Trimethylboroxine (TMB) is used as an additive in the electrolyte for improving the performance of LiCoPO₄ (LCP) in Li-ion batteries. In this work, the role and behavior of TMB are investigated by cyclic voltammetry (CV), impedance spectroscopy (EIS) and on line electrochemical mass spectroscopy (OEMS). It was found that TMB oxidizes from 4.6 V and a low amount in the electrolyte is necessary to obtain good performance. On one hand, its oxidation produces boron trifluoride (BF₃), phosphorylfluoride (POF₃) and carbanion (CH₃−F) linked to a huge increase in impedance. Based on these results, a complete oxidation mechanism is proposed. The catalytic effect of the TMB decomposition products on carbonate polymerization could enhance the performance of LCP on the other hand, an unexplained water and/or HF release was detected. Further experiments need to be done.

Rechargeable lithium batteries were first developed with lithium metal as a negative electrode (anode) and several positive electrode (cathode) materials like LiMnO₂ or Li/LiTTS.² Due to safety issues related to dendrite formation with lithium metal anode, the first Li-ion batteries were commercialized by Sony in 1991 using graphite anodes.³ Later on, layered-oxide based cathode materials like LiCoO₂ were developed, which have specific capacities and specific energies of ≈170 mAh/gLCO₂ and ≈600 mWh/gLCO₂, respectively. In order to improve battery safety, cost and energy density, recent research has focused on new electrode materials. On the cathode side, numerous spinel structure materials were tested and showed good electrochemical performance.⁴ In 1997, phospho-olivine cathode materials of the general formula LiMPO₄ (M = 3d-transition metal) emerged with layered oxides.³ Therefore, many different routes, does not reach the theoretical specific capacity, of 171 mAh/gLFP and the oxidation from FeII to FeIII takes place at 3.4 V, resulting in a specific energy of ≈590 mWh/gLFP. While offering improved safety, its specific energy is very similar to LiCoO₂, so that with respect to energy density, LFP offers no improvement over LiCoO₂.

One approach toward improved energy density required for electric vehicle applications would be the use of LiCoPO₄ (LCP) cathode material, which promises a theoretical specific energy of ≈800 mWh/gLFP based on a charge/discharge voltage of ≈4.85 V vs. Li/Li⁺ and a theoretical specific capacity of 167 mAh/gLFP.⁶ However,⁷ the reported electrochemical performance of LCP, synthesized by many different routes, does not reach the theoretical specific capacity, shows low coulombic efficiency, and exhibits poor cycling stability. For example, Ni et al.⁸ synthesized carbon-coated LCP material by a sol gel route which gave a specific capacity of 131 mAh/gLCP at 0.1 C in the 1st cycle and lost 25% of its initial capacity after only 40 cycles. Slightly higher initial discharge capacities of 145 mAh/gLCP at 0.1 C in the 1st cycle were obtained for an LCP-carbon composite synthesized by a solid state route, but similar capacity fading was observed.¹⁰ The addition of a constant-voltage (CV) step at the end of charge was shown to improve the charge/discharge cycling performances,¹¹ but capacity fading was also very fast (20% of capacity loss after only 10 cycles). Kang et al.¹² demonstrated that cobalt can migrate into the lithium sites during the first delithiation of LCP, thereby blocking lithium ion diffusion, which in turn was suggested to cause the observed capacity fading; iron doping was claimed to suppress cobalt migration and to improve cycle-stability. On the other hand, Markevic et al.¹³ proposed that capacity fading might largely be related to the reaction of fluoride ions (present in electrolytes with LiPF₆ salt) with LCP through a nucleophilic attack of F⁻ on the P atoms of delithiated (charged) LCP, owing to the instability of the high-spin Co³⁺ in CoPO₄. This hypothesis was substantiated by the reduced capacity fading when using a quartz separator compared to a polyethylene separator, assuming that quartz would serve as a fluoride ion scavenger.¹⁴ The use of different additives in the electrolyte should prevent the electrode material from electrolyte corrosion and limit the capacity decrease. Recently, the same group¹⁵ reported improved performance by using a conventional LiPF₆ based electrolyte with trimethylboroxine (TMB) additive and fluoroethylene carbonate (FEC) as co-solvent: a capacity of 100 mAh/gLCP was maintained after 100 cycles at a rate of 0.2 C. Based on XPS studies, they concluded that FEC creates a better SEI layer on the cathode, but the mechanism leading to the reduced capacity fading by the addition of TMB could not be fully resolved.

