Elucidating the Reactivity of Tris(trimethylsilyl)phosphite and Tris(trimethylsilyl)phosphate Additives in Carbonate Electrolytes—A Comparative Online Electrochemical Mass Spectrometry Study

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S Supporting Information

ABSTRACT: The electrolyte additives tris(trimethylsilyl)phosphite (TMPSi) and tris(trimethylsilyl)phosphate (TMSPa) have shown their potential to improve lifetime and decrease impedance build-up in lithium ion batteries (LIBs) in several studies. Online electrochemical mass spectrometry (OEMS) was applied to study the effect of TMPSi and TMSPa on a gas releasing parasitic reaction during cycling of HE-NCM/graphite cells in different electrolytes to elucidate their working mechanisms, for which so far contradictory claims can be found in the literature. The results underline the chemical instability of the two additives in solution and show that they have, with one exception, little or no effect on the release of O₂ and CO₂ which would be expected in the case of a passivating surface layer suppressing electrolyte decomposition. The decreased PO₂ evolution and the formation of Me₃SiF indicates that the main role of both additives is that of a chemical scavenger, e.g., for HF, which leads to decreased acidification of the electrolyte and thus a longer lifetime of LIBs containing these electrolytes.

KEYWORDS: Li-ion batteries, Li-rich NCM, electrolyte additives, online electrochemical mass spectrometry, fluoroethylene carbonate

I. INTRODUCTION

No ideal electrolyte is existing that exhibits all characteristics required for seamless operation of Li-ion batteries (e.g., high Li⁺ conductivity, low viscosity, electrochemically stable in an electrode operating voltage window, chemical inertness toward all cell components, etc.). Modern commercial Li-ion electrolytes are mainly based on LiPF₆ salt dissolved in a mixture of cyclic (e.g., ethylene carbonate EC) and linear (e.g., dimethyl carbonate (DMC) or diethyl carbonate (DEC)) carbonate solvents. The success of these carbonate electrolytes relies largely on their wide thermodynamic electrochemical stability window (~1.3–4.5 V vs Li/Li⁺)¹ and their ability to form a protective and stable solid electrolyte interphase (SEI) on the negative graphite electrode in the first cycle of the Li-ion cell. However, side reactions are yet prevalent, particularly at the positive transition metal oxide electrode operating at high potentials (>4.3 V), leading to loss of active lithium along with cell impedance growth, both of which belong to the main causes for a declining cell performance and shortened lifetime.

Electrolyte additives have been proven to prolong the lifetime of the Li-ion cell, and several additives with varying functionalities can be found in modern cells. For instance, molecular redox shuttles can be used to improve cell safety in the case of cell overcharge,^{2,3} additives such as vinylene carbonate (VC) or fluoroethylene carbonate (FEC) are selected due to their ability to form improved SEIs,⁴ and further additives of interest are scavengers of undesired

electrolyte species such as HF.⁵ Detailed information on the exhaustive number of investigated compounds is found in recent review papers.^{2,3}

Two of the most widely investigated additives are tris(trimethylsilyl)phosphate and tris(trimethylsilyl)phosphite (hereafter denoted TMSPa and TMPSi, respectively), differing solely with respect to the oxidation state of the central phosphorus atom (Figure 1). TMPSi was introduced as an electrolyte additive for Li-ion batteries in a patent from Samsung Ltd. in 2009⁶ and since then has been intensively investigated and shown to improve the electrochemical performance of Li-ion cells based on various electrode

Figure 1. Chemical structures of TMPSi and TMSPa.

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materials.^{7–12} Dahn et al. made in 2014 a first systematic comparison of the performances of TMSPi and TMSPa as electrolyte additives (in blends with other additives) and found that cells with TMSPa only slightly improved the performance compared to cells with blank electrolyte solution.^{8,13} In contrast, cells with TMSPi showed significantly improved charge end point slippage and Coulombic efficiency which they attribute to slower rate of parasitic reactions in the presence of the additive.⁸ Despite these latter findings, several further reports (with sometimes contradictory claims) have emerged showing significantly enhanced cycling performance of cells rather than including TMSPa.^{14–17}

The disparate results on the beneficial role of TMSPi and TMSPa (collectively hereafter abbreviated TMSPx) can largely be explained by the lack of fundamental understanding of how these electrolyte additives operate. The most frequently discussed mechanism is the formation of a protective surface layer on the cathode active material (CAM) for TMSPa^{15–19} and TMSPi^{7,9,11,20–22} due to oxidation of the additive at lower potentials than the conventional carbonate electrolytes. However, the various experimental and theoretical studies make contradictory claims about the oxidative stability of the additives,^{7,15,23,24} and thus it is still unclear if and under which conditions these additives are oxidized in the electrolyte. Recent studies propose that TMSPi or chemical decomposition products of it coordinate to the surface of the CAM to prevent side reactions and stabilize the material.^{23,25,26} As further modi operandi scavenging and/or stabilization of several potentially detrimental compounds were suggested: The most commonly proposed is HF scavenging by the $-\text{SiMe}_3$ moieties of TMSPi^{9–11,22} and TMSPa. Furthermore, oxygen scavenging by oxidation of the P(III) atom in TMSPi to a P(V) as proposed for triethyl phosphite,²⁷ stabilization of POF_3 by the free-electron pair in TMSPi, and subsequent suppression of LiPF_6 hydrolysis¹¹ as well as scavenging of alkoxides by TMSPi and thus preventing EC decomposition²⁸ were proposed.

