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Supporting Information on Article "Mechanistic Insights into Lithium Ion Battery Electrolyte Degradation – A Quantitative NMR Study"

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S1 Experimental

Table S1: Bruker NMR measurement parameters.

Test series	Dilution series		Quantification	
Measurement	^{19}F $\{^{1}H\}$	^{13}C $\{^{1}H\}$	^{19}F	^{13}C $\{^{1}H\}$
Bruker pulse program	zgfhi gqn.2	zgpg30	zg	zgpg
Number of scans	64	256	32	64
d1 delay / s	8	2	2	2
Acquisition time / s	4	4.5	5	3.2

S2 Identification

Figure S1 shows the ^{1}H NMR spectrum of a strongly degraded LP30 sample. Not all of the signals contained in the presented spectrum are assigned to their corresponding compounds in literature. The signals of EC (4.63 ppm), DMC (3.81 ppm) and dimethyl ether (3.37 ppm) were assigned according to previous publications.[10,11] Furthermore, there is a small singlet at 5.80 ppm (out of the displayed range), according to literature it is attributed to ethylene.[11] Signal 2 at 3.67 ppm is previously assigned to -(CH_2-CH_2-O-)$_n$-.[11] However, this signal as well as signal 5 (4.32 ppm) show a coupling pattern of a doublet and a triplet. Whereas an oligomer of this kind would be expected to show a singlet. This means that further measurements are necessary to assign the signals 1-6.

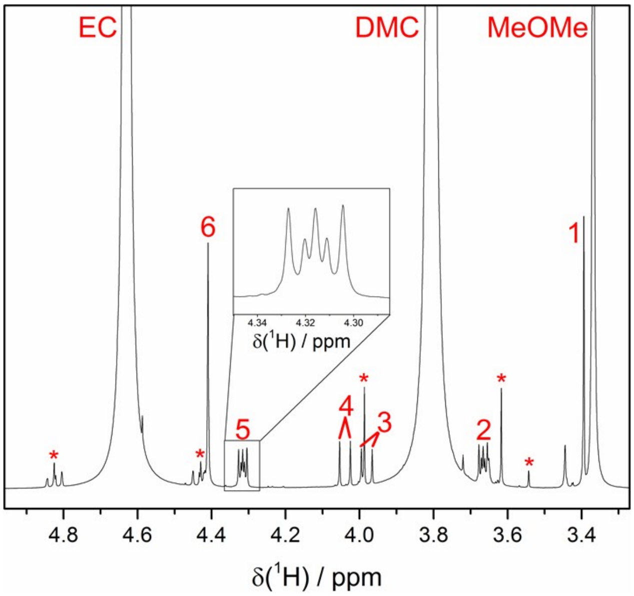

Figure S1: ^{1}H NMR spectrum of strongly degraded LP30 with 1000 vppm H_2O stored at 80 °C. *: ^{13}C satellites.

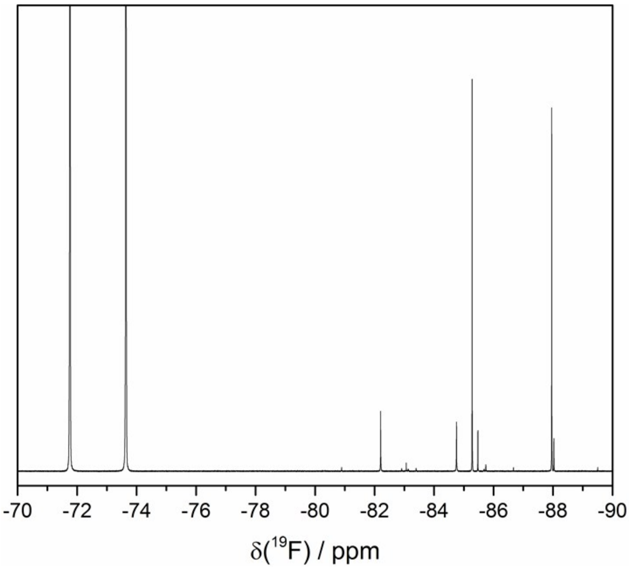

Figure S2: ^{19}F NMR spectrum of LP30 electrolyte after storage at 60 °C for 56 days in a NMR glass tube.

