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Revealing the Formation of Dialkyl Dioxahexane Dioate Products from Ethylene Carbonate based Electrolytes on Lithium and Potassium Surfaces

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In this study, the formation of dicarbonate degradation products of ethylene carbonate-based carbonate mixtures containing dimethyl carbonate, ethyl methyl carbonate or diethyl carbonate that were combined with lithium or potassium metal, is investigated. It is shown by NMR and GCMS that the dicarbonate products dimethyl dioxahexane dioate, ethyl methyl dioxahexane dioate and diethyl dioxahexane dioate are formed from the reactants to different extents and, in particular, the potassium surface initiates the fast formation of the corresponding dicarbonate products. Experiments with deuterated DMC suggest an intermolecular mechanism of the dicarbonate formation. In cell tests, namely potassium vs. graphite, it is shown that the electrolyte formulation with the lowest tendency to dicarbonate formation (EC/DEC) exhibited the best cell stability respectively lowest cell aging.

Introduction

Evaluation of electrode materials and electrode formulation are most commonly performed in so-called two-electrode half-cell setups, in which alkali metals are used as counter-reference electrodes versus the respective material/electrode of interest (i.e., the working electrode). This setup has well-known limitations, mainly the high reactivity of the alkali metal towards electrolyte components.[1] Furthermore, in post-Li systems the effect is amplified as a result of higher reaction rates and presumably a less protective solid electrolyte interphase (SEI). Previous studies reported that SEI components are more likely to dissolve in the electrolyte, thus triggering a significant degree of recurrent SEI formation reactions.[2] Moreover, since alkali metals typically form dendrites or mossy morphologies while aging, short-circuits and increasing cell resistances may adversely affect key performance indicators of the working electrode, such as voltage hysteresis, Coulombic efficiencies and cycle life. The degradation of the counter-reference electrode also affects the working electrode through ‘cross-talk’, in which degradation products generated at the alkali metal electrode commence to deposit on the working electrode thus influencing its surface layer properties. The difference in the surface layer composition and thickness upon mere storage at open-circuit are significant, as recently demonstrated by our group.[3]

The degradation of electrolyte components that lead to the dissolution of the SEI layer has been investigated extensively for lithium over the past thirty years and more recently, also for sodium systems. In this respect, much effort was devoted to characterizing the solid degradation products that deposited on the electrode surface, e.g., by X-ray photoelectron spectroscopy (XPS) or Infra-red spectroscopy (IR).[4] However, the formation of gaseous and soluble degradation products is just as relevant to understand the degradation processes at the electrode interface. For example, online electrochemical mass spectrometry (OEMS) experiments identified ethylene and CO as the major gas phase components from the reduction of ethylene carbonate (EC). Recently, for example, Caracciolo was able to show that storing potassium over electrolytes containing EC/DEC leads to the gaseous products CO_2 and C_2H_4.[5]

Formulations that contain linear and cyclic carbonates are well-known solvent mixtures for Li-ion based electrolytes and often adapted to sodium and potassium-based battery systems.[6] In these mixtures, both carbonates that are used, excellently synergize with each other. However, their use is not entirely straightforward, as reactivity between both carbonate compounds has already been demonstrated in a number of studies,[7] although EC is able to stabilize the linear carbonate.[8] Normally, this has been demonstrated in particular when a voltage is applied. However, there are indications that reaction products are formed even in the presence of alkali metals alone, which can complicate their use as electrolytes.[1,9] While lithium still seems to be quite stable, significant decomposition has already been shown in the case of sodium or potassium metal. With this respect it was already shown that DEC is not stable when mixed with EC using potassium metal.[8,10] Gas chromatog-

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raphy-mass spectrometry (GC-MS) experiments revealed competing processes in the liquid phase with the formation of specific degradation compounds, i.e., ethylene bis(alkyl carbonates). This is one of the main decomposition products of the variety of possible chemical and electrochemical reactions at the electrode interface. Yoshida et al. reported that the formation of ethylene bis(alkyl carbonates) in the liquid phase is the result of a coupled reaction between EC and a linear carbonate, like dimethyl carbonate (DMC) or diethyl carbonate (DEC).[11] As highlighted therein and in follow-up studies by Ogumi and coworkers[7,12] as well as Gireaud et al.,[13] the presence of alkoxides ($R–O^-$) appear to play a decisive role in this side reaction. Sasaki et al. further demonstrated that the presence of defined amounts of ethylene bis(alkyl carbonates) in the electrolyte lead to an instant and considerably capacity decay in graphite–Li half-cells but have little impact on corresponding $LiCoO_2$–Li half cells.[14] Qualitative and quantitative analysis of soluble degradation products is therefore relevant to the understanding of capacity fade in different cell setups. Previous studies referred to these compounds as SEI telltales since their concentration in the electrolyte can serve as a valuable parameter in the evaluation of the battery's state-of-health.[15]

According to Eshetu et al. the concentration of ethylene bis(alkyl carbonates) is larger in sodium half-cells than in lithium half-cells, suggesting that the previously associated capacity fade is amplified in half-cells containing a sodium counter-reference electrode.[15a] In a recent study on Sb–potassium half-cells, Madec et al. identified ethylene bis(ethyl carbonate) *via* GC-MS as well.[16] As recently confirmed by the authors in a separate study, the concentration in an EC:DEC solvent mixtures is depended on the conducting salt.[5] In contrast to the commonly used KPF_6, potassium bis(fluorosulfonyl)imide (KFSI) appears to suppress the formation of bis(alkyl carbonate) to a notable degree. The findings are in general agreement with previous electrochemical results suggesting the use of KFSI over KPF_6 to achieve improved cycle life.[17] Hence, previous literature draws a trend in the reactivity of alkali metal electrodes and the impact of the soluble ethylene bis(alkyl carbonates) on cycle life.

In the following study, we attempt to put previous results on the formation of ethylene bis(alkyl carbonates) on a common basis by comparing their concentration in solvent or electrolyte mixtures exposed to either Li- or K-metal. For our comparison, three common solvent mixtures were chosen, containing EC and either of the linear carbonates DMC, DEC or ethylmethyl carbonate (EMC). Quantitative and qualitative analysis is performed by GC-MS and nuclear magnetic resonance (NMR) spectroscopy. As the most reactive system in this series the focus of this work is placed on the electrolyte degradation in presence of potassium. Our aim is to demonstrate that the rather empirical choice of EC:DEC solvent mixtures in post-Li battery setups is rooted in the higher (electro)chemical stability of DEC over linear carbonates that carry methyl moieties.

Experimental details

Materials

Unless stated differently, materials were used as received und stored under inert gas atmosphere in an Ar-filled glovebox. Li discs (16 mm diameter, purity >99.9%, 250 μm) were obtained from PI-KEM (UK), Na chunks (99%) and potassium ingots (purity >99.9%; in glass ampules) were purchased from Merck (a second batch was ordered from Alfa Aesar, since the product was discontinued). $LiPF_6$ (battery grade) and KPF_6 (99.5% trace metal basis) were bought from Merck. The salts were dried prior to use for 12 h at 120 °C under vacuum. Electrolyte solvent mixtures were prepared from dimethyl carbonate (DMC, BASF, >99.0%, dry), diethyl carbonate (DEC, Merck, >99.0%, dry), methyl ethyl carbonate (EMC, Merck, >99.0%, dry) and ethylene carbonate (EC, BASF, >99.0%, dry). The reference compounds dimethyl dioxahexane dioate (DMDD, TCI Europe, 98%), diethyl dioxahexane dioate (DEDD, TCI Europe, 98%) and ethyl methyl dioxahexane dioate (EMDD, Enamine, 98%) were used for identifying and quantifying the dicarbonate products.

KS6 L graphite and SuperC65 (conductive additive/carbon black) was kindly provided by Imerys Graphite and Carbon (Switzerland). As binders a mixture of polyacrylic acid (PAA, Merck, $M_v = 1.25\ kg\,mol^{-1}$) and carboxymethyl cellulose (CMC–Na, Merck) was employed. All chemical for the electrode preparation were stored outside the glovebox. Glass fiber separators (Whatman, glass microfiber filters, grade GF/B) were cut into 16 mm discs and dried for 12 h at 120 °C under vacuum and then transferred without further exposure to air into an Ar-filled glovebox. 2025 Coin cells (S304 steel) were obtained from MTI.

Gas chromatography measurements

Solvent and electrolyte mixtures. Three different solvent mixtures were prepared, each containing 50 vol.% EC and 50 vol.% of a linear carbonate (DMC, DEC or EMC). From the thus prepared solutions, electrolyte mixtures were prepared by adding the dried electrolyte salt ($LiPF_6$ or KPF_6) in a 10 mL plastic (HDPE) bottle to yield a 750 mM salt solution.

