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Defining Aging Marker Molecules of 1,3-Propane Sultone for Targeted Identification in Spent $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$||AG Cells

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Herein we report on an analytical approach for targeted identification of hazardous 1,3-propane sultone (PS) in spent lithium ion battery material. PS decomposition is investigated with chromatographic techniques coupled to high-resolution accurate mass spectrometry. Speciation of sulfur-containing decomposition products is performed and aging marker molecules are defined. The observed PS decomposition results in characteristic 1-propanesulfonate via electrochemical ring-opening. Based on this, 1-propanesulfonate is defined as an ionic marker molecule for electrochemical PS decomposition. Further, volatile methyl and ethyl esters of 1-propanesulfonate are identified. Their formation is observed mainly caused by elevated temperatures after preceding PS ring-opening during cell formation. Both, ionic and volatile decomposition markers can be applied for targeted identification of hazardous PS-containing lithium ion battery material, despite possible consumption of the initial additive molecule.

1. Introduction

Lithium ion batteries (LIBs) are seen as one of the key technologies for a decarbonized 21st century. Powering electric vehicles and storing energy in grid storage systems, LIBs enable reduction of fossil fuel combustion without electricity or mobility shortage.[1,2]

Ongoing research in the field of LIBs led to various, application tailored, electrode chemistries, enabling long life, high energy, high power, high and low temperature and high safety batteries.[3,4] For most of these cell chemistries, the basic organic carbonate-based electrolyte constitution remained the same.[5–7] However, various additives were reported, enabling, among others, improved voltage ranges, enhanced interphase formation or lowered flammability. Chemically, LIB electrolyte additives range from aromatic compounds over unsaturated species to hetero atom-containing nitriles or sultones.[6,8–13]

Despite limited use in state-of-the-art electrolyte mixtures, hazardous sultone-based additives play a significant role in spent LIBs returns from the last decades.[9,14–17] Therefore, identification e.g., of 1,3-propane sultone (PS) and its decomposition is helpful for reverse engineering approaches regarding cell history.[18] Herein, subjects like original equipment manufacturer (OEM) assignment or risk assessment can play an important role. The carcinogenicity of PS is described for more than half a century and also formed decomposition species should be treated as possible dangers.[19,20] For evaluation of cell histories, the identification of electrolyte additives is inevitable in order to trace back the original cell composition. However, analysis of film–forming agents is challenging and may be limited to aging markers, due to possible quantitative decomposition during cell operation.[21] Moreover, the low amounts of additive addition require sensitive an selective methods. For optimal speciation analysis, chromatographic separation with subsequent mass spectrometric (MS) detection is needed.[22,23]

In this work we report an analytical approach towards understanding of sultone additive aging and utilization of gained insights for targeted analysis of sultone species despite consumption of the original additive molecule. Literature presumed aging mechanisms of PS were evaluated and clarified regarding electrochemical and thermal influence.[9,16,24–26] Ion and gas chromatographic techniques with high-resolution accurate mass spectrometry (IC/GC-HRAM-MS) detection were utilized to identify ionic and volatile aging markers of PS. These markers enable sensitive and selective target analysis of possibly hazardous sultone-based compounds in aged LIB material.

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2. Experimental Section

2.1. Chemicals

The applied base electrolyte containing ethylene carbonate (EC), ethyl methyl carbonate (EMC) and $\mathrm{LiPF_6}$ was obtained from Solvionic (France). Methanol (99.8%), sodium 1-propanesulfonate monohydrate (99%), dichloromethane (DCM, 99.8%), and 1-propanesulfonyl chloride (97%) were obtained from Merck (Germany). Acetonitrile (ACN, >99.9%) and Ethanol (96%) were purchased from VWR (Germany) and PS (battery grade) was purchased from BASF (Germany). 1-propene-1,3-sultone (PES, >99%) was obtained from TCI (Germany).

2.2. Electrolyte Aging

To investigate sultone additive decomposition, thermal and electrochemical aging, as well as a combination of both, were performed. An overview of the aged electrolytes and their respective aging conditions is displayed in **Table 1**. The used electrolytes "EL_x" consisted of 1 M LiPF6 in a mixture of EC and EMC (3:7 (w/w)) with addition of 2 wt% of the sultone additive. The aging conditions were applied for PS addition and comparative analysis with PES.