Regardless of the operating mechanisms, the addition of TMSPx to the electrolyte is expected to reduce the extent of side reactions. Several side products of these electrolyte decomposition reactions are volatile, and a more mechanistic understanding of their formation can be obtained by monitoring their evolution during cycling. Online electrochemical mass spectrometry (OEMS) was shown by us (and others) to provide unparalleled means to monitor such reactions by following the gas evolution inside the Li-ion cell during operation. Both chemical and electrochemical side reactions, involving the active materials and/or the electrolyte, are readily discernible with unrivaled sensitivity. For instance, Li-ion oxide cathode surface instabilities may lead to the release of O_2 ,²⁹ and electrolyte solvent decomposition typically causes CO_2 , C_2H_4 , and H_2 to evolve while the degradation of the LiPF_6 salt generally generates POF_3 .^{30,31} In a recently published study we could already show that the application of TMSPa as electrolyte additive leads also to the formation of Me_3SiF . With the help of this gas we were able to assign the main role of TMSPa in a FEC/DEC based electrolyte to be the one of a chemical scavenger for both HF and LiF .³² Furthermore, the potential dependent evolution of Me_3SiF proved valuable to monitor the operando formation of F^- in LIBs.

The aim of the present study is to apply the knowledge from our previous study and evaluate (1) the differences between

TMSPi and TMSPa and (2) the differences between EC and FEC based electrolyte systems in advanced Li-ion full cells based on state-of-the-art electrodes (graphite vs overlithiated layered mixed transition metal oxide $\text{Li}_{x+1}\text{Ni}_y\text{Co}_z\text{Mn}_{1-y-z}\text{O}_2$, denoted HE-NCM vs Graphite) and electrolyte (1 M LiPF_6 in 12:88 (F)EC:DEC). We primarily target the question of whether these additives and the surface layers they form are effectively preventing reactions at the electrolyte/cathode interface (leading to reduced gas formation), if they suppress as surface complexing agents or O_2 scavengers the release from oxygen from the CAM or if they act as LiPF_6 electrolyte salt stabilizers which would lead to less POF_3 evolution, and aim to answer these questions by *operando* monitoring of the gas evolution with OEMS.

II. EXPERIMENTAL SECTION

II.1. Electrode Preparation. The positive electrodes consist of 89 wt % HE-NCM (BASF SE), 5 wt % polyvinylidene fluoride (PVDF Solef 5130, Solvay), 4.64 wt % Super C65 carbon (Imerys Graphite & Carbon, Switzerland), and 1.36 wt % graphite SFG6L coated on Celgard 2400 monolayer polypropylene. The active material loading was in the range 14.1 mg/cm². Graphite electrodes consisted of 95.7 wt % SFG6 (Imerys Graphite & Carbon, Switzerland), 0.5% Super C65 Carbon, and 3.8 wt % carboxymethyl cellulose (CMC) coated on Cu foil. Detailed information about the electrode preparation of HE-NCM and graphite electrodes can be obtained from previous publications.³²

II.2. Electrochemical Measurements. All cells were assembled in a glovebox filled with argon. HE-NCM ($\text{Li}_{1.17}(\text{Ni}_{0.22}\text{Co}_{0.12}\text{Mn}_{0.66})_{0.83}\text{O}_2$) electrodes were cycled vs SFG6 counter electrodes. All electrochemical measurements were carried out in electrolytes [1 M LiPF_6 , 12:88 (w/w) of ethylene carbonate (EC) and diethyl carbonate (DEC) (battery grade solvents, BASF SE) or (1 M LiPF_6 , 12:88 (w/w) of fluoroethylene carbonate (FEC) and diethyl carbonate (DEC) (battery grade, BASF SE)]. Tris-(trimethylsilyl)phosphate (TMSPa, Sigma-Aldrich, >98%) and tris-(trimethylsilyl)phosphite (TMSPi, Alfa Aesar, 96%) were used as received. If not mentioned otherwise, 1 wt % of TMSPa or 1 wt % TMSPi was added to the reference electrolytes to prepare electrolytes with an additive concentration ~ 40 mmol/L. The amount of trace water in the electrolytes, determined using Karl Fischer titration, was <30 ppm. The additives were added to the blank electrolytes just before assembling the OEMS cells so that the electrolytes were as fresh as possible. The assembled HE-NCM/graphite cells were equilibrated at a constant voltage of 0.2 V (open circuit potential value) for 4 h prior to electrochemical cycling. Galvanostatic cycling was carried out between 2.0 and 4.7 V vs Li^+/Li at a C/10 rate. The specific charges (not reported on the figures) were found similar to those reported previously (~ 300 mAh/g and 250 mAh/g at the end of the first charge and discharge, respectively).³³ All measurements were carried out at room temperature.

II.3. Online Electrochemical Mass Spectrometry (OEMS). The OEMS setup was described elsewhere³⁴ and operates with a quadrupole mass spectrometer (QMS 200, Pfeiffer) for partial pressure measurements, a pressure transducer (PAA-33X, Keller Druck AG) for total cell pressure, temperature, and internal volume determination, stainless steel gas pipes, Swagelok fittings (3 mm compression tube fittings, Swagelok, OH, U.S.A.) to connect the OEMS cell, a set of solenoid valves (2-way magnetic valve, Series 99, silver-plated nickel seal, Parker), and a scroll pump (nXDS15i, EDWARDS GmbH) for efficient flushing. The magnetic valves are electronically controlled with a Solid State Relay Module (NI 9485 measurement System, National Instruments) and connected to a computer with a LabView Software (NI Labview 2013, National Instruments). For partial pressure and gas evolution rate analysis, 1.3 mL of gas are extracted from the headspace (~ 4 mL) of the cell and replaced by pure Ar (quality 5.0). Calibration gas bottles were utilized to relate the MS ion-current signals at $m/z = 2, 26, 32$, and 44 to

Figure 2. Gas evolution rates of O_2 , H_2 , CO_2 , POF_3 ($m/z = 85$), and Me_3SiF ($m/z = 77$) for the two first galvanostatic cycles for HE-NCM electrodes cycled vs graphite between 0.5 and 4.7 V (C/10) in FEC:DEC (A) or EC/DEC (B) (12:88, 1 M LiPF_6) based electrolyte containing no additive (blank, black), 1 wt % TMSPi (blue), or 1 wt % TMSPa (red). The 4 h resting period before cycling is highlighted in light green.

known concentrations of H_2 , C_2H_4 , O_2 , and CO_2 (1000 ppm in Ar), before and after the measurement. POF_3 ($m/z = 85$) and Me_3SiF ($m/z = 77$) were calibrated using a procedure described in a previous study.³² Please note that due the m/z ratio of the Me_3SiF^+ fragment as well as its isotopic pattern can be assigned to the Me_3SiF^+ fragment which therefore rules out that the observed peaks (especially during the resting period) are stemming from evaporation of the TMSPi additive.