Qualitative analysis. The solvent mixtures as well as the pure solvents were stored at 40 °C over a piece of either Li-, Na- or K-metal for a maximum of two months. Samples were taken after 3, 7, 14, 30 and 60 days and analysed by GC-MS.

Quantitative analysis. Electrolyte and solvent mixtures were aged against either lithium or potassium metal in plastic vials for different time intervals. Li discs were cut into smaller discs with a 12 mm diameter and pressed onto a Cu foil of equal size. K pieces were flattened in a plastic bag and the foil was pressed onto a 12 mm Cu disc. Excess material was removed with a ceramic knife or scalpel. Each vial was filled with 2 mL electrolyte and then the alkali metal disc was added to commence the aging process. Quantitative analyses were done within 2,000 min after mixing the electrolyte with the metal. During the reaction time the mixtures were shaken and tempered by a MKR 23.

The GCMS analyses are performed as described in our previous work in detail.[9]

Nuclear magnetic resonance (NMR) spectroscopy experiments

Aged samples were characterised on a Bruker, AVANCE III spectrometer at ambient temperature. The sample was extracted by a capillary and then washed into the NMR tube with deuterated acetonitrile-d_3 (ACN-d_3, D3 >99.8%, water content <500 ppm, Eurisotope, France). The tube was sealed with parafilm while still in the glovebox and then moved to the spectrometer. 1D NMR experiments (^{1}H NMR (500 MHz),proton decoupled ^{13}C{^{1}H} NMR (125 MHz) and ^{31}P NMR (202 MHz), Distortionless Enhancement by Polarization Transfer (DEPT-135) were performed on each sample. 1D NMR spectra were referenced to the residual solvent signal (δ(ACN in CD_3CN) = 2.08 ppm[18]).

Electrochemical measurements

Electrode preparation. Graphite electrodes comprised of 95 wt.% KS6 L, 1 wt.% carbon black and 4 wt.% binder (PAA:CMC–Na, w/w = 1:1), following the description in ref. [19]. A binder solution was prepared from 1.5 mL deionized water, then carbon black is added at the mixture is stirred in a planetary mixer for 5 min at 2000 rpm. Graphite powder is added in two batches together with more deionized water (about 1.5 mL per batch) and the slurry is mixed between each addition in the planetary mixer. The total amount of deionized water used for a total of 2 g of solid material was between 4.5–5.5 mL, depending on the slurry viscosity. The slurry was cast on copper foil (supplier) using a doctor blade and then dried at ambient temperature. The dried coating was cut into electrode discs of 14 mm in diameter and the electrodes were subsequently dried in a vacuum tube (Büchi, Switzerland) at 120 °C under vacuum for 12 h prior to introducing them into the glovebox without further air exposure.

Cell assembly. Coin cells comprised of a potassium counter electrode, a graphite working electrode and a glass fiber separator soaked in 150 μL electrolyte. A piece of potassium was applied onto the coin cell spacer using a ceramic knife. Three electrolyte solutions comprising 750 mM KPF_6 in either EC/DMC, EC/DEC or EC/EMC (each 50:50 vol.%) were studied.

Galvanostatic cycling. Galvanostatic cycling was performed on a VMP-3 potentiostat (Biologic, France) in a 2-electrode setup. All experiments were conducted as Constant-Current-Constant-Potential (CC–CP) technique. The cells were cycled between 25 mV and 1200 mV vs. K/K$^+$. The C-rate in the CC-sequence of the CC–CP technique on the first two cycles was C/20 (1 C = 279 mA g^{-1}) and on following cycles C/10. In the CP-sequence the current cut-off was defined as the current equivalent to C/40 (first two cycles) and C/20 (following cycles), respectively. The CP-sequences ended latest after 1 h. The global time limit on the first two cycles was 35 h per charge/discharge for considering the considerable degree of irreversible reactions during SEI formation. On following cycles, the global time limit was decreased to 12 h per charge/discharge. All time limits were not reached. This means that the current or potential limit was previously exceeded.

Results and discussion

Overview about electrolytes and metals

In this study, the solvents DMC, DEC and EMC were examined in mixture with EC and the decomposition products dimethyl dioxahexane dioate (DMDD), ethyl methyl dioxahexane dioate (EMDD) and diethyl dioxahexane dioate (DEDD) (also called "dicarbonates") were analysed (Figure 1). Additionally, transesterification reactions between DMC, DEC and EMC are considered. The solvent mixtures were studied with and without conducting salt ($LiPF_6$ and KPF_6, respectively), lithium and potassium depending on the metal studied. Based on the solvent mixtures, the formation of mixed carbonates (EMC, EMDD) from the pure dialkyl carbonates was examined, and conversely, the formation of the dialkyl carbonates from the mixed substituted EMC at the metal surfaces was studied. Even though other degradation products are also formed during storage, the present study is devoted to the consideration of the formation of the corresponding dicarbonate derivatives. The concentration of other degradation products was minor compared to high contents of dicarbonate compounds from reactions of EC with linear carbonates.

Reactivity of EMC and transesterification reactions

Reactivity of EMC under storage conditions

The first step was to investigate whether EMC already decomposes when stored over molecular sieve which is often used for drying due to its easy application. However, it seems already possible that EMC can decompose over molecular sieve.[20] Since absence of water plays a prominent role in battery technology, molecular sieves are often used to store individual solvents or even electrolytes in a dry state. Figure 2 shows that keeping EMC over 0.4 nm of molecular sieve leads to a significant formation of DMC and DEC within 9 days.

Thus, cleavage or decomposition of EMC under the molecular sieve conditions is confirmed here. This is important, because one must be aware that a storage of EMC over molecular sieve leads to the consequence that the corresponding EMC is no longer a pure solvent, but contains significant amounts of DMC and DEC, which can then enter into different

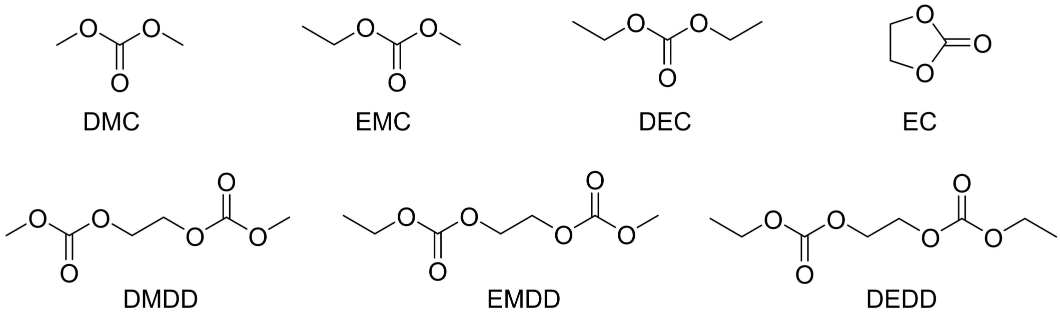

Figure 1. Linear organic carbonates (DMC, EMC, DEC), cyclic carbonates (EC) as well as coupling products DMDD, EMDD and DEDD studied in the manuscript.

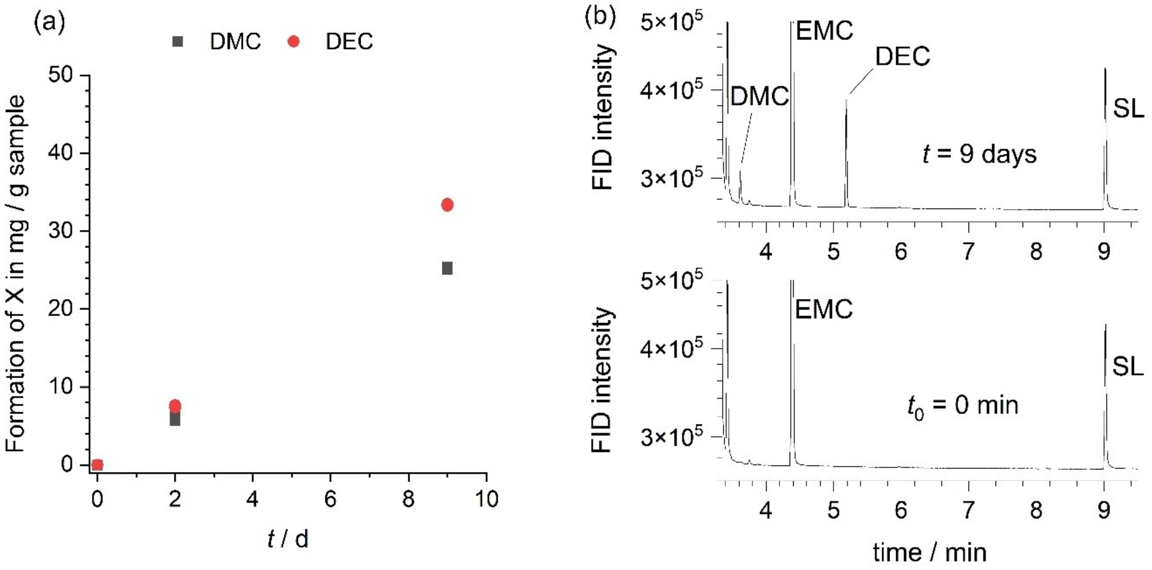

Figure 2. a) Time dependent formation of DMC and DEC within 1 week. b) Formation of DMC and DEC during storage of EMC over molecular sieve observed via gas chromatography (FID) at $t=0$ min and $t=9$ d.

reactions in the course of the later cell chemistry, depending on their quantity. This should also be considered for practical applications.[21] After drying and cleaning, EMC should therefore no longer be stored and/or dried over molecular sieves.