The electrochemical aging was performed in commercially available $\mathrm{LiNi_6Co_{0.2}Mn_{0.2}O_2}$||artificial graphite two electrode pouch cells (Li-Fun Technology, China). The obtained cells were dried at 80 °C under reduced pressure. Afterwards, they were filled with 700 μL of electrolyte and sealed for 5 s at 165 °C under reduced pressure. All cells were wetted for 10 h. Cell formation was obtained in two cycles at C/5 constant current (CC) charge rate up to 4.2 V, a constant voltage step (CV) until the current dropped below C/20 and CC discharge to 3.0 V. Cells that underwent further cycling were degassed, resealed and cycled with 1 C CC/CV ($C < C/10$) charge and CC discharge in a voltage range from 3.0–4.2 V.

2.3. Sample Preparation

The aged cells were opened in an argon–filled glovebox ($\mathrm{O_2} < 0.1$ ppm, $\mathrm{H_2O} < 0.1$ ppm) and the pure aged electrolyte was regained via centrifugation. For GC-HRAM-MS analyses, the regained, the thermally aged and the pristine electrolytes were diluted in DCM (1/100 v/v) for conducting salt precipitation and 1 μL of the supernatant was injected. IC-based investigations were performed after dilution in ACN (1/100 v/v) with an injection volume of 65 μL.

Table 1. Overview of aging conditions of the investigated cells and their denotation as used throughout this work.

Denotation	Aging conditions
$\mathrm{EL}_{\mathrm{form}}$	Formation @ 20 °C
$\mathrm{EL}_{\mathrm{therm.\ stored}}$	Electrolyte storage for 19 days @ 80 °C
$\mathrm{EL}_{\mathrm{200\ cyc\_A}}$	Formation @ 20 °C and 200 cycles @ 20 °C
$\mathrm{EL}_{\mathrm{200\ cyc\_B}}$	Formation @ 20 °C and 200 cycles @ 20 °C
$\mathrm{EL}_{\mathrm{form,\ therm.\ stored}}$	Formation @ 20 °C and cell storage for 2 days @ 60 °C
$\mathrm{EL}_{\mathrm{therm.\ form}}$	Formation @ 60 °C
$\mathrm{EL}_{\mathrm{therm.\ 50\ cyc\_A}}$	Formation @ 20 °C and 50 cycles @ 60 °C
$\mathrm{EL}_{\mathrm{therm.\ 50\ cyc\_B}}$	Formation @ 20 °C and 50 cycles @ 60 °C

2.4. Syntheses of Methyl Propyl Sulfonate and Ethyl Propyl Sulfonate

Methyl propyl sulfonate (MPS) and ethyl propyl sulfonate (EPS) were synthesized using 1-propanesulfonyl chloride and large excesses of the respective alcohol methanol or ethanol in a closed centrifuge vial (15 mL). The reaction mixtures were shaken at room temperature (rt) for 1 h and were not further purified.

2.5. Analytical Investigations

2.5.1. GC-MS

GC investigations with HRAM-MS detection were performed on a Q Exactive GC Orbitrap GC-MS/MS system with a TRACE 1310 GC and a TriPlus RSH autosampler (all Thermo Fisher Scientific, USA). Experimental parameters were applied according to Peschel et al.[27] and target analysis was performed based on extracted ion chromatograms (EICs) of measured accurate masses with a mass window of 1 ppm.

GC-MS measurements with a single quadrupole (SQ) mass analyzer were executed on a GCMS–QP2010 Ultra (Shimadzu, Japan) with assembled AOC–5000 Plus autosampler and a nonpolar Supelco SLB-5 ms column (30 m × 0.25 mm; 0.25 μm; Sigma Aldrich, Germany). Further parameters were applied according to Grützke et al.[28]

2.5.2. IC-CD-MS

IC investigations were performed on an 850 Professional IC (Metrohm, Switzerland) with conductivity detection (CD). For MS detection, the system was further hyphenated to the ion trap-time-of-flight (IT-TOF)-MS (Shimadzu). A Metrosep A Supp 7 column (250 × 4.0 mm; 5 μm; Metrohm) was used for isocratic anion separation at 65 °C and a flow rate of $0.7\ \mathrm{mL\ min^{-1}}$ was applied. The applied method is based on Kraft et al.[29] and further parameters were applied according to Henschel et al.[18]

3. Results and Discussions

To understand the electrochemical and/or thermal decomposition of PS, a matrix of aging conditions including electrochemical aging, thermal aging and combinations of both was investigated (Table 1). IC- and GC-HRAM-MS techniques were applied to understand PS decomposition and define characteristic ionic and volatile aging markers.

