



Challenges in extracting and characterizing electrolytes from automotive lithium-ion cells

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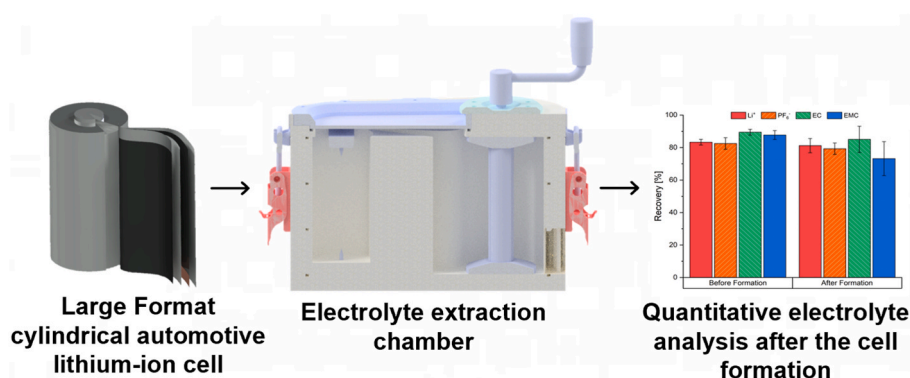
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HIGHLIGHTS

- First method for quantitative electrolyte analysis of cylindrical lithium-ion cells.
- Application variety is presented by investigation of different electrolytes.
- Lithium-ion cells before and after the formation are analyzed.
- Excess electrolyte is no longer a limitation for quantitative electrolyte analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Background: The demand for lithium-ion cells in the automotive industry is rapidly growing due to the increasing electrification of the transportation sector. The electrolyte composition plays a critical role in determining the lifetime and performance of these large-format cells. Additionally, advancements in this field are leading to frequent changes in both electrode materials and electrolyte formulations. As a result, new analytical approaches are required to enable comprehensive characterization of the relevant components of the electrolytes used in lithium-ion cells.

Results: In this research a novel electrolyte extraction method is presented, enabling the quantitative electrolyte analysis in large format cylindrical lithium-ion cells under inert conditions. A liquid-liquid extraction of the cell materials is performed in a newly developed extraction chamber, in which the electrodes are rewound to ensure an efficient extraction. The design of the chamber allows the extraction of volatile and nonvolatile electrolyte components. The cells were filled with various electrolytes and analyzed using high-performance liquid chromatography and ion chromatography coupled with electrospray ionization mass spectrometry. Using the developed method, up to 83% of the conductive salt and up to 89% of the solvents can be recovered. The first application of this method involved analyzing a cylindrical lithium-ion cell after formation.

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Significance: This method provides a crucial tool for mapping electrolyte compounds formed during degradation due to cycling or thermal aging. This analytical approach will offer valuable insights, contributing to a deeper understanding of lithium-ion cell systems and could enhance battery life and performance in the future.

1. Introduction

Lithium-ion cells play a central role in the electrification of the transportation sector and reducing the CO₂ emissions [1]. In this context, lithium-ion cells are gaining popularity and as a result the interest in topics such as fast charge ability and cell lifetime is significantly increasing [2,3]. The lifetime of the battery cell is closely linked to the composition and the stability of the electrolyte [4]. The commercially most used electrolyte is a solution of 1 M LiPF₆ in a mixture of organic carbonates (Fig. 1) [5]. The electrolyte shows a high specific conductivity [6,7]. Charging and discharging of the cell leads to side reactions in the electrolyte causing a reducing of the performance and lifetime of the cell [8].

A requirement for analyzing electrolyte is the representative separation of the electrolyte from cell materials. If no excess electrolyte is present, several methods are described in literature to extract the electrolyte from cell materials. In 2018, Thompson et al. [9] described a method in which small amounts of electrolyte can be separated from pouch cells by centrifugation. Herein, the cell is punctured on both sides of the jelly roll and centrifuged at 30 °C by 2200 rpm for 20 min in a vial. Stockhausen et al. [10]. optimized the extraction method by injecting diethyl carbonate into the pouch cell. The cell was resealed and after eight days a complete homogenization between electrolyte and added solvent could be observed by HPLC-MS. The electrolyte was extracted through a puncture in the pouch foil. Grütze et al. [11]. developed a flow-through supercritical CO₂ electrolyte extraction for small industrially produced cells. For the semi-quantitative extraction solvents as acetonitrile and diethyl carbonate were added to the process and the electrolyte was extracted in almost original composition [11,12]. Disadvantaged of this method are the higher recovery of linear carbonates compared to EC which was retrieved in lower amounts. In addition, the conductive salt was extracted qualitatively and no statement about the concentration can be made. This is demonstrating the challenges in performing a quantitative electrolyte extraction for the entire cylindrical cell. The worldwide increase in electric vehicles indicates the importance for the development of a new quantitative electrolyte extraction approach.

To improve cell lifetime of industrially produced lithium-ion cells, electrolyte degradation reactions have to be investigated further. An electrolyte extraction approach for large format cylindrical cells is necessary to achieve representative separation of the electrolyte from

cell materials. Therefore, a new electrolyte extraction chamber was designed, optimized and validated. With this approach the quantitative electrolyte analysis of lithium-ion cells without excess electrolyte is possible. By extracting the entire cell material, automotive cells with tightly wound electrodes can be analyzed. By liquid-liquid extraction a homogeneous mixture in the developed extraction chamber is formed, leading towards a higher accuracy in the results compared to existing methods. The nonvolatile conductive salt and volatile electrolyte solvents can be analyzed. Furthermore, electrolyte degradation products occurring due to cycling of the cell or thermal aging can be identified and degradation mechanisms can be investigated.

To investigate the electrolyte composition of a lithium-ion cell and to analyze possible degradation reactions numerous detection methods are stated in literature [13–15]. By ion chromatography-mass spectrometry (IC-MS) the concentration of conductive salt LiPF₆ is quantified and ionic organophosphates, which occur due to thermal aging and cycling of the cell, can be identified [16–20]. In literature gas chromatography-mass spectrometry (GC-MS) and high performance liquid chromatography-mass spectrometry (HPLC-MS) are applied to analyze volatile compounds of lithium-ion cell electrolytes and corresponding degradation products [10,21–23].

In this study, we present a quantitative electrolyte extraction approach for large format cylindrical automotive lithium-ion cells that enables the quantitative analysis of conductive salt concentrations and carbonate-based solvents by means of IC-MS and HPLC-MS.

