Decomposition of LiPF$_6$ in High Energy Lithium-Ion Batteries Studied with Online Electrochemical Mass Spectrometry

Aurélie Guéguen,a,d Daniel Streich,a Minglong He,a Manuel Mendez,b Frederick F. Chesneau,b Petr Novák,a and Erik J. Berga

*aElectrochemistry Laboratory, Paul Scherrer Institute, 5232 Villigen, Switzerland
bBASF SE, GCN/EE - M311, 67056 Ludwigshafen, Germany

The chemical and electrochemical instabilities of LiPF$_6$ in carbonate electrolytes for Li-ion batteries were studied with online electrochemical mass spectrometry (OEMS). Decomposition of carbonate electrolytes based on LiPF$_6$ eventually results in the formation of POF$_3$, which is readily detected and followed in situ during operation of Li-rich HE-NCM-based Li-ion cells. Electrode potentials above $\sim$4.2 V leads to carbonate solvent oxidation and presumably the formation of ROH species, which subsequently hydrolyze the LiPF$_6$ salt and initiate a thermally activated autocatalytic electrolyte decomposition cycle involving POF$_3$ as a reactive intermediate. Activation of the Li$_2$MnO$_3$ domains of the Li-rich cathode contributes along with electrolyte and separator impurities to further POF$_3$ generation. Electrode potentials below $\sim$2.5 V vs. Li/Li$^+$ impede POF$_3$ formation and presumably also further electrolyte decomposition by scavenging reactive intermediate species. As a result, much less POF$_3$ gas was detected upon the 2nd charge when using Li metal counter electrode, contrary to delithiated LiFePO$_4$. In situ OEMS confirm that the parasitic reactions involving LiPF$_6$ constitute an intricate reaction scheme, but more importantly, provide further evidence about what the components of this scheme are and how these may interact with each other.

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Rechargeable Li-ion batteries are nowadays extensively used to power electronic devices and are entering the transportation sector by powering electric vehicles (EV). A wide range of both negative (e.g. graphite) and positive electrode materials (e.g. layered cobalt oxides, spinel-type manganese oxides, and olivine-type iron phosphates) have been thoroughly investigated and are now in widespread use in commercial batteries. The specific energy of Li-ion batteries is limited mainly by the positive electrode materials, having typical practical specific charges of $\sim$150 mAh/g and average operating potentials of $\sim$3.8 V vs. Li/Li$^+$, which significantly inhibits the introduction of Li-ion batteries as power source in new applications.

In recent years, the layered Li-rich cobalt-nickel-manganese oxides xLi$_2$MnO$_3$(1-x)(LiMO$_2$) (x = 0.5, M = Co, Ni, Mn), hereafter called HE-NCM, have been shown to exhibit a high and reversible specific charge ($\sim$250 mAh/g) and a competitive average operating potential ($\sim$3.75 V vs. Li/Li$^+$). The origin of such a high specific charge is not yet completely understood, as the exact structure of the HE-NCM materials is highly dependent on the synthesis conditions and models coming from structural characterization are still under debate. Several reports have shown the presence of so-called Li$_2$MnO$_3$ domains in the compound$^5,6$ whereas other groups demonstrated the monophasic character of their materials.$^7$ However, during the first charge, a long potential plateau at $\sim$4.5 V vs. Li/Li$^+$ is not observed for conventional layered oxides, results from the delithiation process of the Li$_2$MnO$_3$ domains accompanied by oxygen extraction. The extracted oxygen species are believed to be very reactive and partly evolve as O$_2$ gas, of species are believed to be very reactive and partly evolve as O$_2$ gas, which strongly accelerated such decomposition reactions.$^{16,21}$ In situ spectroscopic evidence of electrochemically initiated electrolyte decomposition involving the LiPF$_6$ salt and high voltage cathodes is however more scarce.

In previous reports, we used online electrochemical mass spectrometry (OEMS) to follow the evolution of gases, such as O$_2$ and CO$_2$, from the interface of the HE-NCM positive electrodes in Li-ion cells containing typical carbonate electrolytes.$^{32}$ The results, combined with X-ray photoelectron spectroscopy (XPS), allowed us to propose a mechanism for reactions taking place in different potential windows of the two first charge and discharge cycles. Further improvements on the OEMS experimental setup allow us now to monitor the evolution of other gases, such as H$_2$ and POF$_3$, originating from the decomposition of the carbonate electrolyte. The aim of the present work is not only to investigate the formation of O$_2$ and CO$_2$, but also the H$_2$ and POF$_3$ gas evolution from HE-NCM during cycling to further disclose the underlying electrolyte decomposition processes.