To gain more insight into the positive effect of TMB on the capacity fading of LCP, the present work examines the anodic decomposition pathways of TMB using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and on-line electrochemical mass spectroscopy (OEMS).¹⁶ We will show that small amounts of TMB substantially improve the cycle life of LCP, while larger amounts lead to a very large increase of the high-to-medium frequency resistance of LCP, resulting in accelerated capacity fading. The essentially complete anodic decomposition of TMB at the charge/discharge potential of LCP proceeds through the formation of BF₃ and POF₃. The subsequent reaction of BF₃ and other TMB decomposition fragments (CH₂−carbanions) leads to the degradation of alkyl carbonate, which we believe causes the substantial increase of the high-to-medium frequency resistance of LCP via the formation of a passivating surface film when large amounts of TMB additive are used.

Experimental

LCP synthesis and characterization.— LiCoPO₄ was synthesized using a conventional solid state route according to Jang et al.¹⁷

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Stoichiometric amounts of LiOH·H₂O (crystals, 99%, Fluka), NH₄H₂PO₄ (crystals, 99.95%, Puratonic) and Co₃O₄ (powder, 99%, Alfa Aesar) were used. To remove the crystal water, the educts were initially homogenized in a mortar and precalcined at 673 K for 12 h. Subsequently, the educts were homogenized at 400 rpm in a planetary ball mill and then calcined at 1073 K under argon for 10 h in order to obtain pure single phase LiCoPO₄. After the synthesis, a particle size reduction step was conducted, consisting of ball milling (Fritsch Pulverisette 7) in a 45 mL ZrO₂ jar with ZrO₂ balls (1 mm diameter) at 1100 rpm for 1.5 h, followed by annealing at 873 K for 1 h under argon. The powder diffraction data of the samples were collected with a STOE StadiP powder diffractometer with a Mo-Kα X-ray source (Ge(111) monochromator, λ = 0.7093 Å) and a Dectris Mythen 1 K detector. The measured data were processed with the software Jana2006.18

The specific surface area was measured by N₂-adsorption BET (Quantachrome Autosorb iQ) after outgassing of the sample at 150°C for 16 h.

**Electrode preparation.**— For electrode preparation, the synthesized LCP was mixed with Super-C65 (TIMCAL) and PVdF (Kynar HSV 900, ARCHEMA) at a weight ratio of 80:10:10 (LCP:Super-C:PVdF). Upon addition of NMP (Sigma Aldrich), an ink was prepared by ball milling (Fritsch Pulverisette 7) in a 20 mL ZrO₂ jar with ZrO₂ balls (10 mm diameter) at 180 rpm for 1 h and then coated onto aluminum foil (18 µm, MTI corporation) using a gap-bar coater (RK Print). After drying at room temperature, electrodes with 10 mm diameter were punched, pressed under vacuum at 380 MPa (KBr-press, PerkinElmer), and dried at 120°C under vacuum in a Glass Oven (Büchi drying Oven S85). The LCP loading of the electrodes prepared for this study was within the range of 4.10 ± 0.3 mg/cm² (the exact weight for each electrode was determined to ± 0.05 mg/cm²). Carbon electrodes coated onto aluminum foil and consisting of 50%wt Super-C65 (TIMCAL) and 50%wt PVdF were also prepared by the same process, but without subsequent compression of the electrodes. For OEMS experiments, carbon electrodes at a loading of ~0.6 mg/cm² were prepared by spreading similar inks (50%wt Super-C65 and 50%wt PVdF) onto aluminum foam disks with 15 mm diameter (600 µm thickness, 6-8% density; Duocel).

**Electrolyte and battery test cell assembly.**— Electrolytes used for this study were 1 M LiPF₆ in EC/DMC (1:1 wt:wt) (LP30, Merck); either with additive or without with the addition of 0.2% wt, 0.5% wt, 1% wt, and 3% wt of TMB (99%, Aldrich). The water content of each electrolyte was measured by Karl-Fischer titration and was below 10 ppm.