2. Experimental part

2.1. Chemicals

Battery grade electrolytes 1.0 M LiPF₆ in ethylene carbonate (EC) with ethylene methyl carbonate (EMC) 1:1, 1.0 M LiPF₆ in diethyl carbonate (DEC) and EC 1:1 were obtained from Sigma Aldrich (Steinheim, Germany). Lithium hexafluorophosphate was obtained from Merck (Darmstadt, Germany). Deionized water generated by Millipore Milli-Q IQ7000 from Merck (Darmstadt, Germany) and LC-MS grade acetonitrile (Merck, Darmstadt, Germany, 99.9%) combined with formic acid (Avantor, Radnor, USA, 99.0%) was used for HPLC measurements. The following carbonates were obtained from Thermo Scientific (Dreieich, Germany): Dimethyl carbonate (99.0%), ethyl methyl carbonate (98.0%), ethylene carbonate (99.0%), diethyl carbonate (99.0%),

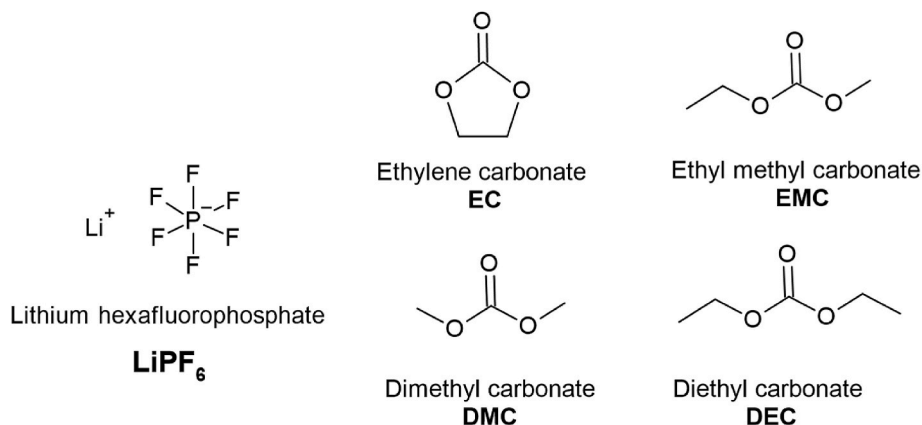


Fig. 1. The chemical formulas of the electrolyte components. The conductive salt lithium hexafluorophosphate (LiPF₆), ethylene carbonate (EC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC) and diethyl carbonate (DEC).

propylene carbonate (99.0%). 2-Butoxyethylacetat (Sigma-Aldrich, Steinheim, Germany, 98.0%) was used as internal standard for HPLC sample preparation. For IC-MS measurements sulfuric acid (97.0%) acetone (99.0%) and sodium carbonate (99.9%) were obtained from Merck (Darmstadt, Germany). Bernd Kraft 1 and 4 multiple element solutions, Yttrium (III) nitrate in HNO₃ 1000 mg/L (Merck, Darmstadt, Germany) and isopropanol (TH Geyer, Renningen, Germany, 99.0%) were used for ICP-OES measurements.

2.2. Cell assembly

The cylindrical automotive battery cells and the utilized electrodes were produced in the pilot plant at BMW Group Munich, Germany. The cylindrical automotive cells used in this research project had a diameter of 46 mm and a height of 95 mm (4695). For this study, LiNi_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC)/Si-Graphite cells were used as active material containing electrolytes with 1.0–1.5 M LiPF₆ in a solvent mixture. The cell assembly was performed in the dry room with a dewpoint lower than – 60 °C. To define the amount of active material per electrode the specific mass loading is implemented, it defines the weight of active material on the current collector in a unit area. In this research the cells consist of one double-sided coated cathode with mass loadings of $m_{\text{NMC}} = 195 \pm 5 \text{ g m}^{-2}$ and one double-sided coated anode with the mass loadings of $m_{\text{Si-Gr}} = 100 \pm 5 \text{ g m}^{-2}$.

For the electrolyte filling the prototype was designed at BMW and constructed at Alpha Modellbau GmbH (Munich, Germany). By using this new prototype for the electrolyte filling, cylindrical automotive cells can be filled with electrolyte on a laboratory scale. A schematic representation of the prototype is shown in Fig. 2. For comparison of the electrolyte amount with other cell formats and a variation of cell chemistries the electrolyte amount filled into the cell was defined as mass divided by electric charge per time (g/Ah). The cells were filled with at least 1.3 g/Ah of electrolyte. For the filling process the cells were placed into the prototype and vacuum was applied. The connection to the electrolyte reservoir was opened and the cell was filled with electrolyte. The electrolyte filling was performed in an argon filled glovebox with H₂O and O₂ values below 1 ppm. After the assembly the cells were dried in a vacuum chamber for 12 h at 45 °C and cooled to room temperature.

Following the electrolyte filling the cell is wetted to distribute the electrolyte evenly through the jelly roll. In the wetting process the cell was sealed temporarily and stored in a vacuum chamber alternating between 10 mbar and atmospheric pressure for 1 h. Afterwards a 5 bar argon pressure was applied to the cell for 1 h. To complete the wetting process the cell was sealed temporarily and stored in a drying chamber

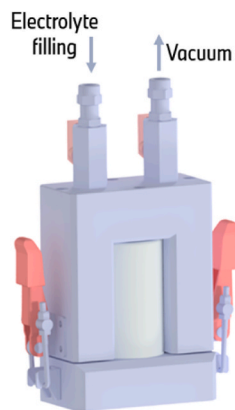


Fig. 2. Schematic representation of electrolyte filling prototype consisting of polyether ether ketone (PEEK) housing for large format lithium-ion cells. Two valves for vacuum and electrolyte filling are implemented in the lid to decrease the pressure before the filling of the electrolyte.

overnight.

2.3. Cell formation

After the electrolyte filling a computer tomography (CT) scan was performed for the visualization of the excess electrolyte. For the pre-charge the cells were charged with 0.1 C (C, battery capacity) for $\approx 2 \text{ h}$ to 3.3 V resulting in $\approx 25 \%$ state of charge (SOC) using constant current (CC). Afterwards the cells were sealed in the dry room. For the formation the cells were charged with 0.1 C for $\approx 8 \text{ h}$ to 4.2 V (100 % SOC) using constant current-constant voltage (CC-CV). The current was set at 4.2 V for 1 h and afterwards the cells were discharged to 2.8 V with 0.1 C (CC). Precharge and Formation were performed by MACCOR series 4000 in a climate chamber (Li plus GmbH) at 25 °C.

2.4. Cell disassembly

The cell disassembly was performed in a glovebox under argon atmosphere. The cap was separated from the can and all surrounding isolations were removed. The jelly roll, consisting of the tightly wound anode and cathode was disconnected from the discs and all tapes were removed. Current collectors, made of a thin aluminum (cathode) and copper foil (anode) were separated from the jelly roll to prevent ripping of the electrodes during extraction process.