**Experimental**

**Electrode preparation.**—The positive electrodes were prepared by coating thin glass fiber sheets (Whatman, GF/C) with a slurry of 93 wt% HE-NCM or stoichiometric NCM111 (LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$) (BASF SE), 3 wt% polyvinylidene fluoride (PVDF) Kynar HSV.
The “wet” thickness of the coating was ∼200 μm and the NMP was evaporated under vacuum at 80 °C for 8 hours. Circular electrodes were subsequently punched out (18 mm diameter) and dried overnight at 120 °C before being introduced into an Ar filled glove box. The average loading for the final electrodes was in the range 4.2 to 6.6 mg/cm² of active material. For comparison, a similar electrode coating (same thickness) was prepared on a Celgard 2400 (Celgard) monolayer polypropylene (PP) sheet with a loading of ∼12 mg/cm². Self-standing LiFePO₄ counter electrodes were prepared by mixing 80 wt% of LiFePO₄ (BASF SE) and 10 wt% Super C65 carbon (Imerys) with 10 wt% polytetrafluoroethylene (PTFE, Sigma-Aldrich) binder in a solution of isopropanol and water (1:1) to form a viscous slurry. The slurry was sonicated and kept under mechanical stirring at 100 °C to evaporate the solvents and obtain a “dough-like” paste. The electrode sheets were obtained by working the paste with a spatula and mechanical rolling (thickness 200 μm), and then dried at room temperature. Electrodes were subsequently punched out (20 mm diameter) and dried (120 °C under dynamic vacuum) before introduction into the glove box. Delithiated LiFePO₄ electrodes were obtained by electrochemical delithiation of these LiFePO₄ electrodes vs. Li₂TiO₃. Carbon electrodes containing 79 wt% carbon Super C65 and 21 wt% PVDF were similarly prepared by coating a NMP-based slurry on the porous glass fiber or polypropylene substrates.

Electrochemical measurements.—A homemade cell was developed for OEMS experiments as described elsewhere. All cells were assembled in a glove box filled with argon. The counter electrode was metallic lithium or delithiated LiFePO₄ (see above). Commercial electrolytes composed of 1 M LiPF₆ or 1 M LiClO₄ in a 3:7 (w / w) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) were used (BASF SE). The amount of trace water in the electrolytes was determined using Karl-Fischer titration and did not exceed 17 ppm. Two types of 28 mm diameter separator were used: thin glass fiber (Sigma-Aldrich) and Celgard 2400 monolayer PP sheets. Before being introduced into the glove box, the PP and glass fiber separators were dried under vacuum at 80 and 120 °C for at least 12 h, respectively. The assembled cells were equilibrated at open circuit potential for 2.5 hours prior to electrochemical cycling. Galvanostatic cycling was carried out between 2.0 and 4.7 V vs. Li⁺/Li at C/15 rate during the first charge and at C/10 rate for the first discharge and following cycles using a computer-controlled battery cycling device (CCCC, Astral electronic AG). The specific charges (not reported on the figures) were found similar to those reported previously (compared to Figures 1a and 1d). The Super C65 carbon electrodes were subjected to cyclic voltammetry (CV) at a scan rate of 0.075 mV/s, starting from 3.2 V and cycling between 4.7 and 2.0 V vs. Li⁺/Li. All measurements were carried out at room temperature.

**Online electrochemical mass spectrometry (OEMS).—**The OEMS setup was described elsewhere 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 and Swagelok fittings (3 mm compression tube fittings, Swagelok, OH, US) 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, EDW ARDS GmbH) for efficient flushing. The magnetic valves are electronically controlled with a Solid State Relay Module (NI 9485 Measurement System, National Instruments) connected to a computer with a LabView Software (NI Labview 2013, National Instruments). For partial pressure and gas evolution rate analysis 0.7 mL of gas are extracted from the headspace (∼3.2 mL) of the cell and replaced by pure Ar (quality 5.0). Calibration gas bottles were utilized to relate the MS ion-currents at 32 and 44 m/z to known concentrations of O₂ and CO₂ (1000 ppm of O₂ and 200 ppm CO₂ in Ar), before and after the measurement. The ion currents for fragments m/z = 2, 85, and 104 were recorded without calibration and converted into approximate gas evolution rates that allow direct semi-quantitative comparison between the different measurements.

