as internal standards was created. Therefore, a stock solution of DMC (212 mg), EMC (202 mg), DEC (195 mg), EC (200 mg), FEC (74 mg) and internal standards were prepared in 8.1 g acetonitrile and sequentially diluted 1 + 1. The samples were stored in the glovebox and for sample preparation the electrolyte extracts were diluted 1:4 in acetonitrile combined with the internal standards.

3. Results and discussion

3.1. Development of the gas analysis chamber

Understanding electrolyte degradation reactions in lithium-ion cells (LICs) is a key factor for producing long lasting cells. Therefore, a comprehensive electrolyte analysis of the gas and liquid phase must be conducted.

For the gas analysis of large format automotive cells few methods are described in literature. The cell can be modified with a gas sample port during production and gases formed during cycling can be analyzed accurately and without contamination. A disadvantage of this method is, that it cannot be transferred towards commercially produced cells [14]. For the analysis of commercial cells *Mattinen et al.* [19] described a gas analysis method in which the cell is punctured and afterwards transferred into a tight chamber to perform gas analysis while cycling the cell. By applying this method, commercially produced cells can be analyzed for their gas degradation products. An aspect that must be taken into consideration is the injection into the steel can before the cycling process, this can result in contamination of the analyzed gas. *S. Kuniyiko et al.* [22] developed a case in which the cell is punctured for gas release which is afterwards transferred to an analyzer. Introducing the first method for gas analysis on commercially produced and tested cells without previous contamination of the investigated gases.

In this research project, the concept of *S. Kuniyiko et al.* [22] gas analysis tool for cylindrical LICs was modified with two analyzers, a pressure sensor and an adapter for gas analysis. With this optimized gas analysis chamber commercially produced and tested cells can be investigated regarding the produced gas amount (pressure sensor), gas composition (gas analysis) and their liquid electrolyte composition (electrolyte extraction from cell materials procedure described in a previous study [10]). Therefore, the electrolyte degradation process is investigated in the liquid phase and in the gas phase.

3.2. Electrochemical data

Increasing the range in which the LIC can be charged and discharged can extend the electric range of an electric vehicle. Cycling the cell towards higher upper cut-off voltages and decreased lower cut-off voltages can affect the lifetime of the cell and lead towards electrolyte degradation reactions. The state of health (SOH) is defined as the ratio of the current maximum capacity of the cell compared to the original maximum capacity and can be used to determine the remaining life

expectancy of the cell. For this study, the cells were cycled in different voltage windows for 1000 cycles (Table 1) and the decrease in SOH is displayed in Fig. 3 (left) combined with the resistance increase during the aging period (Fig. 3 right).

The cells cycled in the range of 2.8 – 4.2 V show a capacity decrease of 20% in the aging period investigated. Cells which were cycled with an increased cut-off voltage of 4.25 V show similar electrochemical behavior with a capacity reduction of 22%. Indicating that the increase of the upper cut-off voltage from 4.2 V to 4.25 V has no significant impact on the long-term cycling behavior of the cell applying 0.5 C and 25 °C. The cells cycled with a lower cut-off voltage (2.5 – 4.2 V and 2.5 – 4.25 V) display an accelerated capacity decrease during the 1000 cycles. The cells cycled in a voltage window of 2.5 – 4.2 V show a capacity decrease of 26% compared to a capacity decrease of 28% (2.5 – 4.25 V).

Fig. 3 (right) displays the resistance increase for the different voltage windows during the investigated aging period. It was found that the resistance increase in the cells is opposite towards the capacity decrease displayed in Fig. 3 left. The cells cycled in the voltage range of 2.8 – 4.2 V and 2.8 – 4.25 V show the least increase. The cells cycled in the voltage window of 2.5 – 4.2 V and 2.5 – 4.25 V have a higher increase.

In the following chapters, the differences in capacity decrease due to the different cut-off voltages in terms of the electrolyte degradation are investigated. The cells are analyzed regarding their gas composition and the liquid electrolyte is analyzed in terms of the conductive salt concentration and the solvent composition.