2.5. Electrolyte extraction

The electrolyte extraction was performed in an airtight electrolyte extraction chamber (Fig. 3). The prototype was designed at BMW and built at Alpha Modellbau GmbH. The extraction chamber was made of polyetheretherketone (PEEK) and the lid had a Perfluoroalkoxy (PFA) inlet for an overview during the extraction. These materials were chosen due to their chemical resistance and durability towards the electrolyte and organic extraction solvents. For transmitting the rotation from the handle to the bar a T20 Torx was implemented in the lid and a matching screw was placed into the bar inside the chamber. To ensure the jelly roll was secured in its place while rewinding, place holders were implemented on both sides of the chamber.

The extraction chamber was dried at 60 °C in a vacuum chamber and transferred to a glovebox with argon atmosphere for the extraction process. For the extraction the first winding of the jelly roll was rewound. The electrodes and separators were attached to the bar below the handle and the jelly roll was hold in place on the left side. Extraction solvent mixtures with internal standard were filled into the chamber and the lid was sealed. The jelly roll was completely rewound using the handle of the chamber and extracted in the solvent. Preliminary experiments were performed demonstrating that an extraction period of 48 h is needed to achieve a homogeneous mixture of the electrolyte and the solvent. To decrease the necessary extraction time the chamber was placed on a shaker while shaking at 10 osc/min. An aliquot of the electrolyte extract was collected with a syringe through a septum in the lid of the chamber to perform the analysis.

2.6. Multiple extraction by centrifuge

For increasing the recovery results achieved with the extraction chamber further, a multiple extraction by centrifuge was performed. For multiple extraction, the cell material was centrifuged after the extraction process in the extraction chamber with 15 mL of DMC. The solvent was decanted after each extraction step and analyzed by HPLC-MS and IC-MS. 15 mL of fresh DMC was added to the electrodes and the process was repeated two times. Each sample was analyzed separately, and the quantified amounts of each analyte were added up. The cell materials were centrifuged at 8000 rpm for 10 min at 25 °C. The multiple extraction was performed in a Biofuge Stratos High Speed by Thermo Scientific. Anode and cathode materials were separated from the cell

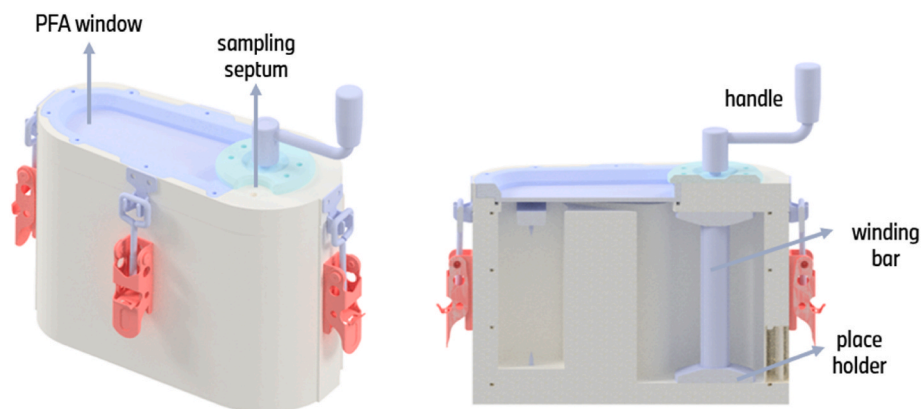


Fig. 3. Schematic representation of electrolyte extraction prototype for large format cylindrical cells consisting of PEEK and a PFA window. The jelly roll is placed in the extraction chamber and rewound by the handle until the electrodes are completely wrapped around the winding bar. Electrolyte aliquot can be collected through the sampling septum.

materials inside the glovebox.

2.7. High performance liquid chromatography - mass spectrometry (HPLC-MS)

The liquid chromatography studies were performed on a Thermo Scientific™ Vanquish HPLC connected to a Thermo Scientific™ Orbitrap Exploris™ 120. The HPLC gradient system consists of a Vanquish™ Core Binary LC (Thermo Fisher Scientific GmbH, Dreieich, Germany) consisting of Vanquish binary pump, an Vanquish autosampler, a Vanquish column compartment and a Vanquish diode array detector) controlled by the Thermo Scientific™ Xcalibur™ software (version 4.6). Heated electrospray ionization (ESI) at 2.0 kV was used to ionize the analytes. The samples were analyzed in positive and negative mode in a low mass range m/z 40–200 and high mass range m/z 150–1500. By MS² mode fragmentation of the analytes were investigated and the collision energy was set to 15%. For appropriate MS/MS detection the ionization parameters were optimized by continuous infusion of standard solutions containing the carbonates: Dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), ethylene carbonate (EC). The data was evaluated with the Software Trace Finder™ 5.1 General Quan (Thermo Scientific™) and Compound Discover™ 3.3 SP2 (Thermo Scientific™).

A gradient of water with 2% acetonitrile and 0.02% formic acid (solvent A) and acetonitrile with 5% water and 0.02% formic acid (solvent B) with a flow rate of 0.4 mL min⁻¹ was used. The gradient started with 100% of solvent A for 1 min. Afterwards solvent B was increased to 100% over 9 min. This solvent mixture was hold for 1 min. Solvent B was decreased to 0% in 1 min and hold at 100% solvent A for 4 min. A pentafluorophenyl column (F5) from Raptor™, with a pore diameter of 2.7 μm from RESTEK (150 × 2.1 mm) was used for the quantification. The column was heated to 45.0 °C and the injection volume was 1.0 μL for each sample. The determination coefficient (R^2) was determined for the quantification of DMC ($R^2 > 0.999$), EMC ($R^2 > 0.998$), DEC ($R^2 > 0.999$) and EC ($R^2 > 0.999$) using an external seven-point calibration in a range of 0.2 g L⁻¹ to 10 g L⁻¹. A stock solution for quantification of DMC (0.3 g), EMC (0.3 g), DEC (0.3 g), EC (0.3 g) was prepared in acetonitrile (10 mL) and sequentially diluted 1 + 1. Electrolyte samples were diluted 1:200 and extraction samples 1:20 in dry acetonitrile inside the glovebox and sealed airtight.

2.8. Ion chromatography – mass spectrometry (IC-MS)

Ion chromatography (IC) was performed using Professional IC AnCat MSM-HC MCS by Metrohm (Filderstadt, Germany) controlled by MagIC Net Version 3.3. The IC was coupled to a 6130 single quadrupole from

Agilent Technologies operated by OpenLabs CDS 5.0. MS. The anionic flow was transferred into the mass spectrometer and an ESI-MS with 3 kV in the negative mode a range of m/z 50–300 was performed. For MS detection of the anionic flow the ionization parameters were improved by continuous infusion of standard solutions containing the anion hexafluorophosphate (PF₆) of the conductive salt.