For charge/discharge life-cycle investigations, two-electrode Swagelok T-cells were assembled in a argon filled glove-box (water activity ≈ 1 μm, 1% rh). Carbon electrodes coated onto aluminum foil and consisting of 50%wt Super-C65 (TIMCAL) and 50%wt PVdF were also prepared by the same process, but without subsequent compression of the electrodes. For OEMS experiments, carbon electrodes at a loading of ~0.6 mg/cm² were prepared by spreading similar inks (50%wt Super-C65 and 50%wt PVdF) onto aluminum foam disks with 15 mm diameter (600 µm thickness, 6-8% density; Duocel).

For charge/discharge life-cycle investigations, two-electrode Swagelok T-cells were assembled in a argon filled glove-box (water and oxygen below 0.1 ppm) using two glass fiber separators (250 µm, VWR) and 80 µl of electrolyte. We note that glass fiber separator is easily wetted by LP30 electrolyte and could act as ~F scavenger.15 A 450 µm thick lithium foil (Rockwood Lithium) with a diameter of 11 mm was used as counter electrode. Tests were conducted with a battery cycler (Maccor, Series 4000) using the following procedure: 12 h rest at open circuit voltage (OCV), then two formation cycles at a constant current rate of C/15, followed by cycling at C/2 between 3.5 and 5.2 V without any constant-voltage step.

EIS and CV experiments were carried out with three-electrode Swagelok T-cells with lithium foil counter and reference electrodes and with three glass fiber separators wetted with 120 µl of electrolyte. EIS measurements were employed to study the high-to-medium frequency resistance of LCP electrodes (working electrode), following a test procedure similar to the one used for the above described charge/discharge cycling experiments: 12 h of OCV, then two formation cycles at C/15, followed by 20 cycles at C/2; impedance spectra between 0.1 Hz and 500 kHz (10 mV voltage perturbation) were obtained after every charge and discharge at potentials of 5.2 and 3.5 V, respectively (after a brief constant-voltage hold at the cut-off voltages prior to recording the impedance spectra). Carbon working electrodes were used to study electrolyte decomposition (with and without TMB additive) by CV, recording three cycles between OCV and 5.5 V at 0.02 mVs. All EIS and CV measurements were conducted with a VMP 3 potentiostat (Biologic).

**OEMS experiment.**— For in-situ gas analysis by on-line electrochemical mass spectrometry (OEMS), the battery test cells were assembled in a special cell hardware, described recently.10 It consists of a 316Ti stainless steel anode current collector and a stainless steel mesh (316 SS) cathode current collector (0.22 mm diameter wire, 1.0 mm openings; Spörl KG), which is contacted and compressed by a compression spring (316 SS; Lee Springs). The described carbon/aluminum-foam served as working electrode and was contacted by the stainless steel mesh; a 17 mm diameter lithium foil (Rockwood Lithium, 450 µm) was placed onto the stainless steel anode current collector. Between the electrodes, the 28 mm diameter glass fiber separators (250 µm, VWR) were placed and 320 µl of electrolyte were added. After assembly and sealing in the glove-box, the cell was placed into a climate chamber held at 25°C (KB 20, Binder). A crimped capillary leak (Vacuum Technology Inc.) connects the OEMS cells to the mass spectrometer system (Pfeiffer Vacuum QMA 410), permitting a constant flow of ~1 µl/min from the cell head space (9.5 ml) to the cross-beam ionization source of the mass spectrometer. The OEMS system is equipped with a secondary electron multiplier (SEM), allowing the detection of masses between 1 and 128 amu. To avoid signal fluctuations due to minor pressure/temperature changes, all mass signal currents, I₂, were normalized to the mass current of the 20Ar isotope, I₂. A linear potential scan from OCV to 5.3 V at 0.2 mVs (Gamry Series G300 potentiostat) was used to study the decomposition of electrolyte with and without TMB additive via OEMS.

**Results**

**Physical-chemical characterization of LCP.**— The X-ray diffraction pattern and the SEM picture of the synthesized LCP after the particle size reduction step and the final annealing at 600°C are shown in Figure 1. Homogeneous spherical LCP particles of 50-60 nm are observed by SEM, which is in good agreement with the measured BET value of 24 m²/g (spherical approximation: d_{mes} = 6/(24 m²/g × 3.6 × 10⁻⁶ g/m³) = 65 nm). The XRD pattern of the synthesized compound reveals sharp Bragg peaks, indicative of a highly crystalline sample, which could all be indexed to an olivine-type LiCoPO₄ cell (space group Pnma – ICSD-99862). The refined lattice parameters of the unit cell (a = 10.1844 Å, b = 5.9138 Å, c = 4.6936 Å, corresponding to a cell volume of 282.7 Å³) are in good agreement with the literature.17-18 No side phases were detected by XRD.