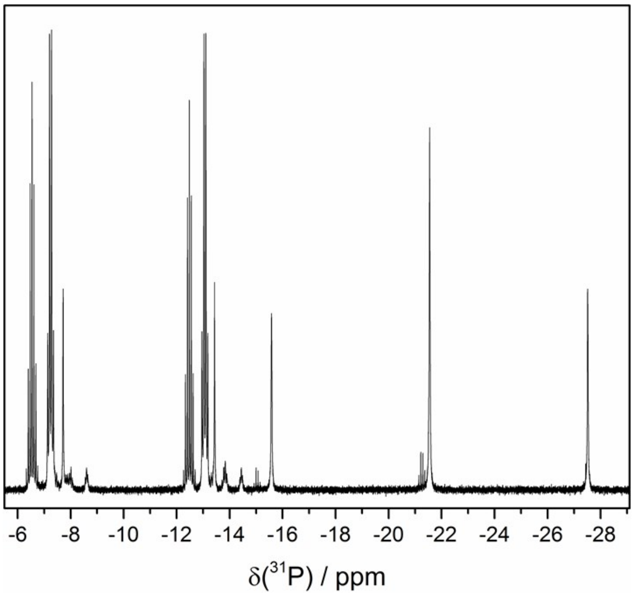

Figure S3: ^{31}P NMR spectrum of strongly degraded LP30 with 1000 vppm H_2O stored at 80 °C.

From the corresponding ^{31}P NMR spectra (**Figure S3**) it can be concluded that all phosphates formed by degradation of PF_6 are fluorinated because all of the signals show characteristic $^{1}J(^{19}F\text{-}^{31}P)$ coupling constants (approx. 700 - 1100 Hz). In addition, the coupling patterns of the ^{31}P signals enable a direct identification of the corresponding compounds because $^{3}J(^{1}H\text{-}^{31}P)$ and even $^{4}J(^{1}H\text{-}^{31}P)$ couplings are observable. The identified compounds are listed in **table 1**. Only in the cases of $OPF_2(OH)\text{-}BF_3$ and $OPF_2(OCH_2CH_2\text{-}O\text{-}CH_3)$ ^{31}P measurements were not sufficient for a complete identification of the compounds. ^{1}H ^{31}P heteronuclear multiple bond correlation (HMBC) NMR measurements (**Figure S4**) reveal that the doublet signals 3 and 4 (**Figure S1**) may be attributed to OPF(OMe)(OH) and $OPF(OMe)_2$, while the doublet at 4.22 ppm reflects OPF_2(OMe).

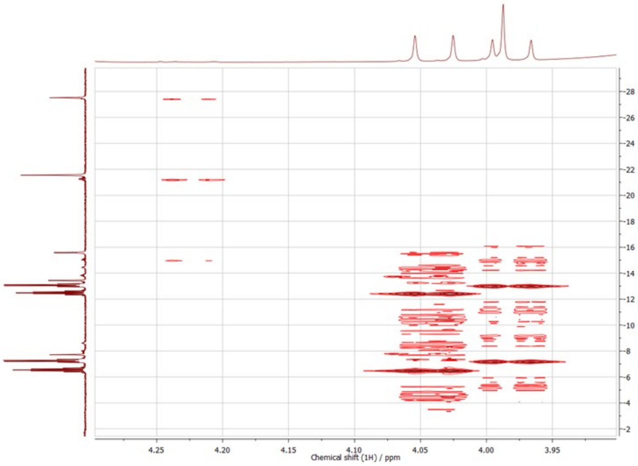

Figure S4: ^{1}H ^{31}P HMBC spectrum of aged LP30.

For the assignments of the signals 1, 2 and 5 several NMR measurements are necessary. ^{1}H ^{13}C heteronuclear single quantum coherence (HSQC) and ^{1}H ^{13}C HMBC NMR measurements reveal that the groups of signal 2 and signal 5 are adjacent and the group of signal 1 is located at a distance of two bond lengths from the group of signal 1. Distorsionless enhancement by polarization transfer (DEPT) 90 and DEPT 135 NMR experiments disclose that the adjacent groups are CH_2 groups and that the other one is a CH_3 group. This means that these signals belong to a $\text{-}CH_2CH_2OMe$ group.