Transesterification of EMC on metal surfaces

Subsequently, the extent to which EMC is stable on metal electrodes was investigated. Based on the measurements shown in Figure 3, it can be concluded that the formation of DMC and DEC is already initiated in a simple storage of EMC over alkali metals, even over lithium metal. The formation of the corresponding products was detected by GC and determined quantitatively. A mixture of 2 mL solvent and a metal disk ($d=12$ mm) was kept under continuous slow shaking. Within 50 h, the formation of DMC and DEC, respectively, could be determined in the range of 100 mg per g of liquid (in case of potassium metal). For lithium, a much less pronounced formation (around 10 mg/g DEC and DEC, respectively) took place. Consequently, it can be concluded that in all alkali metal–EMC carbonate samples, the dialkyl carbonate also undergoes degradation reactions. The rate of formation of DMC and DEC increases steadily from Li to Na (not shown here) to

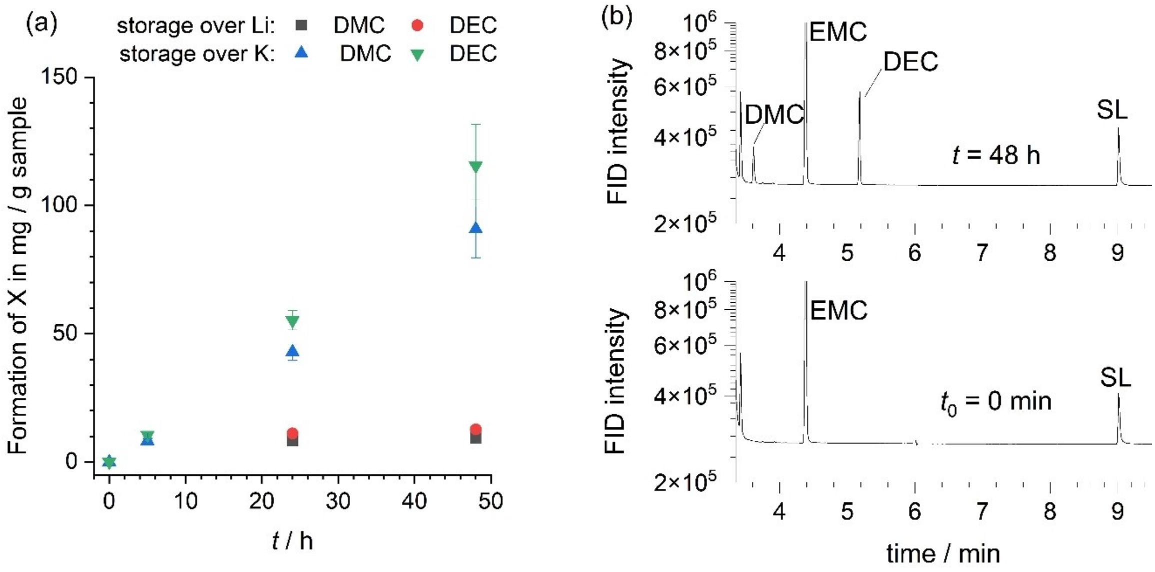

Figure 3. a) Time dependent formation of DMC and DEC within 48 h from EMC solvent over potassium metal. b) Chromatograms (FID) of samples from EMC storage over potassium metal at $t=0$ min and t = 48 h.

potassium metal. Since transesterification is highly dependent on the metal, a surface-induced reaction is expected to ultimately lead to transesterification. No other products such as alcohols or carboxylic acids were detected in the liquid phase. However, this might be due to strong interactions of such alcoholates to metal surfaces.

Conversely, it was shown that EMC also forms as a product in mixtures of DMC and DEC used together as a solvent mixture over alkali metals. In literature it is known that EMC can be formed from DMC and DEC with help of suitable catalysts in a transesterification reaction.[20b,22] This reaction also takes place faster and in higher concentration in the order K > Na > Li. The quantitative evaluation in the case of potassium within 50 h is shown in Figure 4. Compared with the formation of the symmetrical dialkyl products from EMC, significantly lower amounts of EMC were formed under comparable reaction conditions (around 10 mg/g in the case of potassium metal). Finally, it was confirmed that the transesterification reaction is a very fast reaction compared to the battery lifetime, which must always be taken into account for pure metal surfaces (e.g., dendrites or metal electrodes) in the case of carbonates, especially for electrolytes containing solvent mixtures.

Qualitative analysis on the reactivity of electrolyte solvents against Li and K metal and the formation of dicarbonate coupling products

Formation of dicarbonate products studied by NMR

In a first qualitative experiment, individual electrolyte solvents (EC, DMC, DEC and EMC) and electrolyte mixtures (EC:DMC, EC:DEC and EC:EMC) were stored at 40 °C over potassium metal for 60 days (Supporting Information, Figures S1–S4). At 40 °C, ethylene carbonate (EC) is a liquid, making the comparison to the reactivity of linear carbonates easier. After 60 days, a sample of each aged solution was transferred to an NMR tube and diluted with deuterated acetonitrile (CD_3CN). Another fraction of the sample was used to perform gas chromatography-mass spectrometry (GC-MS).

The following discussion will focus on the acquired ^1H NMR spectra in the range between 3.4–4.8 ppm (DMC samples, Figure 5) and 3.9–4.8 ppm (DEC samples, Figure 6), respectively. The full ^1H NMR spectra as well as proton-decoupled ^{13}C NMR and DEPT-135 spectra are provided in the Supporting Information (Figures S5–S13) and all data are listed in Table S1 (Supporting Information). The ^1H NMR spectra in Figures 5 and 6 are zoomed into the CH-satellite regions, as the degradation products show similar intensities. This already outline one of the issues during the analysis, as the satellite peaks overlap with signals of the newly formed dicarbonate degraded species. For easier comparison the pristine solvent mixture, as well as the aged solvent components (i.e., EC and either DMC or DEC) are plotted together with the aged solvent mixture. EC yields as a singlet from its two methylene (CH_2) groups in the 5-membered cyclic carbonate at a chemical shift of 4.49 ppm. DMC shows a singlet from its two methyl (CH_3) groups at 3.75 ppm. DEC appears as a quartet at 4.16 ppm (methylene group) and a triplet at 1.27 ppm (methyl group). The respective, CH-satellites show the same splitting patterns as the proton peaks.

Interestingly, no significant degradation can be seen for EC, DMC or DEC when stored individually over potassium at elevated temperatures. In the region between 3.3–3.8 ppm minor signals characteristic to ethers were found. However, their intensity is significantly lower than the CH-satellites or the concentration of the degradation compounds in solution after aging, which is why these species are not further discussed in the following. In addition to the solvent signals, the aged EC:DMC solvent mixture also shows two new singlet peaks (Figure 5d). The first one is found at 3.76 ppm and thus strongly overlaps with the considerably broader DMC signal. The peak is

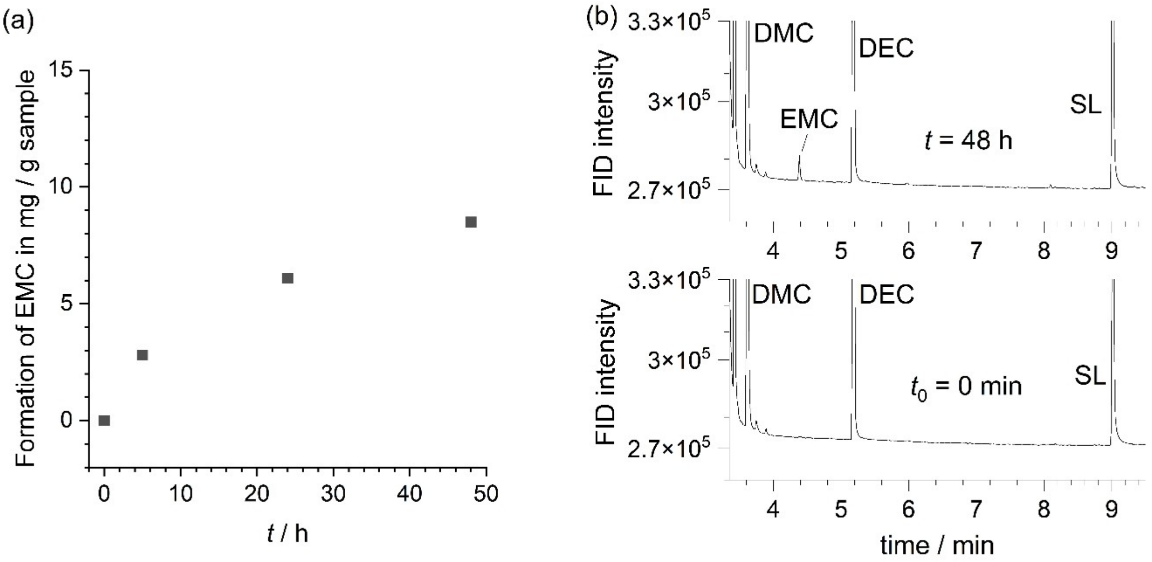

Figure 4. a) Time dependent formation of EMC within 48 h. b) Formation of EMC during storage of DMC + DEC over K observed via gas chromatography.