**Anodic stability via cyclic voltammetry experiments.**— CV experiments were carried out on carbon electrodes in order to study the anodic stability of the electrolyte containing 0.2% and 1% TMB. The standard electrolyte (LP30) without TMB was used as a reference. The results of the first positive-going (anodic) scan at 0.02 mVs are shown in Figure 2a. While no significant anodic currents are observed until ~4.7 V without TMB additive, substantial oxidation currents initiate at ~4.6 V in the electrolyte containing 1% TMB, increasing to ~80 µA (≈100 µA/cm²) at the positive potential limit of 5.3 V. Lower anodic currents and an analogous current vs. potential behavior are observed for the electrolyte with 0.2% TMB, also showing a potential peak at ~4.9 V followed by an exponential current increase at the positive voltage limit. While part of the oxidation current will be due to the corrosion of the aluminum current collector, the substantial increase of the oxidation currents at any given potential with TMB concentration suggests that a large fraction of the observed anodic currents are due to the oxidative decomposition of TMB. This will be demonstrated by OEMS data later on.
Figure 1. X-ray diffraction pattern and SEM picture of synthesized LiCoPO₄ powder after the particle-size reduction step.

Figure 2. Cyclic voltammograms of carbon electrodes in electrolyte (1 M LiPF₆ in EC:DMC (1/1 w/w)) containing different amounts of TMB: a) 1st positive-going scan; b) 3rd positive and negative-going scans. CVs were conducted at 0.02 mV/s at room temperature.

Figure 3. Specific discharge capacity (in mAh/gLCP) vs. cycle number of LCP electrodes in electrolyte (1 M LiPF₆ in EC:DMC (1/1 g/g)) containing different amounts of TMB indicated in the figure. The first two galvanostatic cycles (formation) were conducted at C/15 rate, followed by galvanostatic cycles at C/2 rate; the lower and upper cut-off voltages were 3.5 and 5.2 V, respectively.

Figure 2b compares the 3rd voltammetric cycle in the electrolytes used in the previous CV experiment. While the current decreases only very little from the 1st to the 3rd cycle in TMB-free electrolyte, the oxidation currents decrease substantially by a factor of two in the electrolyte with 0.2% TMB and 1% TMB. This suggests that TMB can be oxidatively decomposed either completely within the examined potential range or partially due to the formation of a passivating layer.

We note that the current values in TMB-free electrolyte and in the electrolyte with 0.2% TMB are similar in the 3rd cycle. Interestingly, the electrolyte with 1% TMB does not reach the current corresponding to the electrolyte without additive. Probably, a high amount of TMB leads to a higher degradation or a lower efficiency in the building of the passivating layer. Next experiments should help to understand this observation.