All gas evolution rates and gas amounts are normalized with respect to the mass of the cathode active material (CAM).

III. RESULTS

For studying the gas evolution with OEMS three HENCM/graphite cells were cycled in (F)EC/DEC electrolyte (12:88, 1 M LiPF_6) without additive (blank) or with either 1 wt % TMSPa or TMSPi, respectively. Figure 2A shows representative curves for the H_2 , CO_2 , O_2 , POF_3 , and Me_3SiF evolution for the three FEC containing electrolytes and Figure 2B the same gas evolutions for the respective cells with electrolyte consisting of EC. The observed gas evolution can be divided in two parts: (1) Initial potential hold period for 4 h when cell stability is monitored and gas formation is assumed to result solely from chemical reactions and (2) the galvanostatic cycling period when the observed gas formation is the result of electrochemical and chemical reactions. These two parts will be discussed separately in the following section.

III.1. Gas Evolution during the Initial Resting Period.

The cells are kept at a constant potential of 0.2 V for 4 h before being cycled in order not only to ensure proper wetting but also to obtain a stable baseline for the gas evolution. Typically,

after attaching the cells to the OEMS setup, minor contaminations of atmospheric gases (N_2 , O_2 , and CO_2) are observed, which drop rapidly to zero. However, for TMSPi containing electrolytes a different behavior is observed for POF_3 and Me_3SiF . For these two gases a continuous gas formation with an overall decreasing evolution rate takes place over the initial 4 h of the resting period. The integration of the gas evolution rates yields the released gas amounts, which are shown in Figure 3 (FEC based electrolytes) and Figure 4 (EC based electrolytes). With TMSPi present in the electrolyte, the amount of POF_3 is $0.5 \pm 0.2 \mu\text{mol g}^{-1}$ in the FEC and the EC containing ones. For the blank or TMSPa containing electrolytes no POF_3 evolution during the initial 4 h is observed. It is important to note here that POF_3 detected by OEMS can be both POF_3 and PF_3 , the latter reacting to POF_3 on the way from the cell to the MS.³⁵ The amount of Me_3SiF is $58 \pm 21 \mu\text{mol g}^{-1}$ in the FEC based electrolyte and $65 \pm 10 \mu\text{mol g}^{-1}$ for the electrolyte containing EC. The amount of Me_3SiF evolution in the initial resting period is therefore not significantly affected by the type of cyclic carbonate used in the electrolyte formulation. The TMSPi containing electrolytes produce more than 80 times more Me_3SiF than for the TMSPa containing ones, which have almost no gas evolution ($0.7 \pm 0.3 \mu\text{mol g}^{-1}$ (FEC); $0.4 \pm 0.1 \mu\text{mol g}^{-1}$ (EC)).

In another series of experiments, the rate of gas release of differently aged LP47 (3:7 EC/DEC, 1 M LiPF_6) electrolytes containing 1 wt % of either TMSPa or TMSPi was studied. The Me_3SiF evolution recorded during the resting period shows that only the 4 day aged electrolyte containing TMSPa has significant Me_3SiF evolution whereas for TMSPi there was

Figure 3. Gas amounts for POF₃ (A) and Me₃SiF (B) from FEC/DEC (12:88, 1 M LiPF₆) based electrolytes for the first two galvanostatic cycles. All values and error bars are obtained from three cells.

Figure 4. Gas amounts for CO₂ (A), POF₃ (B), and Me₃SiF (C) from EC/DEC (12:88, 1 M LiPF₆) based electrolytes for the first two galvanostatic cycles. All values and error bars are obtained from three cells.

a strong evolution only after 2 days and already much less gas evolution after 4 days (Figure S1). Clearly, the addition of TMSPi to the blank electrolytes leads to an immediate chemical reaction, most likely between the additive and the LiPF₆ as was shown by Qi et al.³⁶ In conclusion, there is a quite significant difference in the reactivity toward the electrolyte between the TMSPi additive containing a P(III) atom and TMSPa with a P(V).

III.2. Gas Evolution during Cycling: FEC/DEC Electrolyte. The underlying mechanisms for the evolution of H₂, CO₂, and O₂ in electrolyte formulations with FEC as cyclic carbonate are already discussed in detail in our previous works^{31,32} and thus are only summarized briefly here. O₂ evolution onsets at low rates at a cell voltage of about 4.2 V and undergoes a strong exponential increase above 4.5–4.6 V,

as a result of the formation of a reconstructed O-deficient surface layer on the NCM oxide.³⁷ The subsequent cycle shows only minor release of oxygen. H₂ evolution is mainly observed at the beginning of the first charge, predominantly due to the reduction of FEC and solvent impurities such as moisture or glycols.³⁸ A second peak is observed close to the cutoff potential, when oxidatively formed protic species (e.g., HF) are subsequently reduced at the anode. The CO₂ evolution shows three features in the first charge: First a strong evolution due to the FEC reduction during the SEI formation,^{39,40} second a maximum which was recently assigned to Li₂CO₃ oxidation³⁷ or dissolution due to proton formation, and third an exponential increase close to the cutoff voltage because of electrolyte decomposition triggered by the evolving singlet oxygen⁴¹ as well as further CO₂ release from surface carbonates.⁴² For the subsequent cycle only the latter evolution is observed at an onset potential of about 4.2–4.4 V. The gas evolution profiles for O₂, CO₂, and H₂ in Figure 2 show no qualitative differences between the blank reference electrolyte and electrolyte containing 1 wt % TMSPa, which was already observed in our previous study.³² Replacing TMSPa by TMSPi has also no significant influence on the evolution of O₂, CO₂, and H₂.