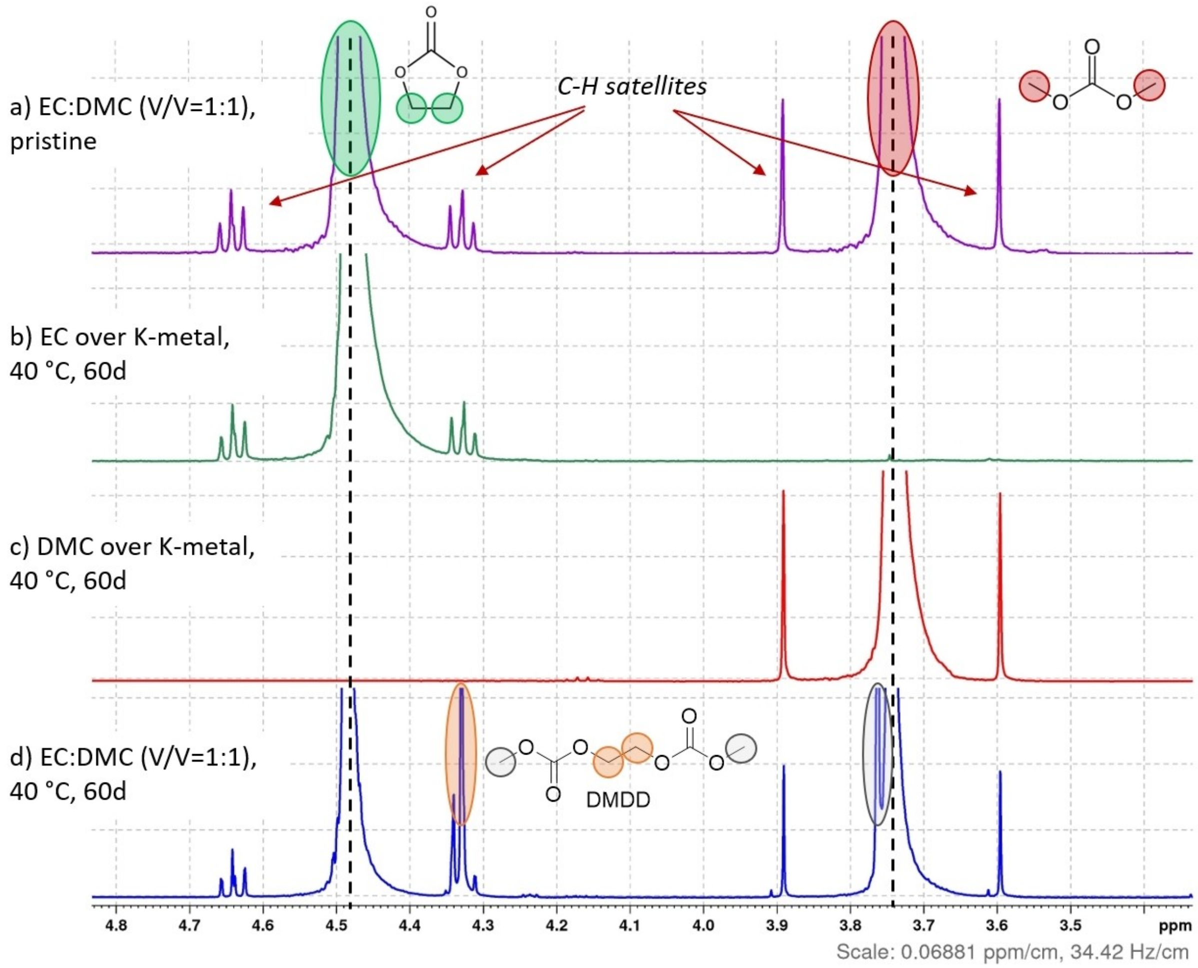

Figure 5. ^1H spectra of the pristine solvent mixture EC:DMC (v/v = 1 : 1) a) before and d) after aging over potassium metal at 40 °C for 60 days. The ^1H NMR spectra of aged EC is shown in (b) and that of aged DMC in (c), respectively. The individual solvent components were subjected to the same aging conditions as the solvent mixture.

associated with two new satellite peaks at slightly higher resonant frequencies than the corresponding satellites of the DMC signal. The close proximity to CH_3-signal of DMC suggest a very similar chemical environment. The other singlet overlaps with the CH-satellite signal of EC at 4.33 ppm. The presence of this additional peak further leads to an intensity increase of the surrounding satellite signals. ^{13}C NMR shows two new signals at 65.12 ppm and 54.56 ppm that are adjacent to solvent signals at 64.99 ppm (DMC) and 54.37 ppm (EC). Using the corresponding DEPT-135 spectrum, where CH- and CH_3-groups have positive and CH_2-groups negative intensities, the signals around 54 ppm can both be ascribed to CH_2-groups. Unfortunately, as a result of the signal overlap of both new signals, integration of the peaks does not yield any meaningful values. A clear assignment based on ^1H and ^{13}C NMR data is not possible from the two new signals alone, therefore complementary GC-MS experiments were conducted (see below) that allowed us to assign the compound to DMDD. This compound has been described in literature previously as one of the dominant degradation products during electrolyte decomposition reactions. As our results demonstrate, the degradation process proceeds only when both EC and DMC are present together, i.e., as coupled EC-DMC-reduction, whereas on their own both solvents appear surprisingly stable towards reduction.

Similar observations were made for the aged EC:DEC mixture, where the corresponding DEDD dicarbonate product was observed as the main decomposition product. In general, the assignment of the NMR spectra in Figure 6 are even slightly more challenging in the case of DEC containing samples, due to the peak splitting of signals assigned to the ethyl group of DEC. The signals of the degradation product DEDD appear as two peaks at 4.19 and 4.20 ppm as part of another quartet signal in the shoulder of the main quartet at 4.16 ppm from the methylene group in DEC. Another peak of the degradation product is visible at 1.30 ppm in the shoulder of the triplet peak of the methyl group in DEC centred around 1.27 ppm. In addition, a singlet peak at 4.32 ppm was found that overlaps with both the CH-satellites of EC and the quartet signal of DEC, making an integration over the peak not possible.

The position of this peak coincides with the CH_2 peak position of DMDD (±0.01 ppm), indicating the same chemical environment of this group. However, in ^{13}C NMR and DEPT-135