For the quantification of the conductive salt LiPF₆ a conductivity detector was used and an external six-point calibration for Li⁺ ($R^2 > 0.999$) and PF₆⁻ ($R^2 > 0.999$) in the range of 0.1–2.0 mol L⁻¹ was prepared. The injection volume for the cationic column was set to 10 μL and for the anionic column to 20 μL. Preliminary experiments, investigating a variety of conductive salts resulted in optimized chromatography parameters. Therefore, 2 mM HNO₃ in water was used for the cationic eluent with a flow rate of 0.9 mL min⁻¹ 10 mM NaHCO₃ in an aqueous solution with 30% acetone was used for the anionic eluent with a 0.7 mL flow rate. For the anionic ions a chemical suppression was applied, decreasing the background conductivity of the eluent and optimizing the signal to noise ratio. Separation of the positive ions was achieved on a Metrosep C4 100/4.0 column using a Metrosep C4 Guard 4.0 column. The separation of the negative ions was performed on a Metrosep A Supp 5–250/4.0 column using Metrosep A Supp Guard 4.0 column. The column oven for the anionic and cationic column was set to 55 °C. The sample was diluted 1:1000 in water and membrane filtered via an 0.45 μm PTFE syringe filter.

2.9. Inductively coupled plasma – Optical emission spectroscopy (ICP-OES)

ICP-OES measurements were performed on a Spectro Acros (AME-TEK) instrument by Spectro Analytical Instruments GmbH (Kleve, Germany) controlled by Analyzer Pro Version 1.40. The samples were injected into the Noordemeer crossflow nebulizer and the aerosol was separated in the quartz twister spray chamber with helix (Scott type) from Spectro. A radial plasma viewing set-up was used with a one-piece quartz torch (1.2 mm injector, Spectro). A sample flow rate of 1 mL min⁻¹ was applied with isopropanol as solvent. The elements were detected at the following wavelengths: Li: 670.780 nm P: 178.287 nm Cu: 327.396 nm. The samples were diluted in isopropanol (1:2000) and yttrium (III) nitrate as internal standard (0.5 mL) was added, which acts as the reference value within the analyzed samples.

2.10. Computer tomography (CT)

CT measurements were performed on a Yxlon comet FF35 CT. The system was equipped with a Yxlon Comet fine focus/micro focus directional tube FXT 225.48 and a digital flat image detector 4343CT

with CsI scintillator. Data reconstruction and visualization was conducted using VGStudio Max 3.5 by Volume Graphics. Electrolyte visualization was performed by gray-level analysis. The cells were scanned with a current of 400 μ A and 225 kV. The data was collected in a 2860 \times 2860 pixel matrix and a voxel size of 0.0518 \times 0.0518 mm with a pixel size of 150 μ m.

3. Results and discussion

3.1. Development of a chamber for extraction of a cylindrical cell

For quantitative electrolyte analysis of lithium-ion cells in order to investigate aging mechanisms, it is necessary to be able to take a liquid electrolyte sample from the cell. Especially in automotive cells, the amount of electrolyte added to the cell in the production process is reduced to a minimum. Usually, no excess electrolyte can be found in the large format cylindrical lithium-ion cells (4695) after the formation process. Conducting a quantification of the main electrolyte components like the conductive salt and the solvents is becoming impossible.

An electrolyte extraction from cell materials is necessary to perform the electrolyte analysis. The method described in literature for the extraction of cylindrical cells (1865) by *Gritzke* et al. [11] using a flow through supercritical CO₂ extraction can only be adapted to large format cells (4695) to a limited extend. The amount of electrodes in large format cells and the tightly wound jelly rolls set a limit on this extraction method. Furthermore, the approach describes a semi-quantitative method only giving qualitative information about the conductive salt. No method is known in literature for the quantitative electrolyte analysis of large format cylindrical lithium-ion cells.

A new electrolyte extraction chamber for cylindrical lithium-ion cells was designed. This approach provides a tool for mapping the electrolyte in cylindrical lithium-ion cells and can give a deeper understanding of the electrolyte composition. An advantage toward existing methods is the accuracy in the quantification results the developed method offers. Additionally, by extracting the entire cell the method can be adapted towards automotive lithium-ion cells. Furthermore, volatile and nonvolatile electrolyte components can be analyzed with the extraction chamber enabling the quantification of the conductive salt and the electrolyte solvents. Making this the first method, which can quantify the complete electrolyte composition of the electrolyte. With the developed approach electrolyte aging mechanisms can be investigated and further studies could therefore enhance the cell lifetime and improve the performance in automotive cells.

3.2. Development of an electrolyte filling tool

The production of a lithium-ion cell is finalized with the formation of the cell after the electrolyte filling. Screening a variety of electrolytes for research purposes isn't implementable into an automotive lithium-ion cell production. The developed tool enables the electrolyte filling for a single cell separate from the production line, by using a vacuum filling method. For this research an electrolyte filling tool was developed (Fig. 2) which allows the electrolyte filling, using laboratory equipment.

For the electrolyte filling process the cell is connected to the tool and vacuum is applied. Afterwards the electrolyte was filled into the cell from an electrolyte reservoir. This process was repeated until the desired amount of electrolyte was added to the cell.

The electrolyte filling process and the formation are coordinated to reduce the time at low potentials and decrease the risk of copper dissolution during the cell production [24]. To verify the concept of the extraction chamber, electrolytes of cylindrical automotive cells were analyzed before the formation process. The cells were produced without electrolyte and filled in the laboratory 24 h before the cell was extracted. The development of the new extraction tool is associated with the advantage that cylindrical cells could be filled with electrolyte separately. By means of this process the time between the electrolyte filling

and the extraction process was kept to a minimum, decreasing the risk of copper dissolution. Additionally, the copper dissolution could distort the electrolyte analysis results described in section 3.3.

Further research projects working with automotive cells could use the developed method for screening a variety of electrolytes on an industrial scale lithium-ion cell.

3.3. Effect of the extraction solvent on the electrolyte composition

First preliminary experiments were performed to identify the optimum conditions for the electrolyte extraction. The liquid-liquid extraction is mainly effected by the extraction solvent and the extraction time. Four different extraction solvents mixtures: Acetonitrile (ACN), acetonitrile/propylene carbonate (PC) (1:3), ACN/PC (3:1) and DMC were investigated and the achieved recovery for each electrolyte component is displayed in Fig. 4.