**Results and Discussion**

**Gas evolution during electrochemical cycling.—**Figure 1 shows the OEMS data collected for HE-NCEM electrodes in 3:7 EC:DEC during the first two galvanostatic cycles, comparing two different electrolyte salts, two different counter electrodes and two different separators. The gas compositions of the cells were continuously probed by analyzing the mass spectra (m/z = 0–110). The gases H₂, O₂, CO₂, and POF were the only identifiable species (appearing at m/z = 2, 32, 44, and 85, respectively) evolving in situ during cycling in our OEMS setup. Under all conditions, the overall evolution of CO₂ and O₂ is similar to previously reported results. Several distinct CO₂ formation contributions are apparent during the first charge. The first contribution (CO₂(1)) is anticipated to extend from ∼4.2 V until the end of charge, and is observed also during charging in later cycles. In the literature there exists a range of independent reports demonstrating that the corresponding CO₂ formation processes are mainly related to the oxidation of EC. There is a presumably superimposed second contribution (CO₂(2)) characterized by a CO₂ evolution maximum at ∼4.4 V. As this maximum is observed irrespective of electrolyte salt and counter electrode during the first charge, but not in later cycles and accompanied by the onset of O₂ evolution, it is obvious to relate it to the activation of the Li₂MnO₃ domain in HE-NCM. Apart from O₂, considerable amounts of reactive oxygen species are expected to evolve from the HE-NCM material during Li₂MnO₃ domain activation, as suggested by the work of Castel et al. and Sathiya et al. The reactive oxygen, or some oxygen-rich species formed thereof via follow-up reactions, probably decompose at higher potential (~4.7 V, resulting in the rapid release of CO₂ (denoted CO₂(3)) and O₂ observed at the end of the first charge. The total amount of O₂ gas detected by OEMS varies between 27 and 89 μmol/gactive material, depending on the cell composition. These quantities correspond to only a small fraction (<5%) of the theoretical O₂ content of the Li₂MnO₃ domains in HE-NCM, which is ~1 mmol/gactive material. Thus the majority of oxygen extracted from the Li₂MnO₃ domains would be expected to be involved in parasitic reactions. Most of the side-products formed are stable at high potential or further react to form products that do not decompose into O₂ gas.

Despite the similarities just described, several important differences depending on the choice of electrolyte salt, counter electrode and separator are apparent from Figure 1. There is an increase in both O₂ and CO₂ evolution when the LiClO₄ electrolyte salt (Figure 1b) or the delithiated LiFePO₄ counter electrode (Figure 1c) are used. The reactive O₂- and C-O-rich species may form in larger quantities and/or be converted into non-reactive products either more slowly or to a smaller extent in absence of LiPF₆ and Li metal, respectively. Both LiPF₆ and Li metal appear to be involved in follow-up reactions with reactive oxygen species generated during Li₂MnO₃ domain activation in such a way that CO₂(3) is substantially enhanced in the absence of LiPF₆ or Li metal. The fact that CO₂(3) is decreasing less or not at all from the first to the second cycle with the delithiated LiFePO₄ counter electrode or LiClO₄, respectively, suggests that both electrolyte salt and counter electrode in addition play important roles in passivating the cell against CO₂ evolution and that LiPF₆ and Li metal are superior to LiClO₄ and delithiated LiFePO₄ in terms of suppressing gas evolution. In this context it should be mentioned that delithiated LiFePO₄ counter electrodes do not have a sufficiently low potential for reducing CO₂. Therefore, an enhancement in CO₂ evolution is expected as this kind of counter electrode cannot act as a sink for CO₂. Obviously, there is a significant interaction between the separator and the LiPF₆ salt as the amount of O₂ increased and CO₂ is reduced when the GF separator is replaced by the PP separator (compare Figures 1a and 1d).
Figure 1. Plots of the CO₂ and O₂ evolution rate and approximate evolution rate for H₂ (m/z = 2) and POF₃ (m/z = 85, 104) for the two first galvanostatic cycles. (a) HE-NCM electrode vs. Li with glass fiber separator and 1 M LiPF₆ in EC:DEC (3:7), (b) HE-NCM electrode vs. Li with glass fiber separator and 1 M LiClO₄ in EC:DEC (3:7), (c) HE-NCM electrode vs. delithiated LiFePO₄ with glass fiber separator and 1 M LiPF₆ in EC:DEC (3:7), (d) HE-NCM electrode vs. Li with PP separator and 1 M LiPF₆ in EC:DEC (3:7).