3.1. Ionic Markers for 1,3-Propane Sultone Aging in LIBs

In literature, electrochemical ring-opening resulting in lithium alkyl sulfonates was reported based on X-Ray photoelectron spectroscopy (XPS) measurements, cyclic voltammetry or density-functional theory (DFT) calculations.[14,16,25,26] However, experiment proves for assumed reaction products are pending. To improve the analysis of sultone aging in spent LIBs, speciation via IC-HRAM-MS was conducted.

Based on literature reports and structural properties of PS, 1-propanesulfonate was suspected as the main target molecule for electrochemical PS decomposition. To determine the IC retention time of 1-propanesulfonate, an aqueous solution of the commercially available sodium salt was measured. (**Figure 1**)

In negative detection mode, the characteristic $CH_3CH_2CH_2{}^{32}SO_3{}^-$ ion was measured with m/z 123.0121. The observed retention time was 7.5 min. Identification of 1-propanesulfonate in unknown samples with more complex matrices could further be confirmed by the characteristic sulfur isotope pattern with $^{33}S/^{13}C$ and ^{34}S. (Figure S1, Supporting Information).

Having defined the targeted ion and its retention time, targeted analysis was performed in all aged electrolytes (Table 1). Moreover, the applicability of the method for dry, solid LIB material was tested by washing a centrifuged and therefore dried negative electrode with water ($EL_{form,\ therm\ stored\_H2O}$). An overlay of EICs with m/z 123.0121 is shown in **Figure 2**.

1-propanesulfonate was detected in all electrochemically aged electrolytes. This proves literature reports on electrochemical ring–opening resulting in alkyl sulfonate species.[24,26] Further, thermally induced ring-opening after 19 days at 80 °C was excluded with no detectable peak for 1-propanesulfonate in $EL_{therm.\ stored}$. Selectivity of the IC-HRAM-MS method was shown with no further detectable peaks for m/z 123.0121 with deviating retention behavior. Slight retention shifts can be caused by the elongated hyphenation and matrix variations due to the different aging conditions. The identification of 1-propanesulfonate in spent LIBs can be used as a marker for both the application of PS and its electrochemical aging. Within the performed IC-HRAM-MS investigations, further, larger sulfur-containing ionic species were detectable. (Table S1, Supporting Information) Exemplarily the twofold negatively charged $C_8H_{16}O_8S_2{}^{2-}$ ion with m/z 152.0149 is shown in the supporting information (Figure S2, Supporting Information). After electrochemical ring-opening, the formed radicals and nucleophiles can, on the one hand, oligo- and polymerize to larger compounds that can suffer from electrolyte solubility above a certain size and therefore are incorporated in the SEI. On the other hand, hydrogen abstractions can occur forming the electrolyte soluble and detected 1-propanesulfonate.

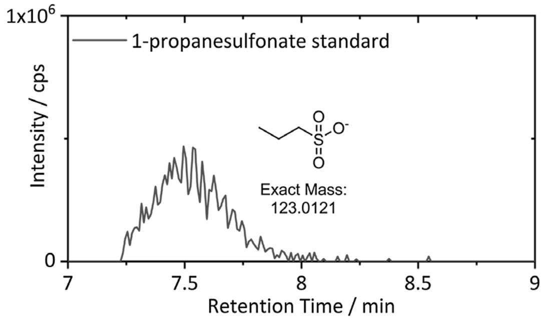

Figure 1. Excerpt of an IC-HRAM-MS chromatogram of commercially available sodium 1-propanesulfonate monohydrate dissolved in water. The EIC of m/z 123.0121 was extracted with a 5 ppm mass window.

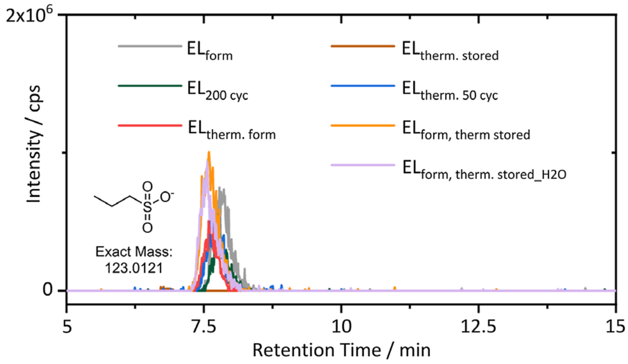

Figure 2. IC-HRAM-MS target analysis of 1-propanesulfonate in the aged electrolytes (Table 1). The shown EICs with m/z 123.0121 were extracted with a 5 ppm mass window.