In contrast, the gases POF₃ and Me₃SiF are strongly affected by the presence of the additives in the electrolyte. We recently demonstrated the main role of TMSPa in its chemical reactivity toward fluorides, such as HF

which in turn suppresses electrolyte acidification and POF₃/PF₅ formation.³² Qualitative comparison of the POF₃ evolution rate in Figure 2A shows that the formation of POF₃ is being affected by the presence of both additives in a similar fashion by strongly suppressing its formation at high voltages. Plotting the POF₃ evolution rate as a function of the cell voltage shows that for the FEC/DEC electrolyte without additive the POF₃ evolution starts clearly below 4 V, whereas there is a clear delay in the presence of TMSPi (~4.1 V) and TMSPa (~4.3 V) (cf. see Figure S2). Especially in the case of the blank electrolyte, two processes may be readily distinguishable during the first cycle. The first process onsets at 3.7 V, is only present in the first cycle, and thus may be ascribed to the oxidation of cell impurities. The second process dominates at cell voltages above 4.3 V when also oxygen release from the material is initiated. The oxygen release leads to electrolyte oxidation and acidification and subsequently to the formation of PF₅ and POF₃.

Integration of the POF₃ in the first cycle (see Figure 3A) shows about three times more gas for the blank electrolyte (6.9 ± 1.5 μmol g⁻¹) compared to the electrolytes containing TMSPa (2.1 ± 0.1 μmol g⁻¹) or TMSPi (1.8 ± 0.7 μmol g⁻¹) and about two times more for the second cycle (3.3 ± 0.7 μmol g⁻¹ vs 1.3 ± 0.3 μmol g⁻¹ (TMSPa)/1.4 ± 0.3 μmol g⁻¹ (TMSPi)). However, POF₃ is overall only a minor contributor to the overall gassing in the first two cycles, and its amount is about five times lower than that for O₂ (55 ± 5 μmol g⁻¹) and 47 times lower than that for CO₂ (471 ± 27 μmol g⁻¹).

The total amount of POF₃ evolved in the first 2 cycles (~0.27 ± 0.03 μmol) corresponds only to a minor part (~0.2%) of LiPF₆ salt (~120 μmol) initially present in the cell. However, if the POF₃ rate keeps evolving constantly during

cycling with the same rate as that observed for the second cycle, all LiPF_6 present in our cell will be decomposed after ~ 1330 cycles. Although the POF_3 evolution rate is reduced in subsequent cycles,³² these experiments clearly show that LiPF_6 salt decomposition is not only an issue with respect to the formation of HF but also with respect to the loss in ion conductivity of the electrolyte for long cycle life. The addition of either TMSPa or TMSPi strongly suppresses the formation of POF_3 and only about one-third (see Figure 3A) of the amount in the blank electrolyte is determined in the first and second cycles when one of the additives is present. This demonstrates the effective mitigation of early salt decomposition and acidification of the electrolyte by adding TMSPx.

As Me_3SiF stems from the $-\text{SiMe}_3$ moiety of TMSPi or TMSPa there is no Me_3SiF evolution observed in the blank electrolyte. The Me_3SiF evolution in the FEC/DEC electrolyte with TMSPa was analyzed in detail in our previous study in which we were able to assign the three evolution maxima occurring during the first charge to different processes such as LiF formation due to FEC reduction (~ 3.5 V), H^+ and HF formation due to oxidation of (surface) impurities (~ 4.3 – 4.4 V), and further H^+ formation due to electrolyte oxidation by reactive singlet oxygen released from the active material (4.7 V).³² In the second cycle only the last maximum is observed, which occurs in parallel with the evolution maxima for CO_2 and POF_3 . If we compare the Me_3SiF evolution for TMSPa with the one for TMSPi (see Figure 2A) we can still see a clear Me_3SiF evolution maximum at the end of charge although its evolution rate is significantly lower than for the TMSPa containing electrolyte (0.05 vs $0.26 \mu\text{mol min}^{-1} \text{g}^{-1}$).

The lower evolution rates for the TMSPi containing electrolyte result in overall lower gas amounts in both cycles. In the first cycle the TMSPa containing electrolyte forms over three times more Me_3SiF ($143 \pm 17 \mu\text{mol g}^{-1}$ vs $39 \pm 12 \mu\text{mol g}^{-1}$), and in the second cycle the gas formation is even more than 7 times higher ($44 \pm 3 \mu\text{mol g}^{-1}$ vs $6 \pm 1 \mu\text{mol g}^{-1}$). In total, during the OCP period and the first two galvanostatic cycles, $2.5 \pm 0.8 \mu\text{mol}$ of Me_3SiF were detected for TMSPi in contrast to $4.7 \pm 0.6 \mu\text{mol}$ for TMSPa. For $120 \mu\text{L}$ of FEC/DEC electrolyte containing 1 wt % of the additive this corresponds to a conversion of $18 \pm 6\%$ of TMSPi and $35 \pm 4\%$ for TMSPa (assuming three reactive sites for the additives) into Me_3SiF . For TMSPa, about 8% of the additive reacts to Me_3SiF during the second cycle, which means that it would take at least 10 cycles to fully convert all silyl groups from TMSPa to Me_3SiF . However, in the case of TMSPi it must also be assumed that due to the fast reactivity toward LiPF_6 ³⁶ parts of Me_3SiF already escaped during the cell assembly, so the amount of reacted TMSPi is very likely underestimated. This also makes it difficult to give any assumptions about how long it would take until all TMSPi has reacted.