Further support of this conclusion is found while comparing the formation and consumption of gaseous species other than CO₂ and O₂. H₂ and POF₃ are particularly important examples of such species. Since H₂ arises from the reduction of protic species ROH, such as H₂O or alcohols, at potentials close to 2 V vs. Li/Li⁺, e.g.,

$$2 \text{ROH} + 2 e^- \rightarrow \text{H}_2 + 2 \text{RO}^- \quad [6]$$

it is an indirect marker for the formation of ROH species inside the battery. Similarly, POF₃ is an indicator of LiPF₆ decomposition, which is supposed to be mediated by ROH species (Equation 3) and/or other oxygen containing species such as Li₃CO₃ and further, similar reactions. Fragments m/z = 85 and 104 evolve in a strongly correlated manner (Figure 1a) and are not observed with LiClO₄ electrolyte salt (Figure 1b) proving that the corresponding signals originate from POF₃ and thus that LiPF₆ decomposition indeed is enhanced by galvanostatic cycling of HE-NCM. Substantial quantities of POF₃ evolve during the first discharge regardless of whether Li metal (Figure 1a) or delithiated LiFePO₄ (Figure 1c) is used as counter electrode. Interestingly, POF₃ formation persists at a roughly constant rate throughout further galvanostatic cycling with delithiated LiFePO₄, whereas it ceases almost completely after the first cycle in presence of a Li metal counter electrode. A wide range of products resulting from both thermally and electrochemically initiated decomposition of LiPF₆ in carbonate solvents have been extensively reported. Although phosphate species are commonly observed, no evolution of fragments at m/z = 79 (PO₃ groups) and 83 (one of the fragments expected for POF₂(OH)) were registered. Possibly, a different range of species are formed during room temperature electrochemical cycling compared to, e.g., high temperature storage of Li-ion battery cells. Alternatively, their volatility and/or concentration are insufficient for in situ detection with the employed OEMS setup.

In the following we will discuss in which ways the observations and differences regarding POF₃ evolution relate to ROH, Super C65, separator, cell potential and counter electrode and how we imagine LiPF₆ decomposition to trigger self-sustained decomposition cycles involving further highly reactive species such as HF.

The role of ROH in LiPF₆ decomposition.—Possible sources of protic species ROH inside the cell are: leakage and contamination such as H₂O (ROH(1)), direct electrochemical electrode or electrolyte decomposition depending merely on potential (ROH(2)), and chemical
follow-up reactions involving primary decomposition products and/or other cell components (ROH(3)).\textsuperscript{13} ROH(1) is expected to be negligible since leak rates were found to be marginal with the employed type of OEMS cell and all electrolyte and cell components were thoroughly dried under vacuum at elevated temperatures for an extended time. Also, the deliberate addition of contaminants, such as water, is known to primarily lead to increased fractions of CO\textsubscript{2} and H\textsubscript{2} during the very early stages of cycling, which is not observed in any of the experiments. In contrast, the gasses in the experimental data in Figure 1 show a substantial potential dependence, suggesting that ROH formation relies mainly on electrochemical decomposition (ROH(3)) or its chemical follow-up reactions (ROH(1)). The correlation observed with LiClO\textsubscript{4} between H\textsubscript{2} evolution rate and cell potential (Figure 1b) supports the assumption that ROH(1) is formed at the HE-NCM electrode by electrolyte decomposition with potential dependent kinetics and subsequently diffuses to the negative electrode where it is reduced, e.g., according to Equation 6. A further comparison of the H\textsubscript{2} traces in Figure 1 provides interesting insights into the interdependence between ROH and LiPF\textsubscript{6}. No potential dependent H\textsubscript{2} evolution, as described above for the cell employing LiClO\textsubscript{4}, is observed in presence of LiPF\textsubscript{6} during the first charge and major parts of the first discharge. Obviously, most ROH(1) is scavenged by reactions, such as Equation 3, under these conditions and the formation of H\textsubscript{2} only occurs upon further reduction of some of the remaining ROH, HF or other residual decomposition electrolyte products at the very end of the first discharge when the positive electrode reaches potentials of \textasciitilde 2 V.