ACN as a polar solvent lead to a recovery for ethylene carbonate (EC) and ethyl methyl carbonate (EMC) in an almost original composition (EC = 78.8% and EMC = 75.6%). A significant distinction between the conductive salt components (Li⁺ = 40.2% and PF₆⁻ = 83.5%) could be observed. To increase the polarity of ACN and enhance the dilution of the conductive salt a mixture of ACN/PC (3:1) was used. Compared to the extraction with ACN higher recoveries for the conductive salt components (Li⁺ = 57.8% and PF₆⁻ = 87.4%) could be reached. The difference between the conductive salt components was still significant but decreased compared to the extraction using only ACN as the solvent. To increase the polarity of the extraction solvent further a mixture ACN/PC (1:3) was used. Overall, a lower recovery for the volatile carbonates (EC = 60.6%), (EMC = 69.5%) and the nonvolatile conductive salt (Li⁺ = 64.3%), (PF₆⁻ = 72.2%) could be observed. During the liquid-liquid extraction, the solvent dilutes the electrolyte from the cell material. The viscosity of PC (η = 2.15 mPa s) is significantly higher than the viscosity of acetonitrile (η = 0.33 mPa s). So it was deduced that the extractant with an increased proportion of PC is not able to extract the electrolyte from the cell materials due to its higher viscosity [5,25,26].

IC-MS measurements displayed a lower recovery for the cation lithium (Li⁺) compared to the anion hexafluorophosphate (PF₆⁻) using ACN as a part of the extraction solvent (Fig. 4). Indicating the solvation of a second cation in the extracted electrolyte. ICP-OES measurements confirmed the presence of copper in the electrolytes extracted with

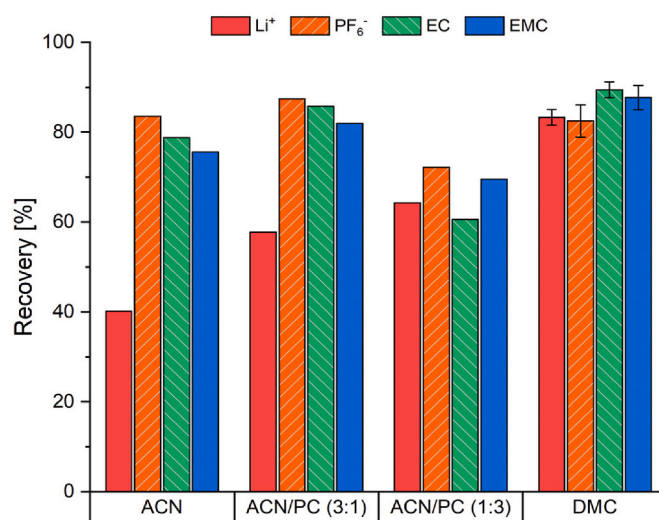


Fig. 4. Recovery [%] for the liquid-liquid electrolyte extraction of large format cylindrical automotive lithium-ion cells using various extraction solvents. All experiments were performed, using 1 M LiPF₆ in EC EMC (1:1) and an extraction time of 48 h. The solvent (DMC) achieved the highest recoveries and was analyzed in three repeated extractions before used in the following experiments as standard extraction solvent.

acetonitrile. The hexafluorophosphate can form an inorganic complex in presence of copper oxide (ICP-OES and HPLC-MS results are attached in the supplementary information Fig S1 and Fig S2). It can be concluded that during the liquid-liquid electrolyte extraction the copper foil of the anode current collector could be oxidized which initiates the reaction shown in Fig. 5 [27]. Resulting in the formation of a copper-hexafluorophosphate complex. The solvation of this complex is favored in ACN indicated by the ICP-OES measurements. In Fig. 4 it can be observed that the Li^+ amount in the electrolyte extract increases by lowering the amount of ACN used as extraction solvent. It can be concluded that ACN is not an appropriate extraction solvent for the conductive salt LiPF_6 .

DMC is known in literature to show high solubility towards LiPF_6 and was therefore investigated as an extraction solvent [28]. By using DMC for the extraction, recoveries of $83.3 \pm 1.7\%$ for the lithium cation and $82.5 \pm 3.6\%$ for the hexafluorophosphate anion as well as $89.4 \pm 1.7\%$ for EC and $87.7 \pm 2.7\%$ for EMC could be achieved. Drawbacks of this solvent include that the DMC content in electrolytes can not be determined. In addition, the degradation process transesterification can result in an increased amount of DMC in the electrolyte, which can not be identified using this method [8].

The liquid-liquid extraction results are significantly effected by the solvents. ACN as part of the extraction solvent leads to the solvation of a cationic complex decreasing the recovered amount of Li^+ . Quantification of the conductive salt couldn't be performed with extraction solvents including ACN and were therefore not used in further studies. DMC as a solvent lead to the highest recoveries within the tested solvents and will be used in the following experiments. Additionally, DMC as extraction solvent allowed the quantification of all electrolyte components.

3.4. Recoveries for electrolyte amount by means of the extraction chamber approach

To give a statement about the electrolyte composition for large format cylindrical lithium-ion cells a quantitative electrolyte extraction of the cell materials is necessary. The electrolyte could be recovered in almost original composition from the cell using DMC as extraction solvent. Afterwards, a multiple extraction is performed to recover the electrolyte remaining in the cell materials. Therefore, the cell was extracted in the developed extraction chamber, followed by three extraction steps in which part of the electrodes (cathode and anode) were centrifuged using the extraction solvent DMC (Fig. 6).

Performing a multiple extraction showed, that a certain percentage of electrolyte components remains in the electrodes after the liquid-liquid cylindrical lithium-ion cell extraction. By multiple extractions the recoveries of the conductive salt components Li^+ could be increased from 83.3% to $96.0 \pm 6.8\%$ and for PF_6^- from 82.5% to $98.8 \pm 9.4\%$. Furthermore, the recovered amount of EC from the electrolyte was increased up to $98.9 \pm 1.1\%$ by multiple extractions. Using this multiple extraction method the recovered EMC remains at $87.7 \pm 2.7\%$ due to the lower vapor pressure of the solvent it evaporates during the sample preparation. The solvent evaporates during the sample preparation and cannot be quantified by means of HPLC-MS. By performing a multiple extraction of the cell components, the electrolyte could be extracted in almost original composition. The lower recovery of EMC could be leading towards the assumption of a lower EMC concentration in the original electrolyte. Further methods for multiple extraction could be investigated aiming towards the recovery of all electrolyte

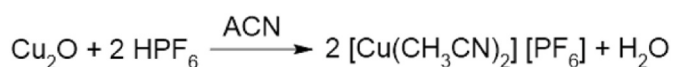


Fig. 5. Reaction of copper oxide with hexafluorophosphate in acetonitrile to a copper-acetonitrile complex with an anionic hexafluorophosphate component and water.