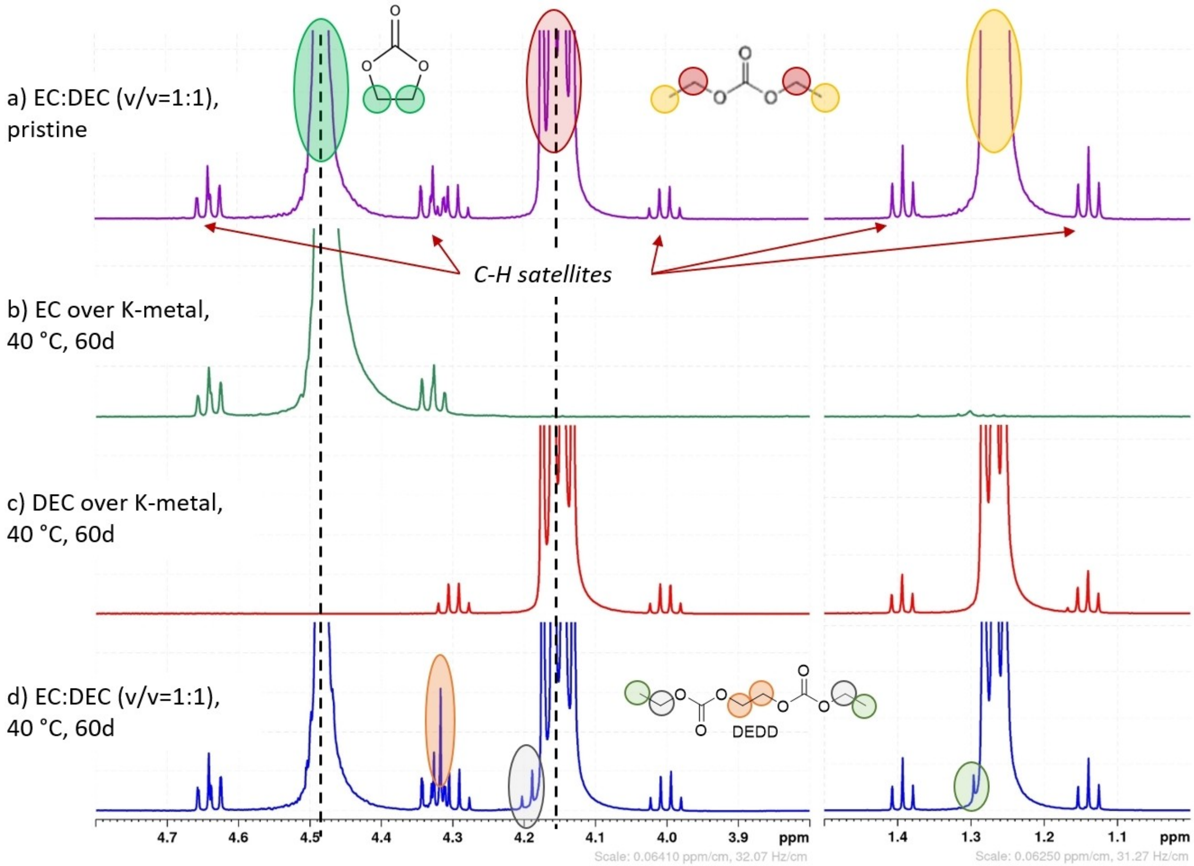

Figure 6. ^{1}H spectra of the pristine solvent mixture EC:DEC (v/v = 1:1) a) before and d) after aging over potassium metal at 40 °C for 60 days. The ^{1}H NMR spectra of aged EC is shown in (b) and that of aged DEC in (c), respectively. The individual solvent components were subjected to the same aging conditions as the solvent mixture.

experiments the signals of DEDD could not be observed, presumably due to the low concentration. Comparison of the peak intensities with the intensities of the satellite signals further shows in a strictly qualitative way that the concentration of DEDD is smaller than the concentration of DMDD in the EC:DMC solvent mixture.

Dioxahexane dioate formation in solvent-metal and electrolyte-metal mixtures

The dicarbonate products DMDD, DEDD and EMDD were identified by means of GCMS without any ambiguity. For this purpose, control measurements were carried out and the corresponding pure substances were analysed (Figure 7). The identification was based on the retention time as well as on the mass decay. Characteristic mass fragments are highlighted (numbered) in Figure 7, namely 59, 45, 74, 91, 103 (DMDD); 45, 59, 77, 90, 103 (EMDD); 45, 63, 76, 89, 91, 104 (EMDD). The formation of such products, investigated by NMR could therefore be confirmed in GCMS analyses. Samples which were taken from stored solvent mixtures over potassium metal (e.g., DMC/EC, EMC/EC or DEC/EC) were analysed in comparison to pure reference compounds. Due to variations in the retention index based on columns and oven programs the more comparable retention index should be used for specifying the retention behaviour. In case of the dicarbonate products such retention indices (RI) were received as follows: DMDD: RI = 1177, EMDD: RI = 1251, DEDD: RI = 1323. These values were calculated based on linear alkanes for comparison as described previously.[9]

Reaction of DMC-EC mixtures with potassium metal

To examine the formation of the dialkyl dicarbonate products, mixed DMC/DMC-d6 samples were prepared and combined with EC and potassium. Figure 8 shows the results of the measurements. A separation of the differently deuterium-substituted DMC products by chromatography was achieved to some extent (retention time: 2.96–3.01 min) and could be confirmed by mass extraction which was also demonstrated by means of mass fragments. This is surprising in so far as usually deuterated compounds are not expected to have any influence on the retention time. It was found that all three deuterated products formed in the mixtures: DMC, DMC-d3 and DMC-d6 product. Likewise, the detection of the three fragments from DMDD, DMDD-d3 and DMDD-d6 was found.

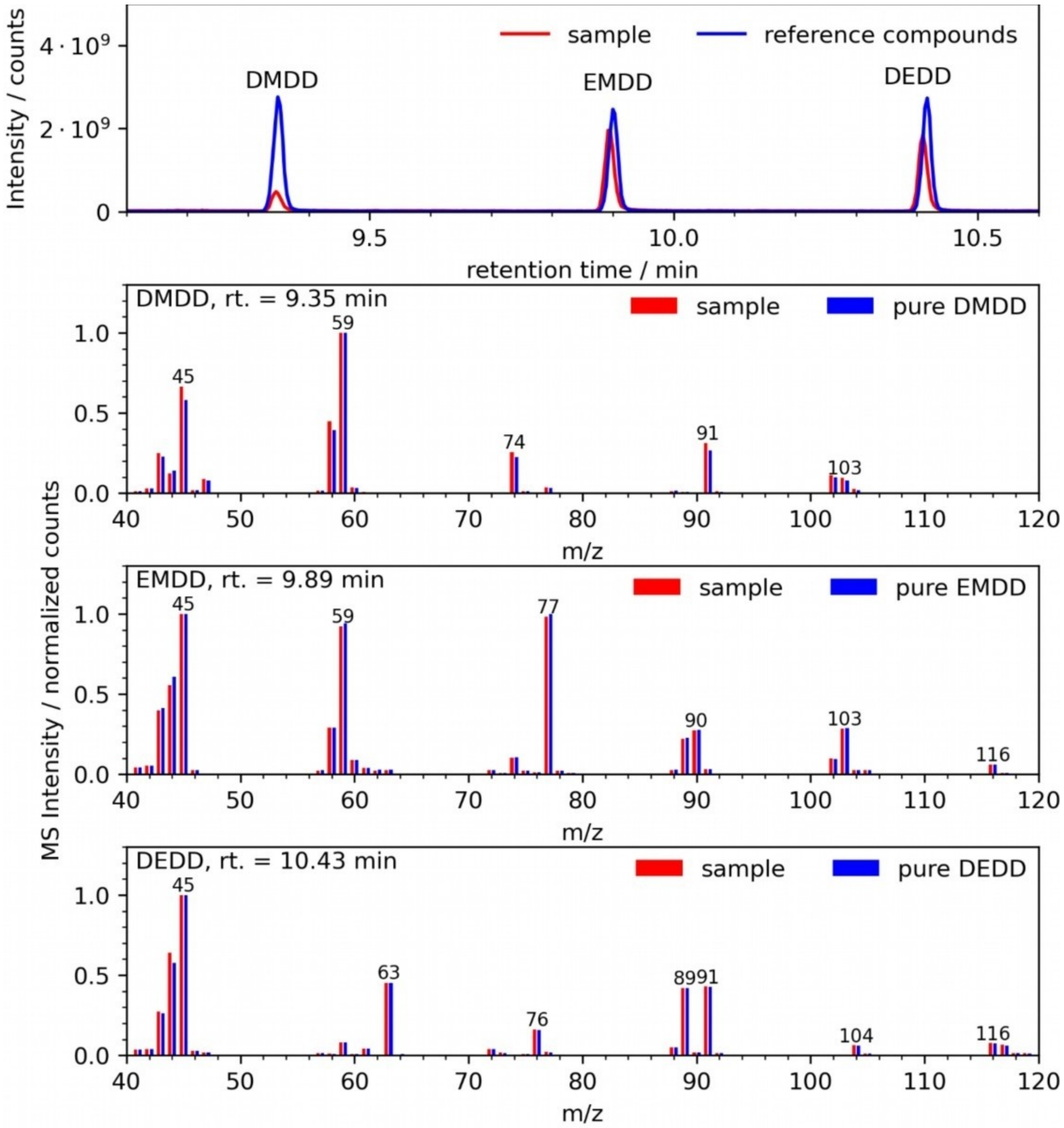

Figure 7. Chromatograms of a mixtures of dicarbonat products DMDD, EMDD and DEDD and their corresponding mass spectra as pure compound and sample in comparison.