The identification of larger sulfonate-based species illustrates the complexity of LIB electrolyte additive decomposition and the need for chromatography-based analyses for reliable speciation. In contrast to surface sensitive X-ray-based techniques, IC-HRAM-MS analysis of the electrolyte offers speciation of the targeted sulfur-containing compounds e.g., by characterizing the $R\text{-}SO_3{}^-$ alkyl chain and separation of monomeric and oligomeric species.[16,25] Moreover, for targeted post mortem identification, measuring the liquid electrolyte or aqueous/organic extracts of randomly chosen aged LIB material, simplifies sample preparation and accessibility.

However, as this work focuses on the identification of characteristic aging markers for reliable target analysis, further considerations will be based on the 1-propanesulfonate anion. To prove the selectivity of 1-propanesulfonate as PS aging marker, the electrolyte aging matrix was repeated with the unsaturated sultone PES, also applied as additive in LIB electrolytes.[9,15,30] Electrochemical ring-opening of PES was also described in literature. Among others, unsaturated, but also saturated $RSO_3{}^-$ species were presumed to be formed.[9,31,32]

For all investigated aging conditions of PES containing electrolytes, target analysis of 1-propanesulfonate was performed analogously to the PS containing electrolytes, but without positive identification. Therefore, the hydrogenation of the unsaturated, ring-opened species appears to be highly unfavorable. Thus, 1-propanesulfonate can be applied as characteristic ionic aging marker for PS decomposition.

3.2. Volatile Aging Markers for 1,3-Propane Sultone Aging in LIBs

Recently, also the volatile species MPS and EPS were considered as PS-based aging markers in spent LIBs.[33] Considering their chemical structure and the well-known propensity of carbonate species for esterification in LIBs, esterification of the previously discussed 1-propanesulfonate appeared reasonable.[34] To prove this assumption and to further clarify the formation of volatile PS

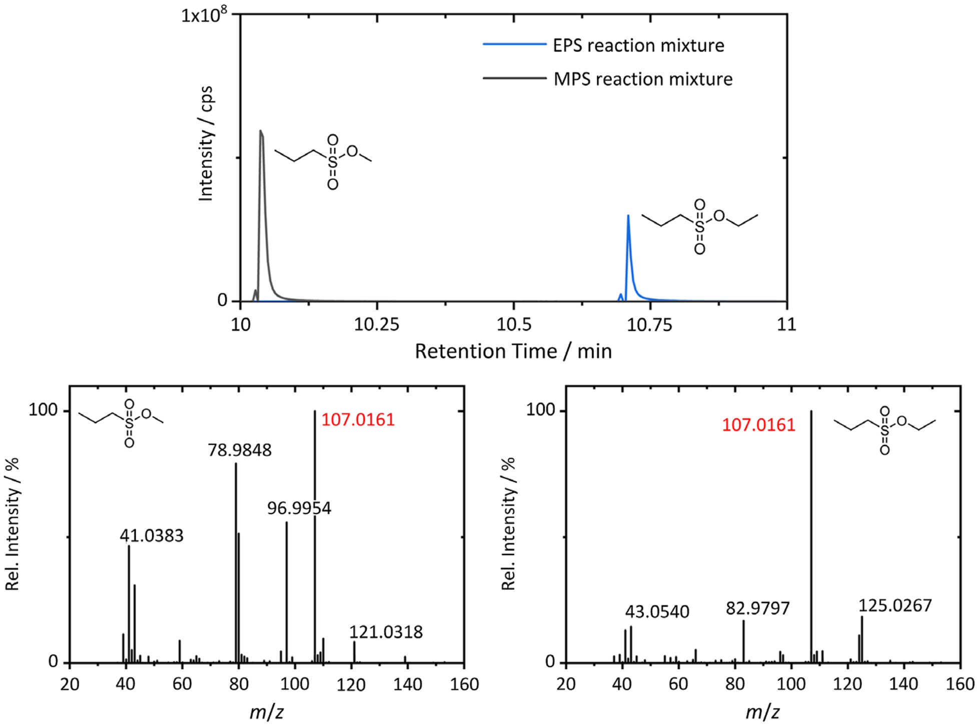

Figure 3. Retention and fragmentation of the synthesized MPS and EPS. The main fragment with m/z 107.0161 ($C_3H_7SO_2$) was used for target analyses.

decomposition species, MPS and EPS formation was analyzed for all previously mentioned aging conditions.