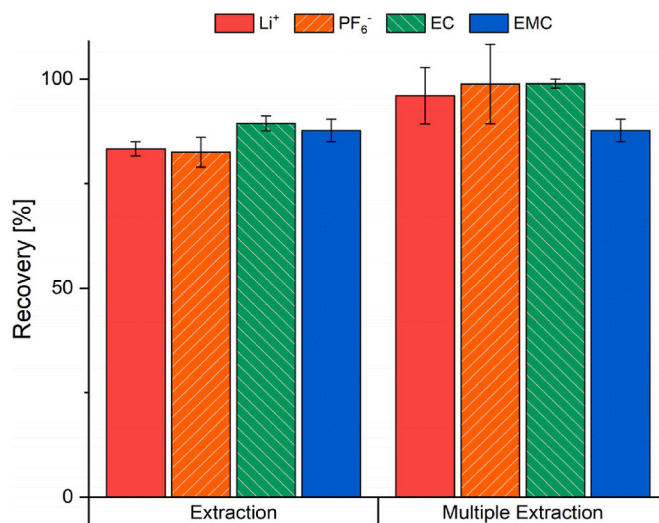


Fig. 6. Recovery [%] for the liquid-liquid electrolyte extraction and after the multiple extraction of large format cylindrical automotive lithium-ion cells. For the multiple extraction the cell was extracted in the developed extraction chamber followed by three extraction steps in which the electrodes were centrifuged in DMC (15 mL). Afterwards the samples were analyzed, and the analytes were added up. EMC could not be analyzed by means of multiple extraction due to evaporation of this component.

components. The partly incomplete electrolyte extraction of the conductive salt and EC after the multiple extraction could be a result of the electrolyte loss during the cell opening. Cell housing and current collectors could contain electrolyte, which are removed in the process for preparing the cell for electrolyte extraction.

By means of multiple extraction it was found that a part of the electrolyte remains in the electrodes after the extraction performed with the extraction chamber. By conducting the multiple extraction, the electrolyte can be recovered in almost original composition. As stated in chapter 3.3 the presented liquid-liquid extraction with the newly developed extraction chamber leads to representative results by using the extraction solvent DMC. The results of the multiple extraction underline these findings by increasing the recovery further. An advantage of the newly developed method is the high extraction efficiency. In further studies electrolyte aging in lithium-ion cells could be investigated to understand electrolyte aging processes.

3.5. Effect of the extraction method on different electrolytes

For validation of the electrolyte extraction method multiple electrolytes with different solvents systems and conductive salt concentrations were investigated. Since this method is intended to cover a wide range of applications two conductive salt concentrations (1 M LiPF_6 and 1.5 M LiPF_6) and a variation of carbonate compositions (EMC and DEC) were tested. For authentication of the presented results every analyzed electrolyte was extracted from three identical large format cylindrical automotive lithium cells.

For the analysis of a variation in carbonates, diethyl carbonate (DEC) was used as an electrolyte component (Fig. 7). By performing the liquid-liquid electrolyte extraction with a variation in carbonates it was found that similar recoveries for all electrolyte components could be achieved. Indicating that the developed extraction method could be used for a variety of electrolyte solvent. The authors are aware that DMC can not be analyzed as a solvent using the developed extraction method. For this purpose, further research would have to identify solvents which dissolve the electrolyte components from the cell materials to the same extent but are not a component of the electrolyte system.

In a second step, the effect of the conducting salt concentration was

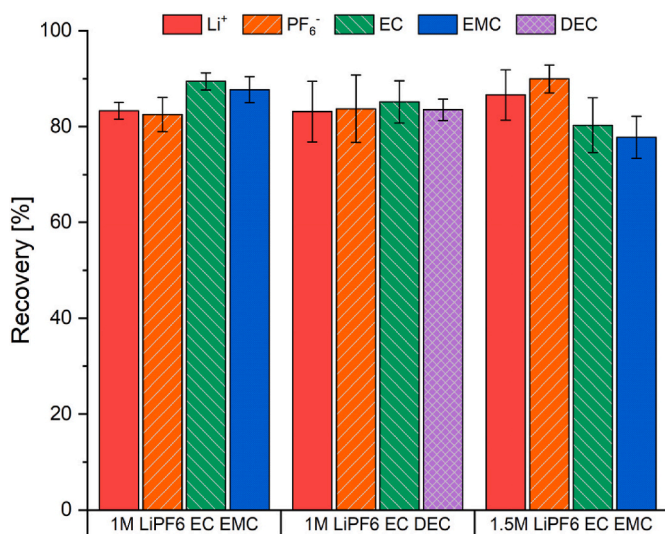


Fig. 7. Recovery [%] for the liquid-liquid electrolyte extraction of large format cylindrical automotive lithium-ion cells filled with different electrolytes (1 M LiPF₆ in EC EMC (1:1); 1 M LiPF₆ in EC DEC (1:1); 1.5 M LiPF₆ in EC EMC (1:1)) extracted in DMC. The recovered conductive salt amount was analyzed by IC-MS and the solvents were quantified by HPLC-MS.

investigated, in which case the LiPF₆ concentration was increased to 1.5 M (Fig. 7). Industrially used electrolytes seem to increase the amount of conductive salts used in automotive lithium-ion cells [4,29]. The increase in conductive salt concentration showed no significant difference in the determined recoveries for the analyzed electrolyte components.

By conducting the liquid-liquid extraction for cylindrical cells with a variety of electrolytes it was found that the developed method could be utilized for different types of electrolytes. These findings indicate a broad application range for further research projects and industrially produced cells.

3.6. Extraction of a cell after formation

In this chapter the electrolyte of a large format cylindrical lithium-ion cell is quantitatively analyzed by means of the developed liquid-liquid extraction method after the formation process. This is intended to represent the first application of the developed tool and highlight the technical opportunities but also point out limits of the method. A cylindrical lithium-ion cell was filled with 1 M LiPF₆ in ethylene carbonate (EC) and ethyl methyl carbonate (EMC) (1:1) electrolyte and formation protocol was applied. For authentication of the results the analyzed electrolyte was extracted from two identical large format cylindrical automotive lithium cells after the formation process. The excess electrolyte amount was visualized by computer tomography (CT) before and after the formation [30]. Fig. 8 left shows the excess electrolyte present in the mandrel and between the current collectors at the top and bottom of the cell, after the filling process. Therefore, a gray layer analysis by means of CT was performed highlighting the excess electrolyte in light blue. The right side (Fig. 8) shows the cell after the formation and the excess electrolyte is limited and concentrated in the mandrel. Indicating the necessity of the electrolyte extraction from the cell materials to perform a quantitative electrolyte analysis of the large format cylindrical cell.