While these results prove the importance of electrochemical ROH(1) generation for LiPF\textsubscript{6} decomposition, the question remains to which extent thermally activated chemical ROH(3) formation processes contribute to LiPF\textsubscript{6} instability and PO\textsubscript{3}F\textsubscript{3} formation.\textsuperscript{39} Diverse sources of ROH(3) formed in chemical reactions can be conceived and have been proposed in the literature.\textsuperscript{10,39} They range from decomposition reactions involving either auxiliary cell components (e.g. conductive carbon additives) or other secondary decomposition products (e.g. HF or OH\textsuperscript{−}) or combinations thereof (ROH(3\textsubscript{b})) to reactions associated with oxygen species formed during Li\textsubscript{2}MnO\textsubscript{3} domain activation (ROH(3\textsubscript{a})).\textsuperscript{9,40} The broad range of conceivable decomposition routes of the carbonate solvent implies that several factors may be influential. This led us to consider the roles of the conductive Super C65 carbon additive, the glass fiber separator, as well as the release of reactive oxygen species during Li\textsubscript{2}MnO\textsubscript{3} domain activation in more detail.

The role of carbon, separator, and Li\textsubscript{2}MnO\textsubscript{3} domain activation in LiPF\textsubscript{6} decomposition.—Based on the BET specific surface areas of 62 and 10 m\textsuperscript{2}/g for Super C65 and HE-NCM, respectively, the 2.64 wt\% of Super C65 contained in our HE-NCM electrodes are expected to make up about 15% of the overall electrode surface area. The results in Figure 2a show that substantial PO\textsubscript{3}F\textsubscript{3} formation occurs with a HE-NCM free Super C65 electrode (solid line, filled squares), verifying that the presence of Super C65 itself contributes to LiPF\textsubscript{6} decomposition. From the concomitant CO\textsubscript{2} release we conclude that oxidation of Li\textsubscript{2}MnO\textsubscript{3} at potentials above 4.3 V occurs upon further reduction of some of the remaining ROH, HF or other residual decomposition electrolyte products at the very end of the first discharge when the positive electrode reaches potentials of \textasciitilde 2 V.

Moreover, very high specific current peaks are observed with the glass fiber separator early on during the first charge and at the end of the first discharge. These are not observed with the PP separator and dwarf all other specific current features. In line with previous reports\textsuperscript{37,41} we are convinced that impurities or reactive surface groups in the glass fiber account for these differences and that reactive electrolyte decomposition products, including ROH(3), are involved in sustaining or promoting further electrolyte decomposition. For instance, SiO\textsubscript{2} is known to react with HF to form H\textsubscript{2}O and SiF\textsubscript{4}.\textsuperscript{42} ROH forming reactions, such as the ones proposed earlier between carbonates and O\textsubscript{2}\textsuperscript{−} radicals,\textsuperscript{3} suggest that oxygen removal from the HE-NCM active material during Li\textsubscript{2}MnO\textsubscript{3} domain activation might also play an important role in ROH(3) mediated LiPF\textsubscript{6} decomposition. In order to test this hypothesis, the gas evolution characteristics of a HE-NCM cell (Figure 1d) was compared with an NCM111 cell (Figure 2b). NCM111 does not contain any Li\textsubscript{2}MnO\textsubscript{3} domains and therefore lacks the 4.5 V plateau with its characteristic CO\textsubscript{2}(2,3) and O\textsubscript{2} evolution. However, the evolution of CO\textsubscript{2}(1) starts at the same potential (\textasciitilde 4.2 V) as with HE-NCM and the release of a small amount of O\textsubscript{2} is also observed at potentials around 4.55 V at which over-oxidation of the NCM111 material occurs, resulting in extraction of oxygen from the lattice and ensuing Mn dissolution.\textsuperscript{43}

For HE-NCM, a small but non-negligible extent of PO\textsubscript{3}F\textsubscript{3} evolution is already observed at potentials between 4.3 and 4.5 V, but not with NCM111 suggesting that there is a contribution of Li\textsubscript{2}MnO\textsubscript{3} domain activation to LiPF\textsubscript{6} decomposition. Thus, contrary to what has been reported in the literature,\textsuperscript{40} reactive oxygen species generated during Li\textsubscript{2}MnO\textsubscript{3} domain activation might indeed affect the cell performance as they are not only involved in the evolution of O\textsubscript{2} but also in parasitic reactions such as PO\textsubscript{3}F\textsubscript{3} formation. However, mere electrode potential appears to be more important in controlling PO\textsubscript{3}F\textsubscript{3} formation, because PO\textsubscript{3}F\textsubscript{3} is found to evolve much more strongly at the end of charge whenever the potential exceeds \textasciitilde 4.5 V, regardless of electrode material and cycle number.