It is assumed that in each case a CH_3 or CD_3 group is always present. Although the statement cannot be made quantitatively by means of MS, a relative incidence of the formation of the triple deuterated products DMC-d3 and DMDD-d3 is nevertheless confirmed. It can be seen that the mixed deuterated DMC product DMC-d3 tends to have a lower concentration than the two symmetrical products DMC and DMC-d6, but that the mixed DMDD-d3 behaves in exactly the opposite manner. Here, the concentration of the mixed DMDD-d3 is higher than that of the two symmetrical products DMDD and DMDD-d6. This is also supported from a statistical point of view. Furthermore, it is confirmed that there is a transesterification to DMC-d3 from the two products DMC and DMC-d6 (as observed from EMC which forms the dialkylcarbonates DMC and DEC). Mechanistically, this consequently indicates an intermolecular dicarbonate formation reaction, so that regardless of the CH_3 or CD_3 group already present on one side of the dicarbonate intermediate, the formation of the second methyl group occurs independently of the first process. As the reaction is heavily dependent on the metal used this intermediate reaction should be also surface triggered or at least surface initiated, which might be a radical start reaction.

Quantitative analysis of degradation reactions in common solvent and electrolyte mixtures with Li and K metal

The dicarbonate formation in each of the three mixtures EC/DMC (Figure 9), EC/EMC (Figure 10) and EC/DEC (Figure 9) was quantitatively investigated with and without conducting salt. For this purpose, the corresponding solvent or electrolyte mixtures were stored over the corresponding metals for a defined time (with shaking) and then samples were taken at defined times for quantitative determination. In this context, it

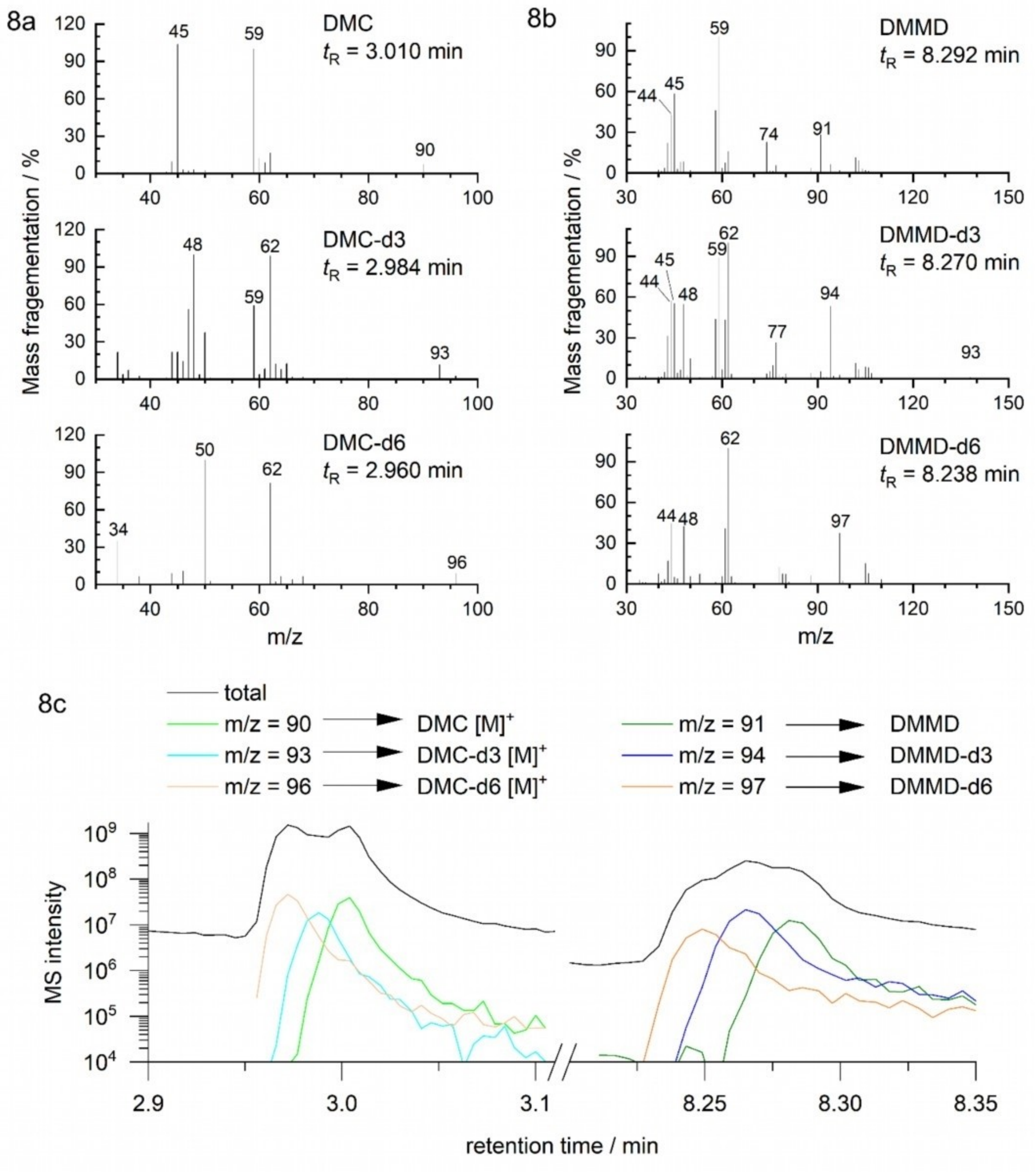

Figure 8. DMC/DMC-d6 + EC mixture over potassium metal. a) Mass fragments during the specified retention times of 2.96–3.01 min (equals to DMC/DMC-d6) and b) mass fragments during the specified retention times of 8.24–8.29 min (DMDD). Please note that the retention times between Figure 7 and Figure 8 differ due to different columns and oven protocols. c) Extracted mass (specified *m/z*) from the total ion count (MS).

is important to emphasize that the glovebox atmosphere strongly influences the formation of the products, because the metal surface reacts very rapidly with traces from the glovebox air during preparation. It is absolutely necessary to ensure a solvent-free interior atmosphere by using appropriate activated carbon. A reproducible concentration response of the individual alkyl dicarbonates could be achieved (especially for potassium metal) when the activated carbon of the glovebox was freshly replaced, thus ensuring that the organic impurities were removed in the glovebox atmosphere.

It was observed that in the presence of lithium, no formation of dicarbonate products (DMDD, EMDD, DEDD) occurs within the first 33 h, neither for the salt-containing electrolytes nor for the pure solvent mixtures. Since in the case of sodium (not shown here) compared to potassium metal the dicarbonate formation was also strongly reduced and delayed, the formation in the lithium samples cannot be excluded in the

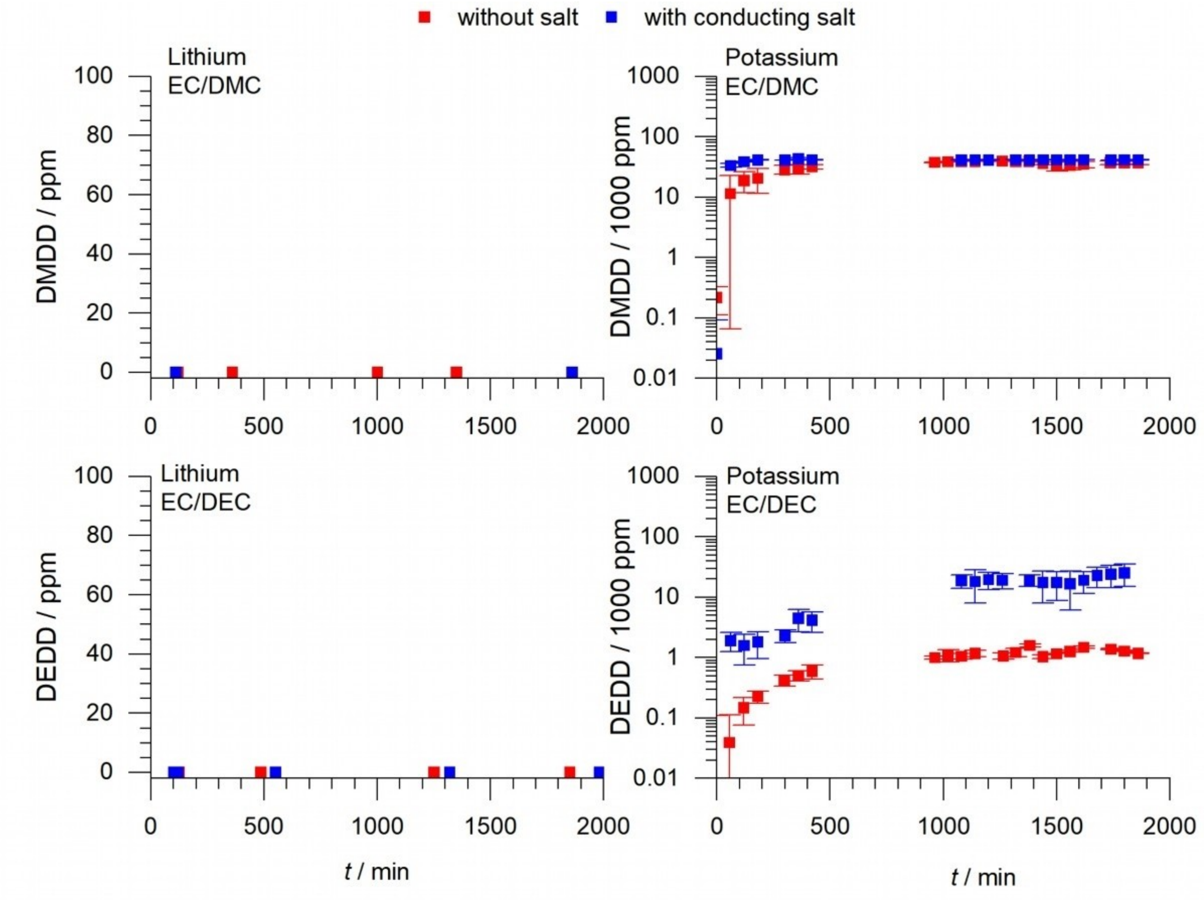

Figure 9. Results of the time-dependent measurements of DMC/EC and DEC/EC solvent mixtures stored over lithium and potassium metal. The formation of DMDD (in case of EC/DMC) as well as DEDD (in case of EC/DEC) was measured quantitatively via GCMS. Additionally, the results of the measurements with conducting salt ($LiPF_6$ for Li metal and KPF_6 for K metal samples) in the solvent mixture is presented as well.