MPS and EPS were synthesized and the respective retention and fragmentation behavior was investigated. (**Figure 3**) Based on the measured HRAM-MS spectra, a characteristic fragment ion (marked in red) was chosen for targeted analysis via EICs.

Remarkably, the fragmentation pattern differed depending on the used MS system. While the GC-SQ-MS spectra (Figure S3, Supporting Information) matched the database (>95% scores with NIST11), the orbitrap-based MS system led to different, but reproducible fragmentation, despite the same ionization energy of 70 eV. This could be explained by the different ion source and mass analyzer geometry of the GC-HRAM-MS instrument.[35] For further targeted analysis m/z 107.0161 ($C_3H_7{}^{32}SO_2$) was used, indicating the propanesulfonate fragment ion, present in both molecules. The overlay of EICs with m/z 107.0161, extracted from the Full MS measurements of all investigated electrolyte aging conditions (Table 1), is displayed in **Figure 4**.

With retention times of 10.03 and 10.71 min, two peaks with varying peak areas were observed, matching the previously determined retention times of MPS and EPS (Figure 3). No significant peak was observed for EL_{form} and $EL_{therm.\ stored}$. The other peak areas increased from $EL_{200\ cyc\_A/B}$ over $EL_{form,\ therm.\ stored}$, $EL_{therm.\ form}$ to $EL_{therm.\ 50\ cyc\_A/B}$.

The absence of MPS and EPS solely after thermal electrolyte aging supports the assumption of a double-stage mechanism for MPS and EPS formation, initialized via reductive electrochemical ring-opening. For subsequent esterification, the thermally treated cells showed larger peak areas, compared to the cells cycled at 20 °C, despite significantly shorter aging durations. In more detail: the largest peaks areas of MPS and EPS correlated with the longest thermal aging duration, premised electrochemical cell formation. In addition, longer cycling at 20 °C also led to MPS and EPS formation, implying kinetic reasons for the amount of esterification.

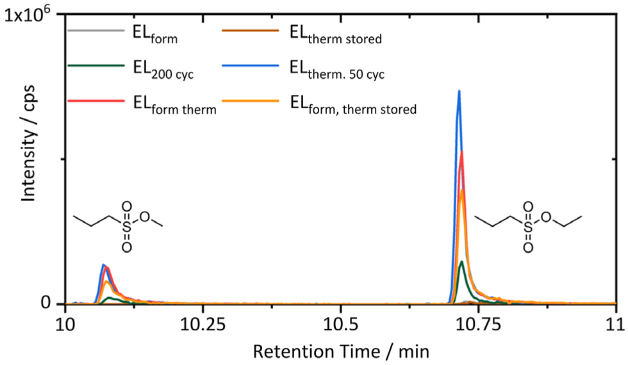

Figure 4. Overlay of EICs (m/z 107.0161, mass window 1 ppm) from GC-HRAM-MS measurements of the aged electrolytes (Table 1). The chemical formulas of the targeted alkyl sulfonic acid esters are shown.

The chosen semi-quantitative approach via measured peak areas could be improved to quantitative values by external calibration with MPS and EPS standard materials or by coupling GC separation to inductively coupled plasma with (HR)MS detection via the $^{32/34}S$ signal and external calibration.[36] To verify the observed esterification and semi-quantitative interpretation, reproducibility was investigated by two separately cycled and