Since elevated potentials promote ROH(3) and ROH(3\textsubscript{a}) formation,\textsuperscript{13} the participation of ROH in these potential dependent LiPF\textsubscript{6} decomposition processes needs to be taken into account. In this respect it is important to realize that the contribution of ROH(3\textsubscript{b}) is likely of minor importance compared to ROH(3) and ROH(3\textsubscript{a}) regarding overall ROH formation inside the cell, because there is hardly any difference in H\textsubscript{2} evolution between the first and second cycle with LiClO\textsubscript{4} (Figure 1b).

The role of the counter electrode in LiPF\textsubscript{6} decomposition.—Counter electrode dependent differences in the evolution of CO\textsubscript{2} and O\textsubscript{2} were already reviewed above. The discussion will now be extended by considerations about the observed similarities and differences in PO\textsubscript{3}F\textsubscript{3} and H\textsubscript{2} evolution (Figures 1a, 1c). In fact, the evolution of PO\textsubscript{3}F\textsubscript{3} is very similar with the two different counter electrodes during the first cycle. Only in the second cycle does the impact of the counter electrode become apparent. While PO\textsubscript{3}F\textsubscript{3} evolution is substantially decreased in the second compared to the first cycle with the Li metal counter electrode, it restarts very early during the second charge and persists at a more or less constant, elevated rate throughout the second cycle with the delithiated LiFePO\textsubscript{4} counter electrode. A drop in PO\textsubscript{3}F\textsubscript{3} evolution accompanied by substantial H\textsubscript{2} evolution is observed at the end of discharge regardless of the choice of counter electrode but only in presence of LiPF\textsubscript{6}. This supports the notion that LiPF\textsubscript{6} decomposition is intimately connected with elevated potentials and that H\textsubscript{2} is generated via reductive reactions involving hydrated LiPF\textsubscript{6} decomposition ROH intermediates.\textsuperscript{9} Interestingly, a similar extent of end-of-charge H\textsubscript{2} formation as with LiClO\textsubscript{4} / Li (Figure 1b) is observed with LiPF\textsubscript{6} / Li (Figure 1a) but not with LiPF\textsubscript{6} / delithiated LiFePO\textsubscript{4} (Figure 1c) during the second cycle. Obviously, further LiPF\textsubscript{6} decomposition ceases after the first cycle in presence of the Li metal counter electrode even though more ROH(3) is being generated. This suggests that ROH is necessary but not sufficient for LiPF\textsubscript{6} decomposition and that the Li electrode acts as a “sink” for ROH products that are required to sustain LiPF\textsubscript{6} decomposition.
Summary.—As schematically depicted in Figure 3, electrochemical decomposition reactions inside the cell – strongly influenced by auxiliary battery components, such as the separator and/or the conductive carbon additive – give rise to many species such as diverse radicals, H₂, O₂, CO₂, and ROH (“Source”). These can enter both chemical and electrochemical follow-up reactions with each other, the electrodes, the solvent, or LiPF₆ and its decomposition intermediates (“Reactant”). Our in situ study allowed us to adapt the thermally activated electrolyte decomposition scheme from previous reports⁴⁻⁵ by showing that similar reactions are also triggered by the potential of the positive electrode. Once the potential reaches the oxidation potential (~4.2 V vs. Li⁺/Li) of the carbonate solvents, ROH species may arise that react with PF₅ to form POF₃. A ubiquitous side-product of the latter reaction is HF,³⁶,⁴⁵ which together with POF₃ cause the generation of more ROH⁴⁵,⁴⁶ in an autocatalytic self-sustaining LiPF₆ decomposition cycle as outlined by Campion et al.¹³ This autocatalytic decomposition cycle can be stopped by competing deposition / degradation processes that inactivate at least one of the involved species. We observed that a key player in controlling the nature and extent of these inactivation processes is the counter electrode (“Sink”).

Conclusions

Further insights into the parasitic reactions involving LiPF₆ can be obtained from in situ OEMS measurements by monitoring POF₃ and H₂ evolution during the electrochemical cycling of HE-NCM based Li-ion batteries and analyzing its dependence on different system components and parameters:

1. Carbonate solvent oxidation (>4.2 V vs. Li⁺/Li) leads to the formation of reactive species, such as ROH, which in turn hydrolyze the LiPF₆ electrolyte salt to form POF₃ species.
2. Li₂MnO₃ domain activation contributes considerably to POF₃ formation between 4.3 and 4.5 V vs. Li⁺/Li during the first charge.
3. The contribution of Super C65 conductive carbon to electrolyte decomposition and POF₃ (and HF) formation is substantial.
4. Impurities or surface functions of glass fiber cause dramatically enhanced and even additional POF₃ evolution.
5. Electrochemically initiated LiPF₆ hydrolysis triggers an autocatalytic electrolyte decomposition cycle involving POF₃ as a reactive intermediate.
6. The autocatalytic electrolyte decomposition cycle, as observed by the maintained POF₃ formation, is impeded by counter- or working-electrode potentials more negative than ~2.5 V vs. Li⁺/Li, which leads to scavenging of reactive intermediates.