III.3. Gas Evolution during Cycling: EC/DEC Electrolyte. In a second set of experiments HENCM/graphite cells were cycled in EC/DEC electrolyte (12:88, 1 M LiPF_6) without additive (blank) or with either 1 wt % TMSPa or 1 wt % TMSPi, respectively. Figure 2B shows representative curves for the H_2 , CO_2 , O_2 , POF_3 , and Me_3SiF evolution for the EC based electrolytes. Please note that during the reduction of EC also C_2H_4 is formed; however, as its formation is well understood and described^{31,43,44} it is not discussed in this study.

Also for EC based electrolytes the mechanisms for the evolution of H_2 and O_2 were already discussed in detail in

previous works.^{31,37,45} No apparent difference in the gas evolution profiles from the earlier works is observed for these two gases. If we compare the evolution profiles between the three EC based electrolytes, it can be easily seen that there is no major difference. There is also no apparent difference between the evolution profiles for these two gases between the FEC based and the EC based electrolytes.

In contrast to the FEC based electrolyte there are clear differences in the CO_2 evolution profile for the EC based electrolytes. While all three electrolytes show the same features, namely, a first peak in the evolution at about 4.35 V, which is only observed in the first cycle, followed by a maximum evolution at the cutoff voltage of 4.7 V, the evolution rate for the electrolyte with TMSPi is significantly lower compared with the others. For example, during the first evolution peak at about 4.35 V the CO_2 evolution rate for the TMSPi based electrolyte is only $0.13 \mu\text{mol min}^{-1} \text{g}^{-1}$ and thus clearly lower than both the blank electrolyte ($0.22 \mu\text{mol min}^{-1} \text{g}^{-1}$) as well as the one containing TMSPa ($0.19 \mu\text{mol min}^{-1} \text{g}^{-1}$). The significantly lower evolution rate is observed all over the first two cycles and subsequently results in a lower amount of CO_2 ($121 \pm 10 \mu\text{mol g}^{-1}$) for the TMSPi based electrolyte compared to the blank ($246 \pm 42 \mu\text{mol g}^{-1}$) and the TMSPa containing one ($208 \pm 9 \mu\text{mol g}^{-1}$).

Significant differences were also observed for the formation of POF_3 . For all three EC based electrolytes the evolution profile for POF_3 only shows one major feature which is the maximum at the cutoff voltage of the cell at 4.7 V. The presence of TMSPa or TMSPi leads also for the EC based electrolytes to a suppression of POF_3 evolution; thus, the evolution rate at 4.7 V is for TMSPi ($4 \text{ nmol min}^{-1} \text{g}^{-1}$) and TMSPa ($10 \text{ nmol min}^{-1} \text{g}^{-1}$) about one-third that of the blank electrolyte ($26 \text{ nmol min}^{-1} \text{g}^{-1}$). Additionally, for TMSPa containing electrolyte a constant but very low POF_3 evolution (max. $1.2 \text{ nmol min}^{-1} \text{g}^{-1}$) was observed directly after the SEI formation until the onset of the high voltage maximum.

Comparison of the integrated gas amounts (Figure 4) shows that there is no significant difference between the blank EC based electrolyte ($0.9 \pm 0.6 \mu\text{mol g}^{-1}$) and the one containing TMSPa ($1.0 \pm 0.2 \mu\text{mol g}^{-1}$) in the first cycle, whereas in the second cycle, in which only the high voltage POF_3 maximum is observed for both electrolytes, the blank electrolyte releases more POF_3 ($0.9 \pm 0.5 \mu\text{mol g}^{-1}$) than the TMSPa containing electrolyte ($0.3 \pm 0.1 \mu\text{mol g}^{-1}$). For both cycles the lowest amount of POF_3 is however produced with the EC based electrolyte containing TMSPi ($0.4 \pm 0.2 \mu\text{mol g}^{-1}$ (1st cycle); $0.2 \pm 0.1 \mu\text{mol g}^{-1}$ (2nd cycle)). In all cases the EC based electrolytes produced significantly less POF_3 than their FEC based counterparts.

Also for the EC based electrolyte the formation of Me_3SiF is observed in electrolytes containing TMSPa or TMSPi. For the one containing TMSPa the evolution profile of Me_3SiF during the first charge has been discussed in detail in our previous study.³² As for the FEC based electrolyte three potential dependent evolution peaks are observed (cf. Figure 2). In the second cycle only the evolution maximum ($0.26 \mu\text{mol min}^{-1} \text{g}^{-1}$) at 4.7 V is observed. For TMSPi no distinguishable potential dependent evolution maxima can be identified during the first cycle due to the strong gas evolution in the resting period. Nonetheless, in the second cycle a small evolution maximum ($0.02 \mu\text{mol min}^{-1} \text{g}^{-1}$) is observed at 4.7 V showing that TMSPi or decomposition products thereof are still undergoing reactions at these voltages. The gassing of

Me₃SiF during cycling with TMSPi as additive is also about four times lower than for the electrolyte containing TMSPa (see Figure 4).

Comparison of the absolute Me₃SiF amounts in FEC based electrolytes (TMSPi: 2.5 ± 0.8 μmol; TMSPa: 4.7 ± 0.6 μmol) with the ones in EC based electrolytes (TMSPi: 2.7 ± 0.3 μmol; TMSPa: 3.1 ± 0.2 μmol) shows that the gas amount measured is largely independent from the cyclic carbonate used in the electrolyte formulation. Additionally, the cyclic carbonate used does not have a major impact on the extent of the conversion of the TMSPi additive into gaseous Me₃SiF (FEC: 18 ± 6%; EC: 20 ± 2%). However, for TMSPa there is significant influence, which can probably be assigned to the formation of LiF during FEC reduction, resulting in a lower conversion to Me₃SiF in the EC based electrolyte (23 ± 2%) compared to the FEC based one (35 ± 4%).