3.3. Gas phase evaluation

In the next step, the gas amount and composition of LICs after the formation, calendar aging and 1000 cycles applying a variation of voltage windows are investigated. Therefore, the cells were punctured in the developed gas analysis chamber and analyzed by μ -GC (Fig. 4). For authentication of the results two identical cells were analyzed for each displayed electrolyte analysis.

By means of the performed gas analysis the amount of gas production in the cell for different aging periods can be investigated. After the formation of the LIC a gas amount of 114 μ mol was determined. The cells cycled in a voltage window from 2.8 to 4.2 V showed a similar gas volume as the cells after the formation, indicating that only few gaseous decomposition products were formed during the cycling process. Cycling in a voltage window with a decreased lower cut-off voltage (2.5 – 4.2 V) lead to an increased gas production after 1000 cycles [11]. By increasing the upper cut-off voltage an increased gas production was

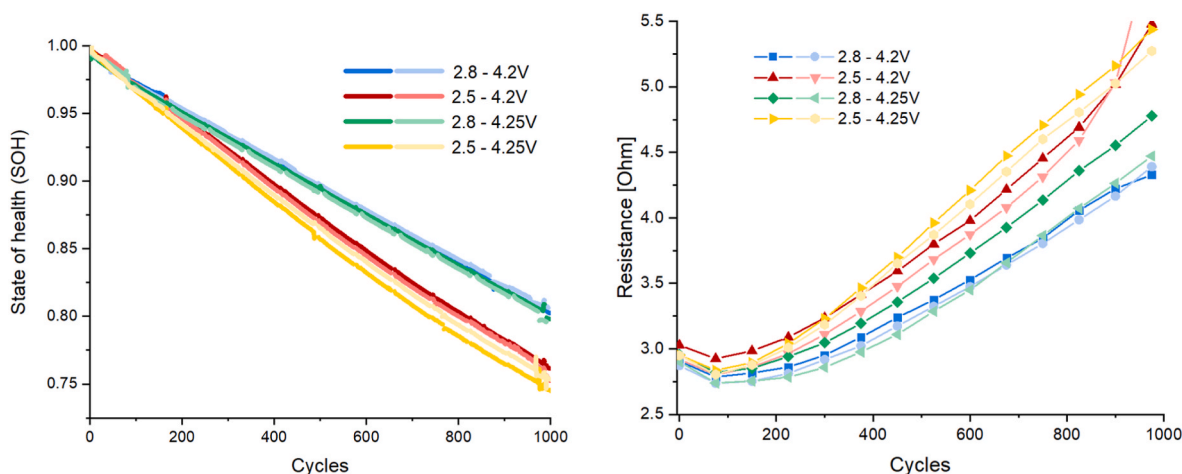


Fig. 3. The cells were aged for 1000 cycles using 0.5 C and 25 °C with four different voltage windows. For each investigated voltage window two identical cells were cycled and analyzed. **Left:** Normalized capacity (state of health) vs. cycle numbers for 1000 cycles, applying the following voltage windows: 2.8 – 4.2 V (blue); 2.5 – 4.2 V (red); 2.8 – 4.25 V (green); 2.5 – 4.25 V (yellow). **Right:** Pulse resistance of the cell vs. cycle numbers at state of charge 50% after 10 s. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

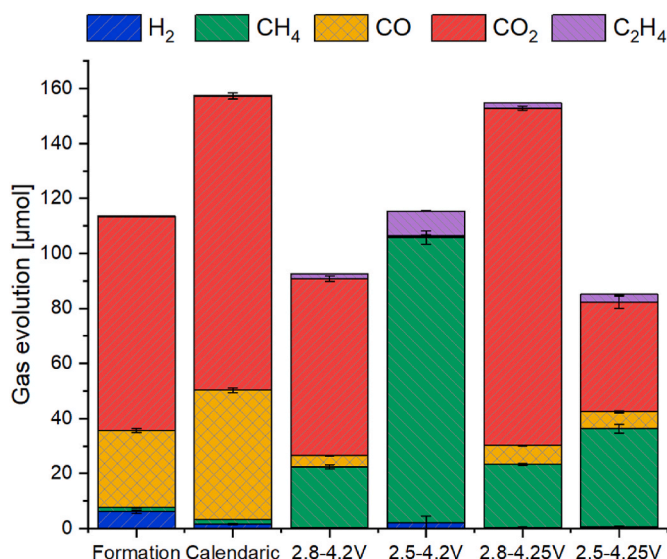


Fig. 4. Gas volume and gas composition of LICs were determined after long-term cyclic aging and compared with calendar aging and cells after the formation process. The cell was punctured in the developed gas analysis chamber followed by pressure measurement and μ -GC analysis. All experiments were performed using an electrolyte containing 1.2 M LiPF₆ in DMC, EMC, EC and FEC.