In addition, it can be concluded that the evolution of POF₃ with concomitant consumption of ROH is indirect proof for the formation of HF (e.g. according to Equation 3), which is one of the major causes for failure of Li-ion batteries during long-term cycling. HF contributes to the leaching of transition metal ions from positive electrode materials, whereby the metal ions and their complexes cross over to the negative electrode and ruin the operability of the SEI. Our results show that POF₃ can be used as a probe to investigate the HF formation in situ, which in turn may be the key to develop rational strategies for its mitigation. Resolving the issues of interfacial electrolyte decomposition
on high energy and potential cathodes is of paramount importance for further development of Li-ion batteries.

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References

1. S. Levasseur, M. Ménétrier, and C. Delmas, Journal of The Electrochemical Society, 149, A1533 (2002).
2. Z. Lu, Z. Chen, and J. R. Dahn, Chemistry of Materials, 15, 3214 (2003).
3. M. M. Thackeray, C. S. Johnson, J. T. Vaughey, N. Li, and S. A. Hackney, Journal of Materials Chemistry, 17, 3112 (2007).
4. M. M. Thackeray, S.-H. Kang, C. S. Johnson, J. T. Vaughey, R. Benedek, and S. A. Hackney, Journal of Materials Chemistry, 17, 3112 (2007).
5. F. Almarj, M. Talianker, B. Markovsky, D. Sharon, L. Burlaka, G. Shafir, E. Zinigrad, O. Haik, D. Aurbach, J. Lampert, M. Schulz-Dobrick, and A. Garsuch, Journal of The Electrochemical Society, 160, A324 (2013).
6. P. Lanz, C. Villevieille, and P. Novák, Electrochimica Acta, 130, 206 (2014).
7. H. Koga, L. Crogueenec, P. Manessiez, M. Ménétrier, F. Weill, L. Bourgeois, M. Duttine, E. Suard, and C. Delmas, The Journal of Physical Chemistry C, 116, 13497 (2012).
8. E. Castel, E. J. Berg, M. El Kazzi, P. Novák, and C. Villevieille, Chemistry of Materials, 26, 5051 (2014).
9. A. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Baradé, P. Novák, and P. G. Bruce, Journal of the American Chemical Society, 133, 8040 (2011).
10. M. Moskovich, M. Ciojcaru, H. E. Gottlieb, and D. Aurbach, Journal of Electroanalytical Chemistry, 497, 84 (2001).
11. N. N. Greenwood and A. Earnshaw, Chemistry of the Elements, Pergamon Press New York (1997).
12. B. Ravel, K. M. Abraham, R. Gitzendanner, J. DiCarlo, B. Lucht, and C. Campion, Journal of Power Sources, 119–121, 805 (2003).
13. C. L. Campion, W. Li, W. B. Euler, B. L. Lucht, B. Ravel, J. F. DiCarlo, R. Gitzendanner, and K. M. Abraham, Electrochemical and Solid-State Letters, 7, A194 (2004).
14. C. L. Campion, W. Li, and B. L. Lucht, Journal of The Electrochemical Society, 152, A2327 (2005).
15. B. Vortmann, S. Nowak, and C. Engelhard, Analytical Chemistry, 85, 3433 (2013).
16. V. Kraft, M. Grützke, W. Weber, M. Winter, and S. Nowak, Journal of Chromatography A, 1354, 92 (2014).
17. V. Kraft, W. Weber, M. Grützke, M. Winter, and S. Nowak, RSC Advances, 5, 80150 (2015).
18. W. Weber, R. Wagner, B. Steipert, V. Kraft, M. Winter, and S. Nowak, Journal of Power Sources, 306, 193 (2016).
19. S. Wilken, M. Treskow, J. Scheers, P. Johansson, and P. Jacobsson, RSC Advances, 3, 16359 (2013).