III.4. Further Analytical Data. Based on gas analysis with OEMS and cyclic voltammetry measurements we have recently concluded that there is no oxidation of the TMSPa additive in FEC based electrolytes and also no formation of a surface layer which should result in suppressed formation of CO₂.³² Analysis of the surface of HE-NCM electrodes in in EC:DEC (12:88) 1 M LiClO₄ containing 0 or 1 wt % TMSPa (Supporting Information Figure S3) confirmed the absence of any surface layer formed due to TMSPa oxidation.

OEMS analysis of FEC electrolyte based cells containing TMSPi shows that there is also no significant suppression of CO₂, and thus the formation of a SPI which effectively prevents electrolyte decomposition is unlikely for HE-NCM. However, cyclic voltammetry on carbon electrodes showed significantly higher currents >4.5 V vs Li⁺/Li for electrolyte containing TMSPi (see Figure S4) which is in contrast to theoretical studies by Kim et al., who predict a stability for TMSPi similar to that for TMSPa.²⁴ The additional oxidative current is rather high and would correspond to >3 e⁻/TMSPi. As discussed in the previous section, the low chemical stability of TMSPi in the 12:88 electrolytes makes it doubtful if there is still a significant amount of TMSPi present in the electrolyte when the cell reaches high cell voltages. We therefore hypothesize that not TMSPi itself, but rather a decomposition product of it, undergoes the observed electrochemical oxidation. Gas analysis by OEMS that was performed during the CV experiments did not provide any further information about the products of this oxidation reaction.

IV. DISCUSSION

IV.1. Stability of TMSPi/a in LiPF₆ Containing Electrolytes. A major difference between TMSPa and TMSPi is the reactivity toward the LiPF₆ salt in the electrolyte which could be observed in the form of Me₃SiF and PO₂F₃ release during the initial 4 h resting period. While the TMSPa containing electrolytes show hardly any evolution of Me₃SiF during the early rest period, the electrolytes with TMSPi release significant amounts of Me₃SiF, and their evolution rates decay exponentially directly after attachment of the cell to the OEMS setup. This observation is a result of the already described reactivity of the TMSPi additive toward the PF₆⁻ anion, which leads to the decomposition of the additive and the salt.³⁶ The high initial amount of Me₃SiF, the evolution of some PO₂F₃ or PF₃, and the low amounts released during cycling indicate that an immediate reaction of TMSPi with the PF₆⁻ anion is taking place once the additive is added to the base electrolyte. One could hypothesize that the free electron

pair of TMSPi allows for the coordination of the Lewis acid PF₅ and that the close proximity of F⁻ and Me₃Si⁻ leads to the cleavage of one or several Me₃SiF from this complex.

For the LP47 electrolyte used by Qi et al.,³⁶ which has a 3:7 (w/w) EC/DEC ratio, the reactivity toward the LiPF₆ salt is much slower (hardly any evolution of Me₃SiF during the resting period for the freshly prepared electrolyte, cf. Figure S1). In contrast the electrolytes containing only 12% (F)EC show a higher reactivity toward the PF₆⁻ anion which is an effect of the lower content of the cyclic carbonate. Borodin et al. showed by DFT calculations that highly EC coordinated Li⁺ cations are energetically more favored, with the 4-fold coordinated as the most stable complex.⁴⁶ Other theoretical studies^{47,48} or experimental studies⁴⁹ indicate that the Li⁺ might even be coordinated by up to 5 or 6 cyclic carbonate molecules. However, in an (F)EC/DEC (12:88) electrolyte with 1 M LiPF₆ the ratio (F)EC:Li⁺ is only about 1.6:1 (compare Figure S5). Therefore, it can be assumed that not all Li⁺ are coordinated by cyclic carbonates and LiPF₆ occurs partly as a contact ion pair as was observed for LiClO₄ in pure DEC.⁵⁰ A recent MD simulation by Hou et al. shows also that coordination to Li⁺ is weaker for FEC than for EC which leads to a higher extent of contact-ion pairs in FEC based electrolytes.⁴⁷ In a contact-ion pair, the direct coordination of Li⁺ to the PF₆⁻ anion weakens the P–F bonds and makes it thus more reactive toward the additives. Therefore, the stabilities of TMSPi and TMSPa are strongly dependent on the composition of the electrolyte.

However, even for electrolytes with higher EC content such as LP47, the 4 day aged solution with 1 wt % TMSPi only shows Me₃SiF evolution during the OCP but no potential dependent gas formation during cycling, indicating that all TMSPi is consumed, forming a less reactive compound. This high reactivity of TMSPi makes it questionable if the additive itself or decomposition products thereof cause the reported long-term effects of TMSPi. A detailed study about TMSPi decomposition products in electrolyte solutions containing 10 wt % additive was conducted by Peebles et al.²⁵ They identified the aging product F₂POSiMe₃ as the effective additive in their system (NCM523) as it is able to bind to NCM surfaces. In general, despite its positive effects of HF scavenging, some reaction products of TMSPi might even be more desirable additives.

IV.2. Main Operation Mechanism of TMSPa/TMSPi in the FEC Based Electrolyte. All of the working mechanisms of TMSPx listed in the Introduction should influence the gas evolution during cycling, and OEMS should thus allow us to study which of these processes play a role in the studied systems. Formation of a protective surface layer which effectively prevents electrolyte decomposition should result in decreased electrolyte oxidation and thus less CO₂ evolution. Additionally an oxidative current should be observable if the surface layer is formed due to additive oxidation. The complexation of the surface should also lead to decreased formation of CO₂ and, in the case of a stabilization of the surface, less O₂ release. The latter should also be observed in the case of O scavenging, whereas HF/PO₂F₃ scavenging should result in decreased PO₂F₃ formation and, in the case of HF scavenging, the evolution of Me₃SiF.