identified in the LIC, this agrees with the reports in literature [23]. By increasing the voltage window from 2.5 to 4.25 V the measured amount of gas decreased compared to the other investigated cycling windows. No gaseous degradation products, which could indicate a leak in the cell, were detected in the analysis. It is assumed that the extended cycling window can lead towards reactions in the electrolyte forming solid degradation products. To confirm this hypothesis further studies would have to be conducted.

In a next step the composition of gas formed during the calendar and cyclic aging were analyzed by μ -GC. Previous studies showed that gas composition result generated by μ -GC can be compared to results generated by means of OEMS [14,17]. Investigation of the gas composition shows significant differences in cycled cells with varying cut-off voltages.

During the formation process the additive FEC is reduced on the anode at low voltages, leading towards CO and CO₂ being the main components in the gas phase. For the SEI formation the reduction of EC in a ring opening reaction lead towards an increased amount of CO and CO₂ being generated (Fig. 1) [24]. Traces of water remained in the cell materials, which were reduced during the first charging process on the anode to form H₂ [7,25].

The cells after calendar aging at 20 °C for 8 months at 3.3 V showed an increase in CO and CO₂. Indicating the cyclic carbonate reduction and the reduction of FEC (Fig. 1) occurring during this time period due to further SEI growth resulting in the formation of the gases CO and CO₂ [26].

The gas composition of the cycled cells showed significant differences due to the variation of the cycled voltage windows. The cells cycled in the range of 2.8 – 4.2 V showed an increased methane production compared to the cells after the formation. This indicated that the linear carbonates EMC and DMC in the electrolyte get reduced on the anode during the long-term cycling (Fig. 1) [27]. Traces of ethylene were observed resulting from the cyclic carbonate reduction on the anode. The CO and CO₂ concentration after 1000 cycles did not show significant differences to the cells after the formation.

For the cells which were cycled with a decrease in the lower cut-off voltage, in the range of 2.5 – 4.2 V a significant increase in the methane concentration could be identified. Resulting from the reduction of the

linear carbonates, which increased at lower potentials [27]. The EC reduction towards C₂H₄ also increased at lower voltages, leading to the increased amount of ethylene [19].

The cells that were cycled from 2.8 to 4.25 V show a high amount of CO₂ in the gas phase. Increasing the upper cut-off voltage can lead towards the oxidation of the lithium oxalate in the cathode [11]. Low amounts of CO and C₂H₄ indicate the reduction of the cyclic carbonate EC. Furthermore, similar amounts of CH₄ could be identified in the voltage range of 2.8 – 4.2 V compared to the cells with an increased upper cut-off voltage.

The cells cycled in a range of 2.5 – 4.25 V showed a lower amount of gas evolution compared to the other investigated voltage windows. A possible explanation could be that the generated gas undergoes further reactions to form liquid or solid electrolyte degradation products. The gas composition of the cells cycled from 2.5 to 4.25 V showed no significant change to the cells cycled in a voltage window of 2.8 – 4.2 V. Further studies must be carried out to investigate the electrolyte behavior in the gas phase.

