



Reactions of the Additive 1,3-Propane Sultone with Electrolyte Compounds Investigated by Capillary Electrophoresis and High-Resolution Mass Spectrometry



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ABSTRACT

In this study, the lithium ion battery (LIB) additive 1,3-propane sultone (PS) was investigated using capillary electrophoresis (CE) connected to a quadrupole time-of-flight mass spectrometer (Q-TOF MS). In the first part, PS was thermally aged with the organophosphates dimethyl phosphate (DMP), diethyl phosphate (DEP) or triethyl phosphate (TEP) at 60 °C for one month. It was observed that PS reacted with traces of water, with organophosphates, with decomposition products of the organophosphates and polymerized to long-chain decomposition products. Due to the large number of in part similar decomposition products, it was not possible to baseline separate them from each other. The structures of the decomposition products were identified and the deviations of the detected m/z -ratios of the decomposition products to the calculated m/z -ratios were lower than 3.0 ppm. Moreover, one of the most interesting aspects was the formation of DEP in the aged samples of TEP and PS. In the second part, PS was mixed with DMP, DEP or TEP in the LIB electrolyte and aged at 60 °C for one month. In these samples, decomposition products were determined, formed by reaction of PS with carbonates, organophosphates and DMP, DEP or TEP. In these electropherograms, the decomposition products were baseline separated.

In this study, the high reactivity of PS with different electrolyte compounds from the electrolyte was shown in battery research for the first time.

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1. Introduction

Sulfur based additives, such as 1,3-propane sultone (PS), were reported for graphitic anode protection by supporting the formation of the solid electrolyte interphase (SEI). The SEI is generated on the anode surface in the first cycles (= formations cycles) [1–5]. PS as an additive in propylene carbonate (PC) based electrolytes in lithium ion batteries (LIBs) suppressed the massive decomposition reactions of PC, [6] related to PC co-intercalation into graphite [7]. In combination with PC or other organic carbonate solvents, PS inhibited gas formation after cycling at higher temperatures [8]. Furthermore, the combination of PS and vinylene carbonate (VC) was reported providing better performance and reducing gas formation during cycling [9]. Zhang *et al.* investigated the effect of different combinations of PS and VC on the SEI formation and ethylene gassing. They showed that this

additive combination reduced the ethylene gassing by more than 60% during formation. On the graphitic anode surface compounds like lithium alkylsulfonate and poly vinylene carbonate were identified [10].

A theoretical density functional theory calculation was done by Leggesse and Jiang to describe the decomposition of PS as SEI forming additive in PC based electrolytes [11]. In literature, PS was described as a monofunctional alkylating agent which reacted spontaneously with a nucleophile. This led to reactions with different reaction partners like amides, imides or organic sulfides [12,13].

Some studies report on the reaction of PS with guanosine and DNA by high performance liquid chromatography (HPLC.) [13,14]. Additionally, several studies reported about synthesized polymers with PS, so that the end-functionalized group was the opened structure of PS [15–18].

Fischer described the ring opening of PS where 3-hydroxypropane-1-sulfonate or hydroxypropanesulfonic acid were formed. This took place under mildly alkaline conditions in combination with different reaction partners like, for example, water, ammonia,

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phosphorus based compounds and carboxylic acids [12]. As PS was described as being very reactive [12], it would be interesting if and how PS reacted in a standard LIB electrolyte. Aging investigations on electrolytes containing organic solvents and the conductive salt lithium hexafluorophosphate (LiPF_6), which are the standard electrolytes in LIBs [19] revealed the formation of organophosphates, which are considered to be highly toxic [20–34].

In this study, PS was aged with the organophosphates dimethyl phosphate (DMP), diethyl phosphate (DEP) and triethyl phosphate (TEP) with and without LP30 electrolyte. This aging behavior of PS after one month of aging at 60 °C was investigated in the fresh sample and by capillary electrophoresis (CE) connected to a quadrupole time-of-flight mass spectrometer (Q-TOF MS).

2. Experimental

For the detection of the anionic decomposition products of PS, the CE 7100 from Agilent Technologies (Santa Clara, CA, USA) connected to 6530 Accurate Mass Quadrupole Time of Flight Mass Analyser (Q-TOF) with an ESI coaxial sheath liquid interface was used. The software MassHunter Acquisition B.05.01 software from Agilent Technologies (Santa Clara, CA, USA) was used to control the connection between the CE and the Q-TOF system and for the interpretation of the data MassHunter Qualitative B.07.00 software was used. The electrolyte SelectiLyte LP30 (50/50 wt% DMC/EC and 1 M LiPF_6 (battery grade purity) were ordered from BASF (Ludwigshafen, Germany, max. 20 ppm water)). PS (99% purity), DMP, diethyl DEP (99%) and TEP (99.8%) were obtained from Sigma Aldrich (Steinheim, Germany).