The absence of any suppressed CO₂ evolution for TMSPa and TMSPi, despite the observation of an oxidative current for the latter in the CV experiments, indicates that any surface

layer formed is not effectively preventing reactions which lead to electrolyte oxidation and CO_2 formation.

The OEMS data also show that there is no suppression of O_2 evolution by TMSPi, thus indicating that TMSPi is not acting as an oxygen scavenger. In addition, it can be also excluded that a coordination of TMSPx additive or its respective decomposition products coordinate the surface in a manner that leads to a significant stabilization of the CAM surface and suppresses formation of a rock-salt surface layer during the initial cycles.

Similar to TMSPa, the main effect of TMSPi in the FEC based electrolyte as can be observed by OEMS is also the suppression of the formation of POF_3/PF_5 as can be seen from the clearly suppressed evolution rates and amounts (cf. Figure 2). As mentioned above, POF_3 and PF_5 cannot be distinguished in the MS and are measured as a fragment of POF_3 . However, the study by Solchenbach et al. shows that the source of it is very likely PF_5 which is formed due to acidification of the electrolyte.³⁵ The suppression of POF_3 formation for TMSPx can be therefore attributed to the decrease of the acidity in the electrolyte by the additives. In our previous manuscript, we already discussed this mechanism for TMSPa and that it goes in parallel with the evolution of Me_3SiF .³² The resulting phosphoric acid derivate is less prone to releasing the proton compared to HF, which is always in equilibrium with Li^+ to form LiF and a “free” H^+ (see Figure 5).

Figure 5. Reaction scheme visualizing the different reactivities of TMSPa and TMSPi with LiPF_6 and LiF and HF leading to different Me_3SiF evolution profiles.

However, in contrast to TMSPa there is hardly any potential dependent formation of Me_3SiF observed for TMSPi and the amount of Me_3SiF released during the first cycle is significantly lower, most of which probably stems from the initial Me_3SiF formation during the OCP period. Therefore, the mechanism for how TMSPi prevents the acidification must differ slightly. The initial reactions of TMSPi with the LiPF_6 salt as observed here and first described by Qi et al. leads to the formation of partly soluble Li-phosphites,³⁶ which is mainly taking place

during the initial resting period (left half of Figure 5). We hypothesize that, during the cycling, when HF is formed due to oxidation of electrolyte and surface groups, the formed HF can react with the Li-phosphites which would lead to the formation of LiF and phosphoric acid derivate. Due to the low solubility of LiF this equilibrium would be pushed toward LiF and thus the acidification of the electrolyte and the formation of POF_3/PF_5 could be prevented even in the absence of the formation of significant amounts of Me_3SiF during the first cycle. A summarized scheme of this reaction is presented in Figure 5.

IV.3. Main Operation Mechanism of TMSPa/TMSPi in the EC Based Electrolyte. In the EC based electrolyte some of the effects of the additives observed by OEMS partly vary from the observations made for the FEC based electrolytes. However, for O_2 no difference in the released amount is observed thus supporting the conclusion that the P(III) atom in TMSPi is not acting as scavenger for O_2 and that none of the additives is complexing the CAM surface in a manner that it is stabilized and the surface reconstruction suppressed.

However, the presence of TMSPi in EC/DEC electrolyte leads to a clear suppression of CO_2 evolution compared to blank electrolyte as well as the one containing TMSPa (see Figure 2B, an additional version of this figure showing only the relevant CO_2 evolution is provided in the SI in Figure S6). Interestingly, the suppression of the CO_2 formation is already very pronounced before (0.07 (blank) vs 0.02 (TMSPi) $\mu\text{mol min}^{-1} \text{g}^{-1}$ at 4.0 V) and during the activation plateau in the first cycle (0.21 (blank) vs 0.12 (TMSPi) $\mu\text{mol min}^{-1} \text{g}^{-1}$ at 4.4 V). However, the formation of an SPI, as proposed by several groups,^{7,9,11,15–22} should occur at a certain voltage until which CO_2 release should be similar to the blank electrolyte and after which it should be suppressed. However, CO_2 suppression already occurs before any additional current is observed (>4.5 V in the CV experiment, see Figure S4), so that the oxidation of TMSPi (or its decomposition products) is not the key step in CO_2 suppression. Keeping in mind that the only component that was changed was the cyclic carbonate, it seems much more likely that TMSPi is acting again as a chemical scavenger. As was shown by Metzger et al., EC is sensitive toward hydrolysis, especially under basic conditions which can occur in a LIB, e.g., due to the formation of alkoxides during the SEI formation, and that this hydrolysis leads to the formation of CO_2 .⁵¹ Also the trivalent phosphoric acid esters such as $\text{P}(\text{OMe})_3$ are known to undergo hydrolysis under such conditions⁵² and are doing that at faster rate than the respective phosphates. The suppression of CO_2 could therefore be an indication that TMSPi is able to suppress hydrolysis of EC and acts as scavenger not only for HF but also for hydroxides and alkoxides in LIBs. This is supported by calculations from Yim and Han who found the reaction of Li^+ coordinated TMSPi with MeO^- energetically more favored than the reaction of EC.²⁸

The POF_3 amounts presented in Figure 4, especially during the second cycle, indicate that also in EC based electrolytes the TMSPa and TMSPi additives suppress the formation of POF_3 by scavenging HF and thus lower the acidity in the electrolyte. However, the amount of POF_3 formed in the blank EC based electrolyte is much lower than in the FEC based one (seven times for the first cycle and three times for the second cycle, respectively); therefore, the HF scavenging effect of the additives is much less pronounced. This indicates that the cyclic carbonate has a strong influence on the reactivity of the

electrolyte salt, which will be discussed in the subsequent paragraph.