The investigated automotive cells within this research do not contain a reference electrode therefore the Li/Li⁺ potential is not available. Rowden et al. [18] describes the gas production for a graphite cathode and a NMC cathode within half-cell set-up. The electrolyte reduction on the anode at a 0.8 V Li/Li⁺ potential is described as resulting in a gas production consisting of ethylene, CO and CO₂, aligning with the findings within this research [18]. Furthermore, the reduction of water on the anode at 2V Li/Li⁺ is resulting in the formation of H₂, aligning with the analysis results within this research [18]. The FEC reduction on the anode is described to occur at a potential of 1.2V Li/Li⁺ resulting in the gas production of CO₂, CO and C₂H₄ [15]. The analysis results within this research project match the previously published gas analysis results in laboratory cells including a reference electrode. It was shown that the gas amount and gas composition are highly affected by the cycling window in which the cell is operated. Furthermore, it was observed that the gases formed during the formation can increase during calendar aging due to further SEI growth [28]. Lowering the cut-off voltage to 2.5 V increased the methane concentration in the gas phase due to the reduction of linear carbonates at lower potentials [27]. Increasing the cut-off voltage to 4.25 V increases the CO₂ amount resulting from lithium carbonate oxidation in the cathode.

3.4. Liquid electrolyte analysis

For a comprehensive electrolyte analysis, the solvent components and the conductive salt concentration were investigated in addition to the gas composition. Therefore, the electrolyte of the cells was extracted with the previous developed electrolyte extraction chamber [21]. The electrolyte used in this research project consists of 1.2 mol L⁻¹ LiPF₆ dissolved in DMC, EMC, and EC using FEC as an additive.

3.4.1. Solvent analysis

The solvent analysis was performed using a headspace GC-FID. Fig. 5 displays the solvent composition of the cells after formation, calendaric and cyclic aging with different voltage windows. The extraction method used DMC as an extraction solvent which does not allow the analysis of this electrolyte component. The results presented in Fig. 5 were normalized on the DMC amount of the original electrolyte filled into the cells.

The solvent analysis of the electrolyte component EMC displayed no significant changes, a small decrease for cyclic aging with a lower cut-off voltage of 2.5 V can be identified. This can be a result of linear carbonate reduction at the lower cut-off voltage, in which the linear carbonates react to CO₂ and CH₄ (Fig. 1). The gas products of the linear carbonate reduction could be confirmed with the gas analysis in chapter 4.3 (Fig. 4).

The electrolyte solvent analysis of the component EC shows the lowest concentration after the calendar aging process. During calendar

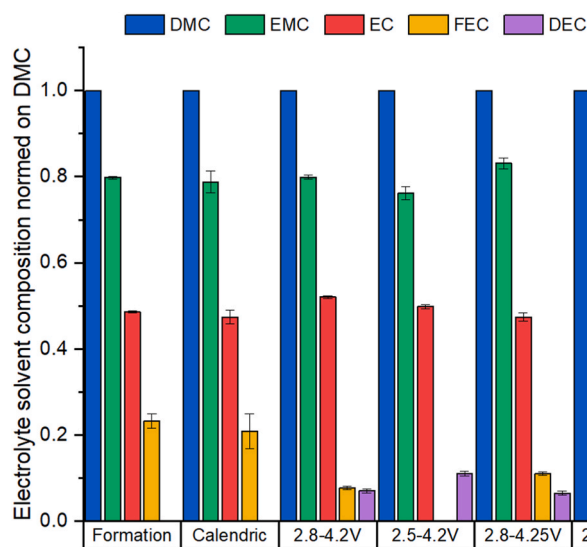


Fig. 5. Headspace GC-FID studies of the solvent composition extracted from the large-format cylindrical cells after formation, calendar aging and cyclic aging using a variation of voltage windows. The electrolyte composition is normalized on the DMC amount of the original electrolyte. Previously determined recovery rates of the electrolyte extraction for the carbonates were considered within this graphic.

aging the cyclic carbonate reduction is occurring (Fig. 1). A high amount of CO and CO₂ can be observed in the gas analysis of calendar aging, confirmed the results from the liquid electrolyte analysis (Fig. 4).

The original electrolyte composition did not include DEC as a solvent. Due to long-term cycling the transesterification of EMC reacting towards DMC and DEC was observed. The transesterification increased at lower potentials which can be identified for the voltage windows 2.5 – 4.2 V and 2.5 – 4.25 V [11].