After the formation process the cell was extracted with DMC using the developed extraction tool (Fig. 9). It could be observed that the conductive salt components could be retrieved in similar amounts (Li⁺ = 81.2 ± 4.4%) and (PF₆⁻ = 79.3 ± 3.5%). During the formation process the solid electrolyte interface (SEI) was build as a protective layer on the anode, which consists of electrolyte degradation products [31]. It can be conducted that the detected reduction of the conductive salt was a result of the SEI formation. The solvent EC exhibits a recovery of 85.1 ± 8.1% after the formation process. EMC can be analyzed with a recovery of 73.2 ± 10.5% which was significantly below the recovery for a filled cell. The diminished recovery of the solvent could be explained by degradation reactions during the formation of the lithium-ion cell. The linear carbonate EMC can initiate the transesterification in which the end groups of the carbonates are exchanged reacting to DMC and EMC [32]. Petibon et al. [8] reported the transesterification in a 1 M LiPF₆

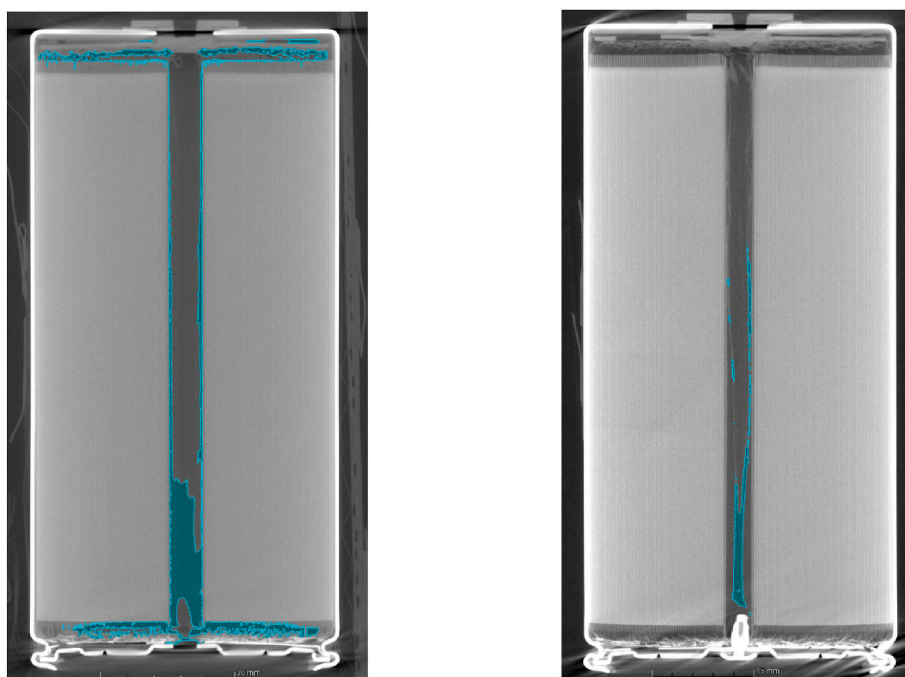


Fig. 8. Computer tomography scans of large format cylindrical automotive cells with the excess electrolyte highlighted in blue. **Left:** Cell after electrolyte filling (no cycling); **Right:** Cell after the formation process with little excess electrolyte. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

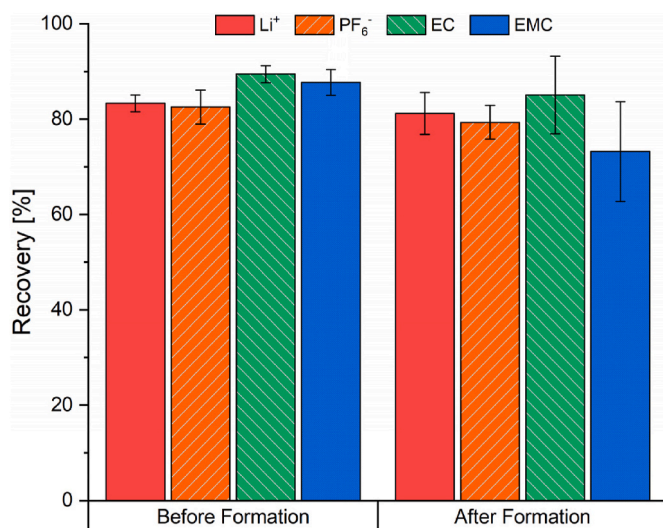


Fig. 9. Recovery [%] for the liquid-liquid electrolyte extraction of large format cylindrical automotive lithium-ion cells after the electrolyte filling (no cycling) and after the formation process. The cell was filled with 1 M LiPF₆ EC/EMC 1:1 electrolyte and extracted after the formation with DMC.

EC/EMC electrolyte starting at a cell potential of approximately 2.8 V. The reaction of EMC towards DMC and DEC during the formation process is displayed in Fig. 10. It was expected that 1 wt% of EMC will degrade into 0.57 wt% of DEC and 0.43 wt% of DMC within the transesterification.

In the performed cell formation, the transesterification can be observed partly with the developed electrolyte extraction method. By means of HPLC-MS the DEC amount was analyzed in the original electrolyte and compared with the electrolyte after the formation process. Fig. 11 shows the signal for DEC ($m/z = 119.0703$) in the original electrolyte 1 M LiPF₆ EC/EMC (1:1) (black) and the MS² spectrum for DEC, confirming the absence of DEC in the original electrolyte. After the formation a substantial amount of DEC was identified in the extracted electrolyte.

Due to the use of DMC as solvent in the developed electrolyte extraction method the DMC which may be formed during the transesterification cannot be quantified by HPLC-MS. By using the calculation suggested by Petibon et al. [8], the formed amount of DMC could be calculated.

By using electrolyte additives, for example vinylene carbonate (VC) or fluoroethylene carbonate (FEC), SEI formation can be enhanced. Hereby VC reacts in a polymeric reaction improving the stability of the SEI. Furthermore, with the use of film formers the transesterification of the carbonates can be reduced [33].

Further electrolyte degradation reactions which can be initiated through electrochemical or thermal aging include the oligomerization of carbonates [34]. Here a ring opening reaction of EC followed by a reaction with linear carbonates can produce the oligomeric carbonates. In this reaction the end groups of the linear carbonates effect the resulting oligo carbonates [13]. In Fig. 12, the HPLC-MS chromatograms of 2,

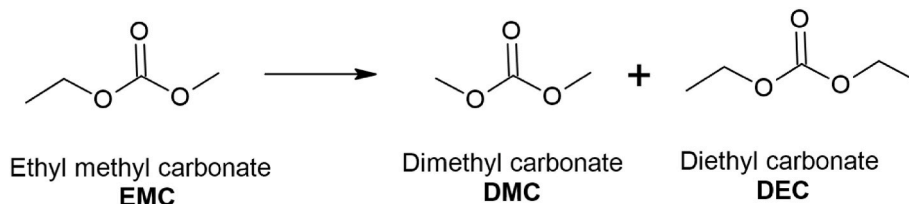


Fig. 10. Transesterification reaction of ethyl methyl carbonate (EMC) to dimethyl carbonate (DMC) and diethyl carbonate (DEC) due to thermal or electrochemical aging of the electrolyte.