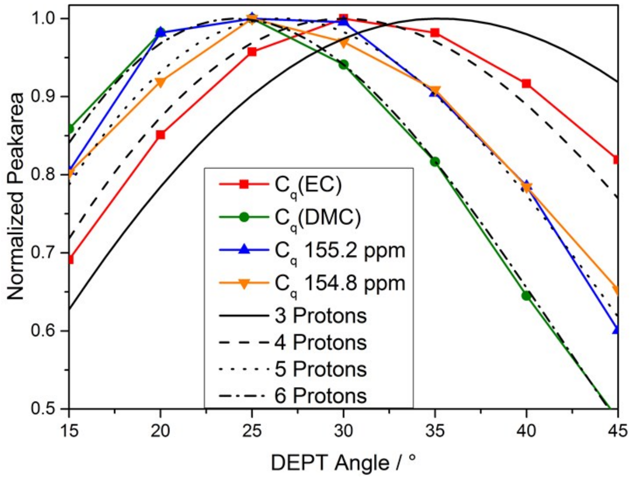

Figure S5: Integrated signal areas of quaternary carbon signals at different DEPT angles. All curves are normalized to their maxima. Black lines represent theoretical calculations for different numbers of protons according to $I(n,\beta) \propto sin(\beta) \cdot cos(\beta)^{n-1}$. Where n is the number of protons coupling with C_q and β is the DEPT angle. Colored lines serve as guide to the eye.

Furthermore, the ^{1}H ^{13}C HMBC measurements show a coupling of the CH_2 signals 5 and 6 to two quaternary carbons (C_q) of two different carbonate groups at -157.3 and -157.7 ppm. Due to the low sensitivity of ^{13}C measurements without decoupling, the coupling pattern of these quaternary carbons is not clear enough to identify the second group bound to the carbonate groups. In order to find out whether it is an H, CH_2 or CH_3 group, a series of DEPT measurements were performed (**Figure S5**). The pulse sequence intervals were adapted to the $^{3}J(^{1}H\text{-}^{13}C)$ coupling constant and the DEPT angle was varied from 15° to 45°. By means of product operator formalism[27] it can be deduced that the curve shape of the integrated NMR signal area *I* is described by the following equation: $I(n,\beta) \propto sin(\beta) \cdot cos(\beta)^{n-1}$. Where n is the number of protons and β is the DEPT angle. The curve of the integrated signal areas of EC and DMC fit well to their corresponding calculated curves for four and six protons (**Figure S5**). The two unidentified carbon signals fit well to the calculated curve for five protons, indicating that both carbonate groups are bound to methyl groups, thus identifying signal 6 as dimethyl-2,5-dioxahexane dicarboxylate (DMDOHC) and the signals 1, 2 and 5 as 2-methoxyethyl methyl carbonate (MEMC) (**Figure S6**). The ^{1}H signals of these methyl groups do most likely overlap with the broad DMC signal. The presence of these compounds is in accordance with the findings of gas chromatography and mass spectrometry measurements of similar samples.[7, 13, 17, 28, 29] However, the identification of their NMR signals is necessary as mentioned above because the ethylene groups of these compounds indicate that they are degradation products of EC.

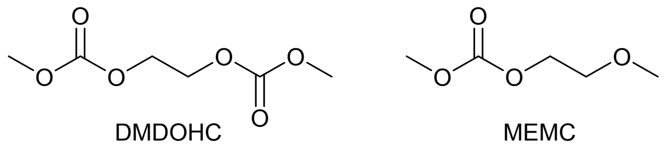

Figure S6: Structures of the main degradation products of EC, dimethyl-2,5-dioxahexane dicarboxylate (DMDOHC) and 2-methoxyethyl methyl carbonate (MEMC).