Galvanostatic charge/discharge cycling with and without TMB.—To determine the effect of TMB on the capacity fading of LCP, we chose a galvanostatic cycling procedure between 3.5 and 5.2 V with two initial formation cycles at low rate of C/15, followed by fast cycling at C/2 (=0.34 ± 0.03 mA/cm²). At C/2 rate cycling following the two slow formation cycles, the contribution from TMB oxidation to the charge/discharge capacities should be negligible based on the CV data in Figure 2b. The evolution of the discharge capacity versus cycle number for LCP electrodes in electrolyte containing different concentrations of TMB is depicted in Figure 3, illustrating...
the strong effect of TMB additive on capacity fading. At the first cycle, a capacity of 125 \pm 2 \text{ mAh/g}_{\text{LCP}} is obtained in all the electrolytes except those containing 3\% TMB, which only yields \approx 60 \text{ mAh/g}_{\text{LCP}}. Once the current is increased after the two formation cycles, higher capacity fading is noticed for the TMB-free electrolyte compared to electrolytes containing between 0.1\% and 0.5\% TMB. The lowest capacity fading is observed for the electrolyte containing 0.2\% TMB. Table I summarizes the number of cycles for which \geq 100 \text{ mAh/g}_{\text{LCP}} can be maintained throughout this cycling procedure, with a maximum of 30 cycles (2 at C/15 followed by 28 at C/2) for the electrolyte with 0.2\% TMB and substantially lower cycle numbers for higher or lower TMB concentrations. This may be compared with the galvanostatic charge/discharge cycling at C/5 for LCP conducted by Sharabi et al.,\textsuperscript{15} where in the same standard electrolyte without additive or co-solvent the specific capacity drops below 100 \text{ mAh/g}_{\text{LCP}} in the first cycle. Using FEC co-solvent (i.e., 1 M LiPF\textsubscript{6} in FEC:DMC (1:4 wt:wt)), 100 \text{ mAh/g}_{\text{LCP}} can only be maintained over 4 cycles, while 100 cycles at \geq 100 \text{ mAh/g}_{\text{LCP}} can be obtained when 0.5\% TMB are added to the FEC:DMC electrolyte (this may be compared to the 30 cycles we observe with 0.2\% TMB, see Table I). Unfortunately, addition of FEC as co-solvent to our electrolyte with 0.2\% TMB did not improve the number of cycles at \geq 100 \text{ mAh/g}_{\text{LCP}}.

At first glance, it is surprising that Sharabi et al.\textsuperscript{15} obtain the lowest capacity fading with 0.5\% TMB in their LCP half-cell measurements (using a lithium metal counter electrode as in our study) and that they suggest 0.5–1\% TMB to the optimum concentration range, while we observe very high capacity fading with 0.5\% TMB (see Figure 3). This, however, can be easily explained when considering the volume of electrolyte per milligram of active material, which is 25 \pm 2 \mu\text{L}_{\text{electrolyte/mg}_{\text{LCP}}} in our experiments instead of 5 \mu\text{L}_{\text{electrolyte/mg}_{\text{LCP}}} in the work by Sharabi et al. in conjunction with the assumption that the critical variable is not the additive concentration in the electrolyte, but the additive/active-material mass ratio. The latter is identical for the optimum 0.1–0.2\% TMB concentration in our case and the optimum TMB concentration of 0.5–1\% reported by Sharabi et al.,\textsuperscript{15} namely 0.03–0.06 mg_{TMB}/mg_{LCP}, (using a density for the reference electrolyte of 1.3 g/cm\textsuperscript{3}). In general, these calculations point out that the optimization of the additive/active-material mass ratio in the assembled cell, and thus depends on the ratio of electrolyte volume to active-material mass, which is vastly different for small-scale test cells (5–25 \mu\text{L}_{\text{electrolyte/mg}_{\text{active material}}, see above}) vs. commercial cells (0.3–0.5 \mu\text{L}_{\text{electrolyte/mg}_{\text{active material}}}). Therefore, optimum additive concentrations determined from small-scale test cell evaluations would likely have to be increased by at least an order of magnitude for use in commercial cells.

Additionally, Table I exposes the irreversible capacity loss (ICL) for the 1\textsuperscript{st} cycle in electrolyte containing different concentrations of TMB. The ICL at the 1\textsuperscript{st} cycle are increasing with the TMB content. However, in electrolyte with 0.1–0.5\% TMB, the ICL are similar, as well as the discharge capacities for 15 cycles. Those high values are consistent with the oxidation on charge of the TMB additive. According to CV results, a low amount of TMB (0.2\% for example) leads to a higher current only in the first cycle (see Figure 2) whereas similar values are observed for the 3\textsuperscript{rd} cycle. A passivation layer is probably formed during the first cycle and could be a reason of the stable ICL for the electrolyte containing 0.1–0.5\% TMB. Those amounts of TMB appear to be an optimum to allow a good passivation. For higher amount of TMB, an additional mechanism is probably taking place.