The additive FEC enhanced the SEI formation of the cell. During the long-term cycling the FEC amount is reduced due to degradation reactions in the electrolyte resulting from continuous interfacial reactions like repeated SEI cracking and repairing or SEI growth. It can be observed that the decrease of the lower cut-off voltage to 2.5 V decreases the FEC amount significantly compared to the lower cut-off voltage of 2.8 V [29]. These results align with the gas analysis data reported in Fig. 4. The headspace GC-FID and μ -GC results indicate continuous interfacial reactions during the cyclic aging period of the cells. The analysis of the FEC concentration remained in the electrolyte indicated that the cells with a decreased lower cut-off voltage of 2.5 V experienced an accelerated SEI cracking and repairing or SEI growth. The electrochemical data presented in Fig. 3 (right) shows a resistance increase for the cells with lower cut-off voltages, confirming the electrolyte analysis results. The gas analysis results in the conclusion that the difference in the capacity decrease (Fig. 3 left) resulted from continuous interfacial reaction, an increased SEI growth or repeated SEI cracking and repair for the cells with a decreased lower cut-off voltage. In the following paragraph the conductive salt of the electrolyte will be investigated regarding the degradation behavior during long-term cycling.

3.4.2. Conductive salt analysis

For conductive salt analysis the electrolyte was extracted from LICs and analyzed by means of IC-CD-MS [10]. The lithium and hexafluorophosphate concentration for the investigated cells including the recovery rates of the extraction chamber are displayed in Fig. 6.

The electrolyte which was originally filled in the cells consisted of 1.2 mol L⁻¹ LiPF₆. During the formation of the cell, two charging and discharging cycles were conducted to form the SEI. The analysis results after the formation indicated a small decrease in the lithium and hexafluorophosphate concentration, resulting from part of the SEI being

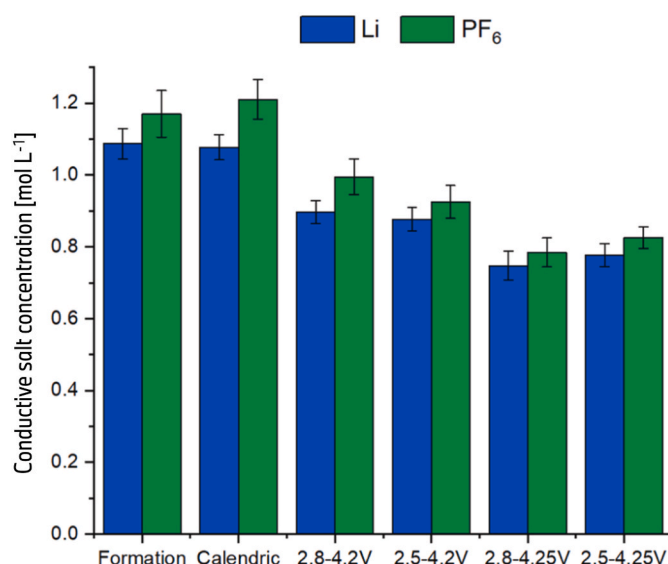


Fig. 6. IC-CD-MS studies of the conductive salt concentration extracted from the cylindrical automotive cells after cycling for 1000 times in a variation of voltage windows. By extracting the electrolyte from the cylindrical cell the recovery rate of the extraction method is included [10].

formed from conductive salt degradation products [16].

The cells analyzed after long-term cycling showed a decrease in conductive salt concentration compared to the cells after the formation and calendar aging. These observations indicate that conductive salt depletion occurred during long-term cycling, which can affect the cell capacity. It was identified that the cells cycled to a cut-off voltage of 4.2 V showed a similar decrease in conductive salt concentration. Furthermore, the cells cycled to an increased cut-off voltage of 4.25 V showed a similar trend with a lower conductive salt concentration compared to the cells cycled to 4.2 V. These results indicate that the upper cut-off voltage affects the decrease in conductive salt concentration during long-term cyclic aging significantly.