5-dioxahexanedioic acid dimethyl ester (DMDOHC), 2,5-dioxahexanedioic acid ethyl methyl ester (EMDOHC) and 2,5-dioxahexanedioic diethyl ester (DEDOHC) are displayed [34]. These findings confirm the identification of electrolyte degradation products with the developed extraction method for large format cylindrical lithium-ion cells.

4. Conclusion and outlook

In this study a quantitative electrolyte extraction method for large format cylindrical automotive lithium-ion cells was presented. A new electrolyte extraction chamber for cylindrical cells which extracts the electrolyte from the cell materials was developed, optimized and validated. This research presents the first method for the quantification of all electrolyte components including volatile and nonvolatile compounds in automotive lithium-ion cells.

The effect of different extraction solvents on the electrolyte composition was investigated, resulting in the finding that DMC lead towards the highest recoveries within the tested solvents. Due to multiple extraction by centrifugation of the cell materials the electrolyte recovery could be increased further. Investigating a variety of electrolytes containing different electrolyte solvents and a range of conductive salt concentrations displayed the wide application for the developed liquid-liquid extraction method. The developed approach can be implemented at research projects from universities using a wide variety of electrolyte compositions or on industrial lithium-ion cells with increased conductive salt amounts. By performing the first quantitative electrolyte analysis on an automotive cylindrical cell after the formation the applicability of the developed method could be presented. Furthermore, it was indicated that degradation products formed in the formation process can be identified using the developed tool.

By means of the presented extraction method, electrolyte can be extracted from large format cylindrical automotive cells and excess electrolyte is no longer the limit for quantitative electrolyte analysis. Further research projects can take up this method including the electrolyte analysis of aged lithium-ion cells, which didn't use to be possible due to the lack of excess electrolyte. Investigations on the electrolyte aging mechanisms, aging due to fast charging or performance loss can be conducted and the effect that the electrolyte has on the different aging process can be quantitatively studied. The electrolyte is a key factor in the aging process of the large format automotive cells and can be analyzed using the developed method.

CRedit authorship contribution statement

Sabrina Schönemeier: Writing – original draft, Visualization, Validation, Methodology, Investigation, Data curation, Conceptualization. **Verena Peters:** Writing – review & editing, Methodology, Conceptualization. **Fabian Horsthemke:** Writing – review & editing. **Heewoo Seo:** Investigation, Data curation. **Frank-Michael Matysik:** Writing – review & editing, Supervision.

Declaration of competing interest

The authors declare that they have no known competing interest or

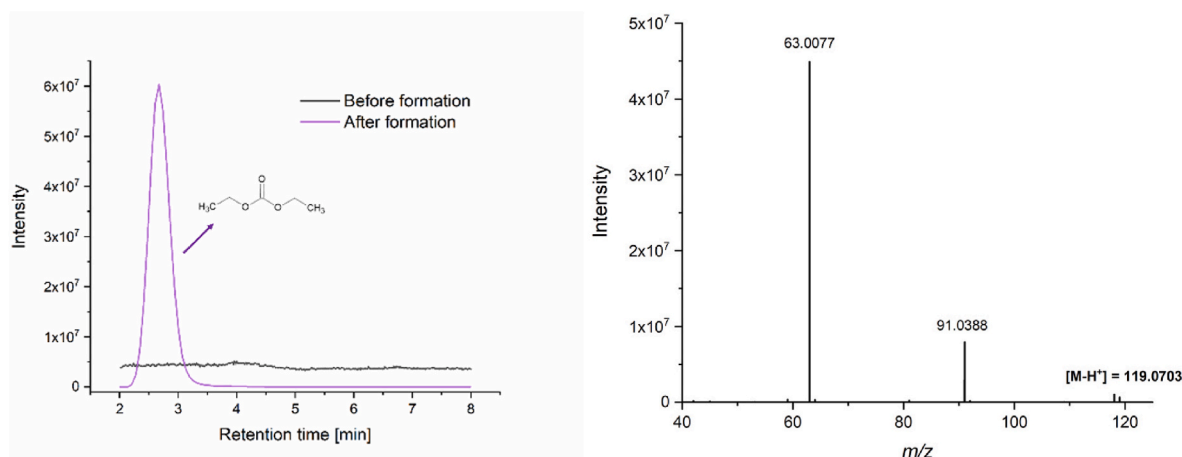


Fig. 11. Left: HPLC-MS signal of the original electrolyte (1 M LiPF₆ EC/EMC (1:1)) in black and the formed DEC in the extracted electrolyte after the formation process in purple. **Right:** HPLC-MS² spectrum for the formed DEC ($m/z = 119.0703$). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

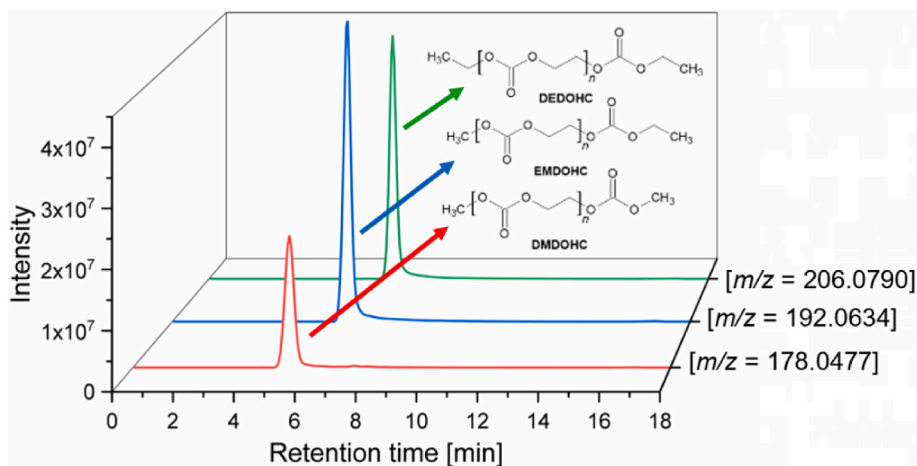


Fig. 12. HPLC-MS studies of the formed oligo carbonates (2,5-dioxahexanedioic acid dimethyl ester (DMDOHC) - red, 2,5-dioxahexanedioic acid ethyl methyl ester (EMDOHC) - blue and 2,5-dioxahexanedioic diethyl ester (DEDOHC) - green in the extracted electrolyte after the formation process. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2024.343530>.

Data availability

Data will be made available on request.

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