Overall, the observed effects on the gas evolution in EC based electrolytes by the TMSPi and TMSPa additive indicate that also in this system surface layers do not lead to an effective prevention of electrolyte oxidation and thus gassing and that the main effects result from chemical scavenging, in the case of TMSPa solely of fluorides and for TMSPi both fluorides and possibly alkoxides.

IV.4. Stability of the Conductive Salt in FEC Based Electrolytes vs the EC Based Electrolyte. In a previous study from our group, Streich et al. reported significant differences in the formation of POF_3 between EC based and FEC based electrolytes containing 30 wt % of cyclic carbonate³¹ in a similar manner as is observed in this study with the 12:88 composition. Streich et al. suggested that POF_3 is formed by the reaction of PF_5 with Li_2CO_3 , the latter formed either in the cell by CO_2 reduction or present as impurity on the CAM, and that differences in the electrolyte composition affect either the solubility of Li_2CO_3 or the concentration of PF_5 .³¹ However, the authors could not reach a final conclusion about this matter.

In the meantime, new studies allow us to cast new light on this open question. A recent study from Solchenbach et al. shows that a significant amount of POF_3 detected by MS is in fact PF_5 which reacts on its way to the ionization source with surfaces of the setup.³⁵ It was also shown that a main contributor to the formation of PF_5/POF_3 in OEMS experiments is not the content of water impurities but protons in the electrolyte which subsequently lead to the further formation of PF_5 in a self-sustaining loop as described by Plakhotnyk et al.⁵³ A further study by Kim et al. showed that FEC is labile toward attacks by strong Lewis acids, which can lead to the formation of vinylene carbonate and protons.⁵⁴

We therefore propose that, in FEC containing electrolytes, a combination of these two processes is taking place (cf. Figure 6): (1) Electrochemically initiated deprotonation of carbonate

Figure 6. Schematic for the PF_5 driven decomposition cycle in FEC based electrolytes.

electrolytes leads to the formation of HF that decomposes LiPF_6 into LiF , HF , and PF_5 . HF in turn decomposes more salt as suggested by Solchenbach et al. and Plakhotnyk et al.⁵³ (2) The thus formed PF_5 dehydrofluorinates catalytically the FEC leading to even more HF (which can subsequently attack further electrolyte salt), and VC as products similar to the reaction described by Kim et al.⁵⁴ or polymeric species as described by Xu et al.⁵⁵ The second part of this mechanism, the attack on the cyclic carbonate, cannot take place in EC

based electrolytes, and the lower acidification of the electrolyte can thus explain the observed differences in the POF_3 evolution between the two electrolytes. The presence of an HF scavenging additive such as TMSPa or TMSPi in FEC based electrolytes is therefore crucial to reduce the acidity in the electrolyte and, thus, prevent the PF_5 formation and subsequent FEC dehydrofluorination, allowing longer cycling life as shown in the long term cycling experiments (cf. Supporting Information Figure S7).

V. CONCLUSIONS

Our complementary OEMS studies on gas evolved during cycling of HE-NCM full cells with 1 M LiPF_6 in FEC:DEC (12:88) or EC:DEC (12:88) containing 0 or 1 wt % TMSPa or TMSPi provide further understanding of the reactivity of TMSPa and TMSPi in the Li-ion cell.

1. A main operation mechanism of TMSPa and TMSPi in EC and FEC based electrolytes is HF scavenging and reduction of electrolyte acidity as is shown by the formation of Me_3SiF and the decreased evolution of POF_3 in electrolytes containing one of the additives. The reduced acidification of the electrolyte leads subsequently to less transition metal dissolution and more stable cathode surfaces, which were observed in previous studies but exclusively assigned to the formation of a passivating surface layer.
2. The interface layers observed in previous study in the presence of TMSPx additives do not display significant impact to affect the O_2 and CO_2 evolution which indicates that they only have limited impact on suppressing these side reactions.
3. Only for EC based electrolyte containing TMSPi was a lower amount of CO_2 observed. However, decreased CO_2 formation occurs already at low cell voltages and not close to the high cutoff voltage where it would be expected in case of the formation of a protective interface. Our hypothesis is that TMSPi due to its reactive P(III) atom also scavenges hydroxide and alkoxide and thus prevents the hydrolysis of EC which is observed under alkaline conditions.
4. TMSPi is effective in suppressing the formation of PF_5/POF_3 despite its high reactivity toward the PF_6^- anion. The finding is supported by other studies showing that not TMSPi but one of its decomposition products effectively enhances long-term stability. The findings suggest that previous studies of the electrochemical stability of these additives need to be reevaluated with the respect to the chemical reactivity of the TMSPx.
5. Comparison between TMSPa and TMSPi and electrolytes with different contents of (F)EC shows that the TMSPi additive undergoes side reactions with the electrolyte much faster than the TMSPa additive. The rate of this side reaction also depends on the content of the cyclic carbonate and takes place much faster in electrolytes with a low content of cyclic carbonate. Likely, the formation of contact-ion pairs in electrolytes with low cyclic carbonate amounts promotes chemical kinetics of the reactions.
6. Previous observations of a higher content of POF_3 in FEC based electrolytes compared to identical formulations containing EC were confirmed. However, our findings let us conclude that this is likely an effect of the

instability of FEC toward PF_5 that is formed under acidic conditions in the cell. Therefore, for long-term cycling in FEC containing electrolytes the usage of HF/H^+ scavengers is recommended. Despite the higher oxidative stability, FEC based electrolytes lead to the formation of more CO_2 during the SEI formation. This source of gas evolution could be suppressed by adding a suitable additive which is reduced at higher potentials compared to the electrolyte formulation.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsaem.9b01551>.

OEMS data during OCV in LP47; figure on the potential dependence of POF_3 release; calculation of the $\text{Li}^+/\text{F}(\text{EC})$ ratio; XPS data of HE-NCM electrodes after 2 cycles; CV data for EC and FEC based electrolytes; and long-term cycling data for FEC/DEC electrolytes (PDF)

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Notes

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