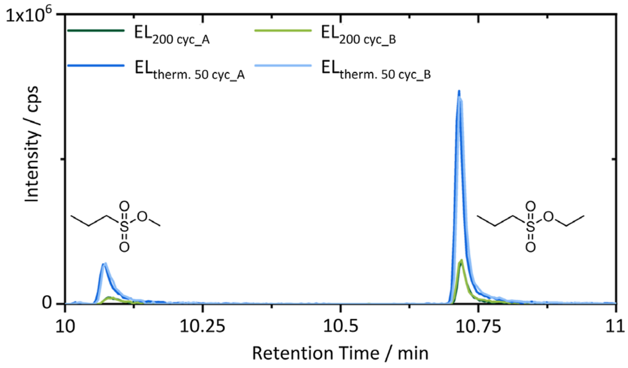

Figure 5. Exemplary visualization of reproducible MPS and EPS formation in two equally aged electrolytes. The overlaid EICs (*m*/*z* 107.0161, mass window 1 ppm) were extracted from the Full MS measurements.

measured cells (indicated by "A" and "B") with 200 cycles at 20 °C and 50 cycles at 60 °C, respectively. The obtained EICs of the marker fragment ion *m*/*z* 107.0161 are shown in **Figure 5**, illustrating reproducible alkyl sulfonate ester formation.

To prove the selectivity of MPS and EPS as PS aging markers, the electrolyte aging matrix was also repeated with the unsaturated sultone PES. Target analysis of MPS and EPS was performed analogously to the PS-containing electrolytes, but without identification in any aged electrolyte. Due to the previously discussed absence of 1-propanesulfonate in PES containing electrolytes, also the absence of its esterification products was reasonable.

Based on these findings, MPS and EPS can be applied as marker molecules for PS in GC-HRAM-MS-based target analysis. Methodologically, EICs with sub-ppm mass deviation enabled quasi background free, sensitive and selective detection of PS decomposition species in the complex LIB electrolyte matrix. Mass resolutions > 60 000 ensured reliable measurement of the characteristic sulfur mass defect and isotope distribution. Moreover, residue analysis of intact, ring-structured PS is accessible by means of GC-HRAM-MS, as shown in the supporting information.

4. Conclusions

In this study, hyphenation of ion and gas chromatographic techniques to HRAM-MS systems was used to understand the decomposition of PS in LIB electrolytes. Thus, characteristic decomposition species were defined, enabling selective target analysis in the complex matrix of aged LIB electrolytes.

The literature described, electrochemically induced ring-opening reaction of PS was proven, resulting in a variety of sulfur-containing anionic species. The hyphenation of IC separation to HRAM-MS detection enables organic sulfur speciation and exceeds XPS-based literature reports on PS decomposition species, limited to R–SO_3^- identification. Further, a GC-HRAM-MS target analysis method was reported, based on presumed esterification of the formed 1-propanesulfonate. MPS and EPS were defined as volatile PS decomposition markers after a concluded double-staged formation mechanism (**Figure 6**).

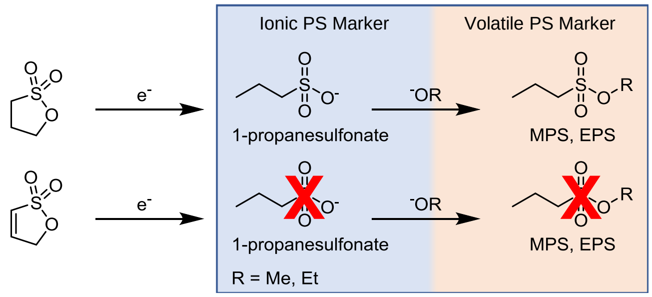

Figure 6. Summarizing scheme of double-staged PS decomposition resulting in the characteristic PS aging marker molecules 1-propanesulfonate, MPS and EPS. Lithium cations, hydrogen abstractions and leaving groups were neglected for simplification.

The discussed anionic and nonionic decomposition species can be selectively applied for PS identification in spent LIB material despite quantitative electrochemical PS consumption. The presented GC/IC-HRAM-MS methods are applicable for both, aged liquid electrolytes and dry, solid LIB material, such as electrodes or separators, after sufficient simple liquid extraction. Combination of chromatographic separation and HRAM-MS detection ensured reliable and sensitive decomposition product identification and extends literature reports on sultone decomposition based on X-Ray methods regarding species information and differentiation.

Possible application of PS identification via MPS and EPS as marker molecules was already reported for analysis of shredded LIB recycling material history, absent experimental evidence for their relation to PS decomposition.[33]

With this, the reported investigations pave the way for more sensitive and selective LIB electrolyte additive identification in spent LIB material, taking mechanistic understanding of decomposition reactions and chromatographic techniques hyphenated to HRAM-MS systems as a basis.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

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