Cells cycled with an upper cut-off voltage of 4.2 V showed a conductive salt decrease of 25% (2.8 – 4.2 V) and 27% (2.5 – 4.2 V) compared to the cells cycled to 4.25 V with a conductive salt concentration decrease of 38% (2.8 – 4.25 V) and 35% (2.5 – 4.25 V). These results align with the study of Petz et al. [30] which identified a decrease in conductive salt concentration of 24% for cylindrical cells cycled from 2.5 to 4.2 V for 1100 cycles. The performed analysis indicates that conductive salt depletion occurs during long-term cycling resulting in the loss of active lithium. However, the identified conductive salt concentrations (Fig. 6) do not match the observed SOH decrease (Fig. 3) indicating that the salt depletion may not be the main factor for the capacity loss.

Hartmann et al. [31] investigated the mechanism of conductive salt decrease at different upper cut-off voltages. For cells after 4 weeks of calendar aging at 45 °C he identified a conductive salt loss of 11% (stored at 4.2 V); 15% (stored at 4.3 V) and 36% for cells stored at 4.4 V. Furthermore, the effect of the conductive salt decrease on the cell capacity was investigated. Therefore, cells with a decreasing conductive salt concentration (0.2 mol L⁻¹ – 1.0 mol L⁻¹) were cycled with different charging rates. A strong impact on fast charging rates (≥ 1 C; battery capacity) for cells with a low conductive salt concentration was identified. Otherwise, it was shown that charging rates below 1 C do not have a significant impact on the cell capacity. The conclusion drawn from Hartmann et al. [31] aligns with the results from this study; showing a decrease of up to 38% conductive salt concentration does not affect the cell capacity for the investigated charging rates of 0.5 C (Fig. 3 left). It can be assumed that an effect on the electrochemical data would be visible if charging rates ≥ 1 C would be applied on the cells.

In summary, the IC-CD-MS measurements for long-term cycling showed a significant decrease in conductive salt concentration especially for increased upper cut-off voltages. This can result in the loss of active lithium which could lead towards the observed capacity fade during the long-term cycling. It is concluded that the difference in the cell capacity (Fig. 3 left) for cycling to different cut-off voltages is originated by continuous interfacial reactions on the anode (discussed in chapter 4.3) and that the decrease in the conductive salt concentration does not affect the cell capacity during long-term cycling.

4. Conclusion and outlook

A comprehensive electrolyte analysis including a novel gas analysis and conductive salt analysis for large-format cylindrical lithium-ion cells is presented. The developed method enables the analysis of the pressure within the cell combined with the analysis of permanent gases and liquid electrolyte components.

The results demonstrate that current challenges in lithium-ion cell research can only be effectively addressed through the complementary application of advanced analytical techniques, forming a flexible and versatile analytical toolbox.

The novel methods presented in this publication enable the analysis of electrolytes in automotive cells after long-term aging without excess electrolyte, which allows for a correlation between electrochemical aging and material analysis.

Large-format automotive LICs after 1000 cycles were investigated and various voltage windows regarding the electrolyte degradation were analyzed. It was identified that cells with a lower cut-off voltage of 2.5 V show a significant capacity loss and a resistance increase during the investigated aging period. The electrolyte analysis displayed a significant FEC loss for the cells with a lower cut-off voltage of 2.5 V indicating a continuous interfacial reaction on the anode resulting in the observed capacity decrease. Furthermore, the conductive salt analysis displayed that an increased upper cut-off voltage results in a conductive salt concentration decrease of up to 38% which can result in the loss of active lithium, however this does not necessarily affect the cell capacity during charging below 1C [31,32]. By means of the electrolyte analysis method for large-format LICs it could be concluded that the difference in cell capacity loss results from continuous interfacial reactions on the anode during the investigated aging period. The developed comprehensive electrolyte analysis method could be optimized by implementing a reference electrode, leading towards the identification of the Li/Li⁺ potential for the identified gas reactions. Furthermore, the developed analysis procedure could be applied and optimized to analyze transition-metal dissolution or further gaseous components as HF and POF₃.

CRedit authorship contribution statement

Sabrina Schöne-meier: Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Christoph Stinner:** Data curation, Conceptualization. **Michael Rampfl:** Validation, Methodology. **Verena Peters:** Writing – review & editing. **Fabian Horsthemke:** Writing – review & editing, Methodology. **Frank-Michael Matysik:** Writing – review & editing, Supervision.

Declaration of competing 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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Data availability

Data will be made available on request.

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