20. S. Nowak and M. Winter, Journal of The Electrochemical Society, 162, A2500 (2015).
21. U. Heider, R. Oesten, and M. Jungnitz, Journal of Power Sources, 81–82, 119 (1999).
22. P. Lanz, H. Sommer, M. Schulz-Dobrick, and P. Novák, Electrochimica Acta, 93, 114 (2013).
23. F. Okamoto and P. Novák, in ECL Annual Report, Paul Scherrer Institut, Villigen, Switzerland (2012).
24. L. Boulet-Roblin, M. E. Kazi, P. Novák, and C. Villevieille, J. Electrochem. Soc., 162, A1297 (2015).
25. K. Xu, Chemical Reviews, 104, 4303 (2004).
26. L. Yu, H. Liu, Y. Wang, N. Kowata, M. Osawa, J. Kawamura, and S. Ye, Angewandte Chemie International Edition, 52, 5735 (2013).
27. T. Li, L. Xing, W. Li, Y. Wang, M. Xu, F. Gu, and S. Hu, Journal of Power Sources, 244, 668 (2013).
28. L. Xing and O. Borodin, Physical Chemistry Chemical Physics, 14, 12838 (2012).
29. L. Xing, W. Li, C. Wang, F. Gu, M. Xu, C. Tan, and J. Yi, The Journal of Physical Chemistry B, 113, 16596 (2009).
30. M. Metzger, C. Marano, J. Steckinger, D. Haring, and H. A. Gasteiger, Journal of The Electrochemical Society, 162, A1123 (2015).
31. M. Okumi, S. Kinoshita, Y. Sakata, M. Yanagidate, Y. Otake, M. Ue, and M. Deguchi, Journal of The Electrochemical Society, 155, A794 (2008).
32. H. Wang, X. Z. Lan, D. L. Jiang, Y. Zhang, H. H. Zhong, Z. P. Zhang, and Y. Jiang, Journal of Power Sources, 283, 187 (2015).
33. H. Koga, L. Crogueenec, P. Manessiez, M. Ménétrier, F. Weill, L. Bourgeois, M. Duttine, E. Suard, and C. Delmas, The Journal of Physical Chemistry C, 116, 13497 (2012).
34. M. Sathiya, K. Ramesha, G. Rousse, D. Foix, D. Gonzalez, A. S. Prakash, M. L. Doublé, K. Hemalatha, and J. M. Tarascon, Chem. Mater., 25, 1121 (2013).
35. M. Sathiya, G. Rousse, K. Ramesha, C. P. Laisa, H. Vezin, M. T. Sourgrati, M. L. Doublé, D. Foix, D. Gonbeau, W. Walker, A. S. Prakash, M. Ben Hassine, L. DuPont, and J. M. Tarascon, Nat Mater, 12, 827 (2013).
36. Y. Okamoto, Journal of The Electrochemical Society, 160, A404 (2013).
37. K. Tsuchiya, H. Tsutsumi, K. Morii, and H. K. M. Lai, Journal of Power Sources, 81–82, 180 (2013).
38. S. Nowak and M. Winter, Journal of The Electrochemical Society, 162, A1297 (2015).
39. R. Sharabi, E. Markevich, V. Borgel, G. Salitra, D. Aurbach, G. Semrau, M. A. Schmidt, N. Schall, and C. Stinner, Electrochemistry Communications, 13, 800 (2011).
40. S. F. Lux, J. Chevalier, I. T. Lucas, and R. Kostecki, ECS Electrochem. Lett., 2, A121 (2013).
41. R. Sharabi, E. Markovich, V. Borgel, G. Salitra, D. Aurbach, G. Semrau, M. A. Schmidt, N. Schall, and C. Stinner, Electrochemistry Communications, 13, 800 (2011).
42. S. F. Lux, I. T. Lucas, E. Pollak, S. Passerini, M. Winter, and R. Kostecki, Electrochemistry Communications, 14, 87 (2012).
43. H. Zheng, Q. Sun, G. Liu, X. Song, and Y. S. Battaglia, J. Power Sources, 207, 134 (2012).
44. J. Jiang and J. R. Dahn, Electrochem. Acta, 51, 3413 (2006).
45. N. P. Pieczonka, Z. Lan, P. Lu, K. L. Olson, J. Moose, B. R. Powell, and J.-H. Kim, J. Phys. Chem. C, 117, 15947 (2013).
46. R. Benedek and M. M. Thackeray, Electrochim. Solid-State Lett., 9, A265 (2006).