The coupling pattern of signal 2 and signal 5 (**Figure S1)** can be explained by the Karplus equation that describes the correlation between ^3J coupling constants and the dihedral torsion angle. If the rotation around the C-C axis was hindered the protons of one CH_2 group would have different dihedral torsion angles to their couplings partners of the other CH_2 group. This can explain the presence of two different coupling patterns of the protons of one CH_2 group caused by three different ^3J coupling constants in this case, namely 0, 1.9 and 9.1 Hz.

As mentioned above, $OPF_2(OH)$-BF_3 cannot be identified solely from the coupling pattern of its ^{31}P signal. In this case the chemical shift and the coupling pattern of the ^{19}F signals (**Table 1**) provides the required information. $^{19}F\{^1H\}$ measurements confirm that protons do not take part in the coupling.

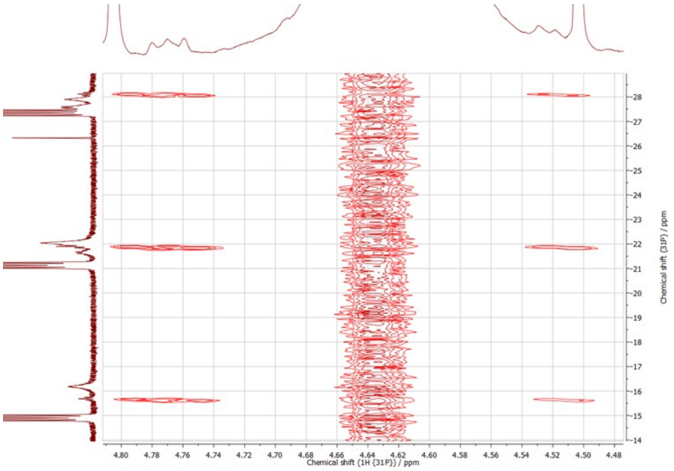

Figure S7: ^1H ^{31}P HMBC spectrum of aged LP30 containing NMR signals of a $-POCH_2CH_2$- group.

A ^{31}P signal at -21.9 ppm of the samples stored in glass tubes shows a coupling pattern of three triplets. The observed coupling constants (1007 Hz, 9.4 Hz, 1.9 Hz) indicate two fluorine atoms and a $-OCH_2CH_2$- group as coupling partners of the phosphorous atom. ^1H ^{31}P HMBC measurements (**Figure S7**) reveal that the ^1H signals of the two methylene groups are at 4.51 ppm and at 4.77 ppm. However, there is no signal found which corresponds to the group bound to the other side of the $-OCH_2CH_2$- group. According to literature the compound is $OPF_2OCH_2CH_2F$ and the missing signal belongs to a fluorine atom.[9] The ^{19}F signals of the two fluorine atoms bound to the phosphorous are clearly observable but no corresponding ^{19}F signal is found in the region of fluorinated alkanes (approx. -300 ppm to -150 ppm). Therefore, it is assumed that the missing part is a methoxy group, which would be in accordance with the findings of Kraft et al.[23] The compound is most likely $OPF_2(OCH_2CH_2OMe)$. Furthermore, this assignment is supported by the signal shapes of the above-mentioned ^1H signals in a $^1H\{^{31}P\}$ NMR spectrum (**Figure S7** horizontal trace) which are similar to the methylene ^1H NMR signal shapes of the $-OCH_2CH_2OMe$ group of MEMC (**Figure S1**).

S3 Quantification - Internal standards

The aromatic compounds meet the requirements for this application in NMR glass tubes. Their signals neither overlap with any other signal, nor decrease over time and no influence on the electrolyte degradation is observed. Trichlorofluoromethane show a decreasing signal after a few days, i.e. it is not stable at these conditions. However, the samples stored in PTFE tubes show different results. The signals of monofluorobenzene and hexafluorobenzene decrease slowly. This is most likely due to diffusion of these compounds into the PTFE material. The signal of monofluoronaphthalene does not decrease but a slight positive effect on the electrolyte stability is observed. This effect is probably too low to make any use of it in a battery cell but too high to be neglected. Trichlorofluoromethane is not stable in these samples either. This means that a quantification cannot be realized this way.