long run. However, it was shown that within the total time of 30 days (1 month) investigated under the reaction conditions, no formation of the products DMDD, DEDD and EMDD occurred in case of lithium metal. It should be noted that different conditions are present in a real half-cell due to the applied voltage and that the corresponding dicarbonate formation can already take place relatively quickly in that case, as already be shown in literature.[7,15b,23]

In contrast to the lithium metal, the samples with potassium metal already revealed the formation of the dicarbonate products immediately after mixing. Without conducting salt, the formation of the coupling dicarbonate products was slower in all three variations (DMDD, EMDD and DEDD). Likewise, a lower concentration was achieved (e.g., 1,000 ppm in the case of EC/DEC without salt vs. approx. 25,000 ppm for EC/DEC with KPF6 after 30 min). The reaction was faster and at higher concentrations for the short-chain DMC than for the longer-chain DEC (approx. 40,000 ppm vs. 1,000 ppm, both without salt, Figure 9). It is remarkable that, despite starting with the pure solvent EC/EMC, the coupling products DMDD and DEDD were found in considerable quantities (around 15,000 ppm) after only a short time in the case of salt-containing EC/EMC electrolytes (Figure 10). Without salt, the formation was significantly delayed and slowed down in this case. This underlines the fast transesterification reaction and/or the intermolecular reaction of the formation of the dialkyl dicarbonates, discussed above.

It was found that the concentration of dicarbonate products formed after each 30 min decreased in the order DMC > EMC > DEC (with conducting salt: approx. 40,000 ppm EC/DMC; approx. 24,000 ppm EC/EMC; approx. 15,000 ppm EC/DEC). Without conducting salt, the formation is reduced but follows the same trend: DMC > EMC > DEC (after 30 min: approx. 25,000 ppm EC/DMC; approx. 3,000 ppm EC/EMC; approx. 1,000 ppm EC/DEC). In Figure 10, it is noticeable that the concentration of DEDD is higher than that of DMDD. However, since it was shown above (Figure 2 and Figure 3) that the formation of DEC is beneficial compared to DMC from EMC, this can be explained by a higher concentration of DEC over DMC. The influence of the conducting salt may be caused by several factors, e.g., acid-catalyzed reactions as a result of HF formation from the conducting salt, surface-induced reactions by contact of the conducting salt with the potassium surface including the formation of a reactive surface species, which then accelerates reactions, or salt-solvent interactions (dipol or ionic interactions) with change of polarization during the dicarbonate formation.

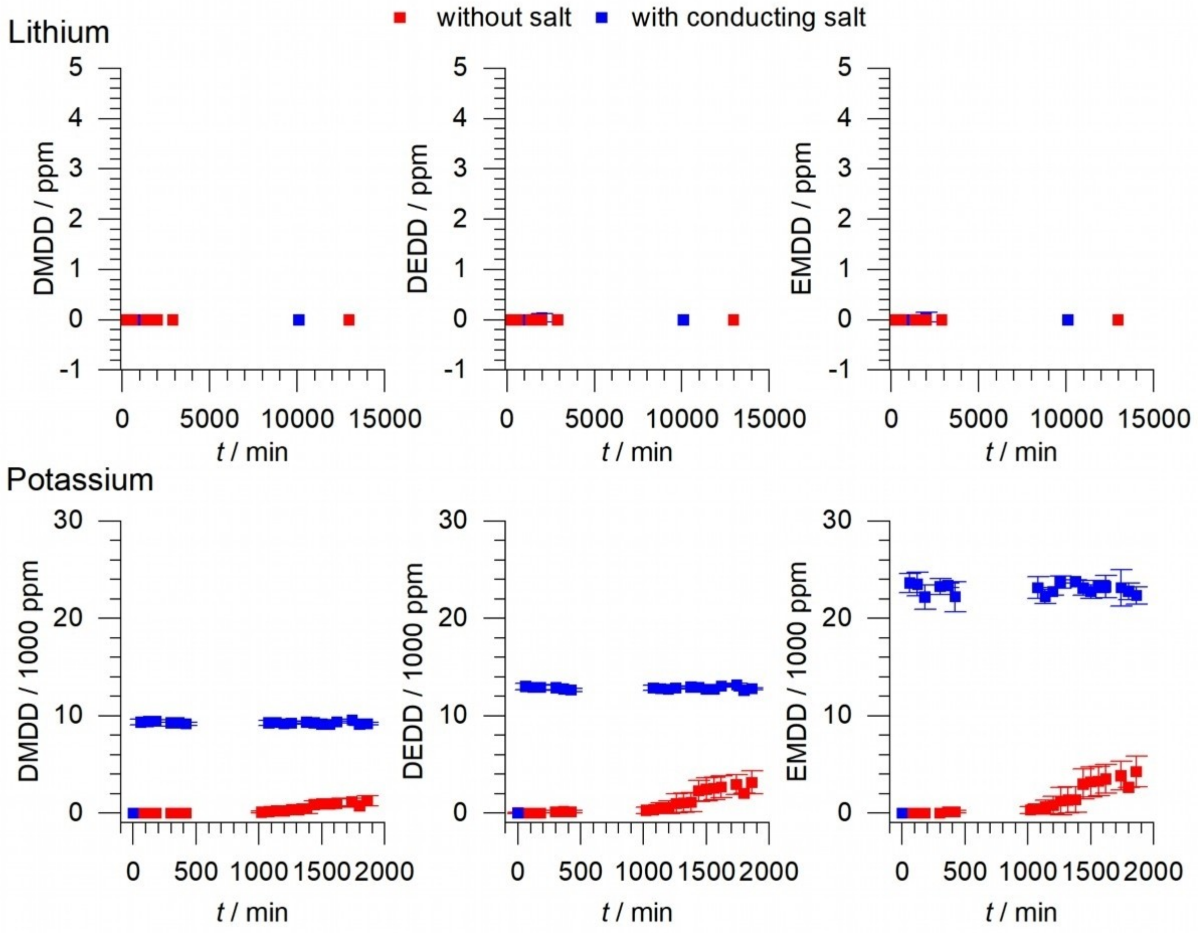

Figure 10. Results of the time-dependent measurements of EMC/EC solvent mixtures stored over lithium (above) and potassium metal (below). The formation of DMDD, EMDD and DEDD was measured quantitatively via GCMS. Additionally, the results of the measurements with conducting salt ($LiPF_6$ for Li metal and KPF_6 for K metal samples) in the solvent mixture is presented as well.

Based on the results, it can be concluded that the solvent combination EC/DMC is less favourable than EC/DEC with respect to the formation of dicarbonate products (if it is assumed that the formation of dicarbonates is unfavourable) and the formation of the corresponding products DMDD, EMDD and EMDD will definitely play a role due to the very short reaction times in potassium half cells. This must always be kept in mind when discussing cell results. In the case of lithium, the reaction is significantly slower, but the formation of the dicarbonate products in the case of half cells might also play a role there due to the applied voltage and must be taken into account.[11]

How linear carbonates impact the cycle life of graphite electrodes in half-cell configurations

In this section the cycle life of graphite–K half-cells was tested in dependence of the choice of electrolyte. The half-cells were cycled in one of the three electrolyte solutions containing 750 mM KPF_6 dissolved in either EC:DMC, EC:DEC or EC:EMC. The graphite electrode composition and the cycling conditions were established in our previous work, where a strong correlation between capacity fade and binder content was found.[19] Following these results, graphite electrodes with an active material content of 95 wt.% offer a good basis for material screening, as capacity decay commences within the first 100 cycles, but are cycle stable enough over the first 50–60 cycles (in a 750 mM KPF_6, EC:DEC electrolyte) so that improvements and adverse effects imparted by changes to cell components and materials are distinctly visible.