The sheath liquid consisted of 5 mM ammonium hydroxide obtained from Merck KGaA (Darmstadt, Germany) was diluted in 50.0% methanol (HPLC grade) from Merck KGaA (Darmstadt, Germany) and 50.0 Vol.-% Milli-Q water (v/v), produced by an in-house Millipore filter system (18.2 M Ω cm, TOC < 3 ppb, Milli-Q Advantage A10, Millipore GmbH, Schwalbach, Germany). The sheath liquid was pumped by an isocratic pump 1260 (Agilent Technologies, Santa Clara, CA, USA). The sheath liquid was delivered with a flow rate of 8 $\mu\text{L}/\text{min}$. The standard bare fused silica capillary was obtained from Polymicro (Phoenix, AZ, USA) and had an inner diameter (i.d.) of 50 μm and a total length of 100 cm. The capillary was preconditioned by rinsing with the background electrolyte (BGE) for 10 min. The BGE consisted of 10 mM ammonium acetate purchased from Acros Organics (98.0%, Geel, Belgium). The pH-value of 10.3 was adjusted by ammonia. The system was rinsed with BGE for 10 min between the measurement steps to protect the capillary from contamination of the previous run. The applied ESI-Q-TOF MS parameters, which were optimized for a m/z range of 50–1000, were as follows: for ESI (-) mode, the voltage was 3000 V, dry gas was set up to 8 L/min and nebulizer pressure to 10 psi with a dry gas temperature of 250 °C.

The samples were injected hydrodynamically with a pressure of 50 mbar for 2 s. After that, the BGE was injected as well for 2 s.

Beside the MS measurements, MS/MS measurements for each new detected m/z -ratio were done. The MS/MS measurements were carried out at a collision induced dissociation (CID) of 20 eV. The mass range in the MS/MS measurements started with 20 m/z and ended by the fragmented m/z of the anion.

PS and the organophosphates DEP, DMP or TEP were mixed in a ratio 1:1 (wt/wt) and aged at 60 °C for one month to investigate the decomposition and reaction products of PS and the organophosphates. For the measurements, the aged mixtures were diluted in a ratio of 1:500 with the BGE solution.

Additionally, the fresh and aged standard electrolyte was investigated. The aging of the LP30 electrolyte mixed with PS and

the organophosphates DEP, DMP or TEP electrolyte was carried out at 60 °C for one month. For all measurements, the electrolyte samples were diluted in a ratio of 1:500 with the BGE solution.

3. Results and Discussion

3.1. Reactions of 1,3-Propane Sultone with Dimethyl Phosphate, Diethyl Phosphate and Triethyl Phosphate

In this part, PS was aged in combination with the organophosphates DEP (3), TEP and DMP (23) at 60 °C for one month. Figures S4, S5, S7 and S8 can be found in the supplemental information.

In Figure 1, the electropherogram of the fresh mixture of PS and DEP is depicted. The calculated and measured m/z -ratios with the deviation in ppm of the detected peaks are given in Table 1. The deviations show that the measured m/z -ratios are in a good agreement with the calculated m/z -ratios when the deviation is lower than 5 ppm like in these measurements (see Tables 1 and 2). In the CE electropherogram (Figure 1), five peaks with the following m/z -ratios were detected 181.0176 (1), 138.0233 (2), 153.0323 (3), 139.0069 (4) and 260.0271 (5).

The m/z -ratio of 153.0324 was assigned to the DEP (3) peak. The opened structure of PS, 3-hydroxypropane-1-sulfonate (4) with the m/z -ratio of 139.0069 was determined (see Figure 1). The decomposition product (2) is formed by a reaction of 3-hydroxypropane-1-sulfonate (4) (139.0069 m/z) with the ammonia of the buffer. In literature, it is described that PS reacts with ammonia under mildly alkaline conditions to sulfopropylated amines [35]. PS can react with acetate to form carboxylic acids [36]. This reaction leads to the formation of the detected m/z ratio 181.0176 (2). Accordingly, PS reacted with the ammonia cation and the acetate anion of the buffer. Therefore, the detected m/z ratios 138.0233 (2) and 181.0176 (1) are not decomposition products of PS.

For a clearer overview, the detected peaks of the aged DEP and PS sample are illustrated in four separate figures (see Figure 2–5). The DEP peak was found in all electropherograms. The peaks of the reaction products of PS and the BGE were not visible, but still the reaction products (2) and (5) were detected in the aged sample. In contrast to the electropherogram of the fresh sample, the m/z -ratio of 181.0176 (7) was not detected in the electropherogram of the aged sample.

In Figure 2 (A), the detected m/z -ratios 139.0069 (4), 261.0108 (6), 383.0147 (7), 505.0183 (8) and 627.0219 (9) are depicted in the electropherogram. The m/z -ratios indicated a polymerization of 3-

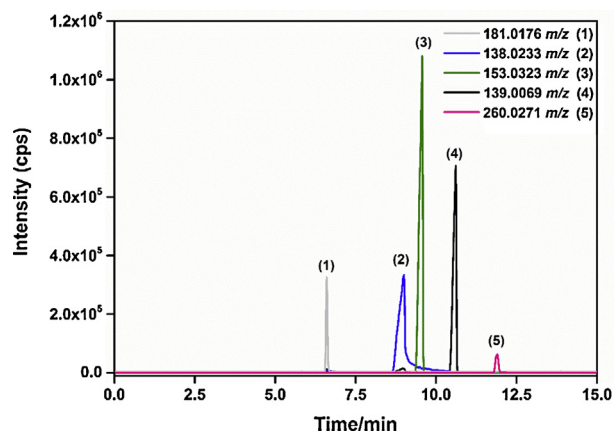


Figure 1. Electropherogram of a freshly mixed DEP and PS sample.

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