Figure 11 shows the galvanostatic cycling results as well as the corresponding Coulombic efficiencies for the three different electrolyte formulations employed in the graphite–K half-cells. The results clearly indicate an adverse effect on cycle life in presence of EMC and DMC compared to the DEC-containing solution. In other words, in solutions where the linear carbonate carries either one (EMC) or two (DMC) methyl groups, the capacity degradation proceeds significantly faster than in the DEC case where methyl groups are absent. A similar trend, that EC:DMC-based electrolytes fade faster, was observed previously by Zhao *et al.* who tested the capacity retention of graphite electrodes (KS4, Imerys) in electrolyte mixtures comprising EC: DMC, EC:DEC and EC:PC.[24] The GCMS measurements presented

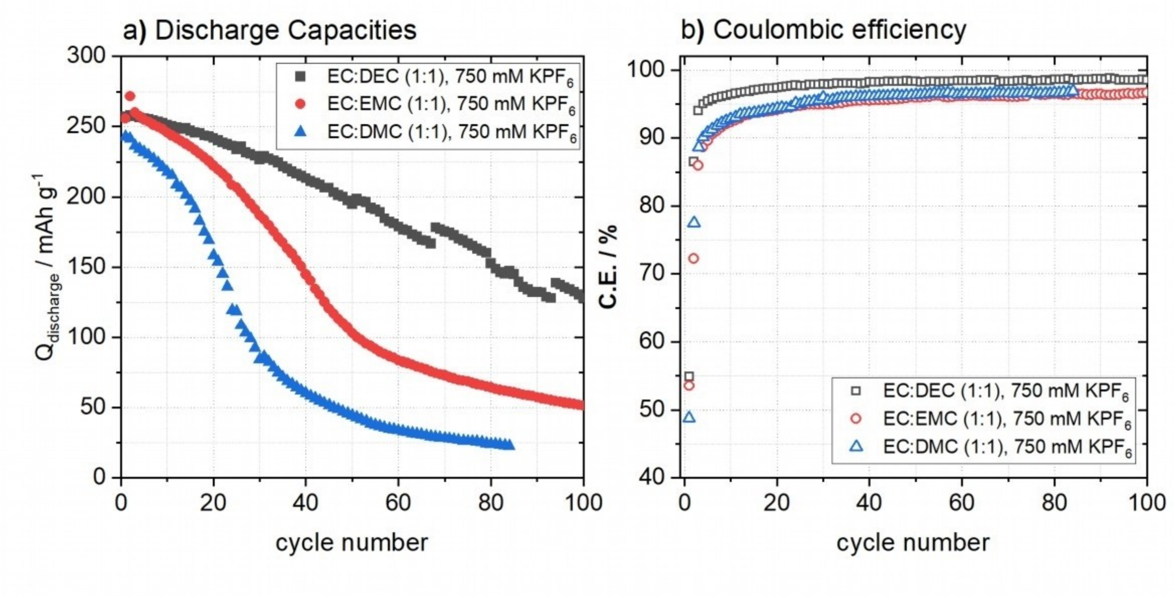

Figure 11. a) Discharge capacity and b) Coulomb efficiency of potassium//graphite coin cells in half cell configuration.

above, put the electrochemical data from previous works and herein into further context as the results strongly suggest that capacity retention appears to be associated to faster reaction rates of linear carbonate solvents with methyl moieties (as compared to ethyl moieties) on potassium metal. Nevertheless, it should be noted that the storage tests shown above can not be linked directly to materials or conditions which are under influence of a potential difference, since additional potentials may have an influence on the formation of degradation products also.

Based on the results of our storage test, the DMDD and DEDD concentrations approach a stable value in less than 2000 min (Figure 10). The steady state concentration is likely a result of the formation of a passivation layer on the K-metal electrode. In our experiment cell cycling commenced after 120 min under OCV conditions. Recurrent degradation reactions are expected during cycling due to repeated stripping and plating processes at the K-metal counter electrode, which could further facilitate the formation of dicarbonates.

Therefore, in half-cells a certain amount of DMDD and/or DEDD dicarbonates is already present before the SEI has formed on the working electrode. The presence of these compounds in the electrolyte mixture has a notable impact in the surface chemistry of the graphite working electrode through crosstalk, i.e., diffusion and deposition on the graphite electrode surface. Significant chemical changes by surface deposits were clearly observed already during short OCV storage times by XPS analysis, as demonstrated in previous works.[3,16] Interestingly, in this context it is worth to mention that Hosaka et al. recently correlated parasitic side reactions caused at the positive electrode to bicarbonate formations at the K-metal counter electrode.[25] The degradation processes are thus a phenomenon that appears to be related to the use of the metallic electrodes in half cell setups. According to Sasaki et al. the dicarbonates then cause deterioration of the graphite electrode.[14] In other words, half cells provide an obscured view on the cycling stability of positive and negative electrodes alike, due to the formation of parasitic dicarbonates formed at the metallic counter electrode. In K-ion systems this effect is strongly amplified in comparison to corresponding Li-ion cells, which appears to be a main cause for accelerated capacity decay.[19] Amongst the linear carbonates those with methyl moieties accumulate in higher concentrations thus accelerating electrode degradation even further.

Ultimately, a self-accelerating degradation cycle could be initiated: deterioration of graphite and recurrent consumption of dicarbonates also lead to reformation of these detrimental compounds, which affects the ageing processes at both electrodes. Loss of K-ion through SEI surface deposits is compensated by the K-metal electrode, but may also lead to dendrites formation and mossy surface deposits, i.e., an overall larger electrode surface area. This gives rise to more side reactions and bicarbonate formation. In addition, the SEI on K-metal will grow continuously, thus rapidly increasing the voltage hysteresis and internal cell resistance.[19]

A comprehensive overview of the changes in voltage profiles for a set of selected cycles for the three cell configurations is provided in the Supporting Information (Figure S-14). The findings are in agreement with our previous study,[19] where a rapidly increasing voltage hysteresis was found with increasing cycle number. The cells thus approached the lower cut-off limit in less time as the hysteresis increases. As a result, cycling ends prematurely and the capacity decreases. However, lowering the cut-off limit would risk potassium plating. The voltage profiles underline the trends in Figure 11, as the voltage hysteresis builds faster with increasing number of methyl groups from DEC showing the slowest build up, to EMC and finally DMC with the fastest build-up.

Conclusions and outlook

In this study, we have investigated in detail the formation of transesterification products and alkyl dicarbonate coupling products when electrolyte components are brought into contact with lithium or potassium metal, respectively. The following conclusions can be drawn on the basis of gas chromatography measurements:

- Metal surfaces (Li, K) in the presence of EMC or DMC and DEC lead to fast transesterification reactions that change the initial solvent composition.
- The formation of dialkyl dioxahexane dioate compounds ('dicarbonates') can be detected by NMR and particularly GCMS.
- The formation respectively reaction rate of dicarbonate coupling products decreases in the order EC/DMC $>$ EC/EMC $>$ EC/DEC and K $>$ Na $>$ Li, respectively.
- Conducting salt (KPF_6) leads to accelerated formation of the corresponding dicarbonates
- Experiments with deuterated DMC indicate an intermolecular reaction between cyclic and linear carbonate
- From the quantitative analyses of the solvent mixtures with and without conducting salt as well as the results of the coin cells, it can be concluded that the DEC-based EC/carbonate mixture is more advantageous compared to the EC/DMC and EC/EMC carbonate mixtures in potassium-based half cells.

The results raise questions as to how transferable degradation phenomena in half cell setups are to full cell tests, especially in the light of accelerated degradation processes in post-Li storage systems, like K-ion batteries.

In literature, it has already been shown that additives (e.g., 1,3,2-dioxathiolane 2,2-dioxide, DTD[25]) can suppress or inhibit the formation of dicarbonate derivatives via passivation of the alkali metal. This allows the use of shorter-chain linear carbonates, some of which have better flow and solubility properties and is topic for upcoming studies.

Author Contributions

A.H.: Conceptualization (equal), Investigation (equal), Formal Analysis (equal), Resources (equal), Visualization, Writing – Original Draft Preparation (lead), Writing – Review & Editing (equal), Supervision (equal).

F.J.: Conceptualization (equal), Formal Analysis (equal), Investigation (equal), Resources (equal), Supervision (equal), Visualization, Writing – Review & Editing (equal), Writing – Original Draft Preparation (supporting).

F.M.: Investigation (equal), Formal Analysis (equal), Writing – Review & Editing (equal).

S.S.: Investigation (equal), Writing – Review & Editing (equal).

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in zenodo.org at https://doi.org/10.5281/zenodo.8355291.

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