\begin{table}[h!]
\centering
\caption{1) Number of cycles with specific discharge capacities of \geq 100 \text{ mAh/g}_{\text{LCP}} for 1 M LiPF\textsubscript{6} in EC:DMC (1/1 g/g) electrolyte with different amounts of TMB additive. Galvanostatic cycles between 3.5 and 5.2 V at C/2 rate after two initial formation cycles at C/15 rate. The discharge capacities in the first cycle for all electrolytes are 125 \pm 2 \text{ mAh/g}_{\text{LCP}}; ii) Irreversible capacity loss at the 1\textsuperscript{st} cycle in electrolyte with different amounts of TMB additive.}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\text{%wt TMB in LP30} & 0 & 0.1 & 0.2 & 0.5 & 3 \\
\hline
\text{i) number of cycles with} & 6 & 18 & 30 & 10 & 0 \\
\text{\geq 100 mAh/g}_{\text{LCP}} & & & & & \\
\text{ii) Irreversible capacity loss} & 57 & 94 & 94 & 92 & 1095 \\
\text{1\textsuperscript{st} cycle (mAh/g}_{\text{LCP}}) & & & & & \\
\hline
\end{tabular}
\end{table}

**LCP impedance vs. cycle number.**—The following impedance analysis is aimed to gain further insights into the observed strong capacity fading at high TMB additive concentrations. The Nyquist plots of the LCP impedance (Z_{LCP}, i.e., recorded vs. the lithium metal reference electrode) at the end of discharge after the 1\textsuperscript{st} cycle at C/2 rate for different electrolytes are shown in Figure 4a. The LCP impedances in the electrolyte containing no additive and 0.2\% TMB are quite similar, and the frequencies at the maximum of the semi-circle (0.4 kHz). Both, the larger medium-frequency resistance and the lower frequency at the maximum of the semi-circle (note: \omega_{\text{max}} \propto 1/(R \cdot C)) indicate an overall vastly increased charge-transfer and/or interface resistance of LCP in electrolyte with 0.5\% TMB compared to 0\% or 0.2\% TMB.

After 20 cycles (Figure 4b), a huge increase of the LCP impedance is noticed for the electrolyte containing 0.5\% TMB, with a
≈200-fold larger medium-frequency resistance (≈3 kΩ \cdot cm²) compared to the values obtained for electrolytes with 0% and 0.2% TMB (≈15 Ω \cdot cm²). Quite clearly, the impedance data suggest a continuous growth of a highly resistive interface layer on the LCP electrode in the presence of large amounts of TMB. This is consistent with the excessive capacity fading observed with 0.5% and 3% TMB in the electrolyte.

Further analysis of the EIS spectra were done following a circuit proposed by Rajalakshmi et al. for LCP electrodes (see inset of Figure 3). This model, \( R_sei \) and \( R_{ct} \) are the resistance of the liquid electrolyte. For the passivation layer, \( C_{sei} \) and \( R_{sei} \) are the capacitance and the resistance of the SEI layer on the LCP respectively. To model the electrode/electrolyte charge transfer, \( C_{dl} \) corresponds to the double layer capacitance and \( R_{ct} \) is the charge transfer resistance. Finally, W represents the Warburg impedance, representing the diffusion of charge carriers in the electrode. The fitted values for the 3 resistances after the 1st and the 20th discharge at C/2 rate are given in Table II, whereby two fits with different initial parameter estimates were used (fit 1 and fit 2).

In the following, we will examine the gas evolution products derived from anodic TMB decomposition on carbon electrode.— In the following, we will examine the gas evolution products via OEMS during the anodic oxidation of 1 M LiPF₆ in EC:DMC without TMB and with 0.5% TMB additive using a carbon working electrode in a linear voltammetric scan experiment (0.2 mVs) from OCV to 5.3 V. The linear sweep voltammetry (LSV) curves (Figure 6a) are very similar to what was shown in Figure 2a, displaying very large oxidation currents in the presence of TMB additive, with a potential peak near 4.9 V. The mass spectrometer currents at various m/z values normalized by the mass spectrometer current of the ¹⁶O isotope, \( I_m/I_{16} \), are shown in Figures 6b–6e. The relevant mass signals 85, 44, 15, 19, 69, 31, 16 arising from the anodic decomposition of the electrolyte without additive are shown in Figure 6b. Most of the mass signals start to evolve at ≈4.5 V, concomitant with the onset of the anodic current in the LSV curve (Figure 6a). Novák and coworkers showed CO₂ (mass 44) evolution coming from electrolyte oxidation and proposed a mechanism of the oxidation of DMC which leads to CO₂ evolution. The other signals are probably related to either mass fragments of anodic oxidation products from the carbonates or from decomposition products of the LiPF₆ salt (see also below discussion). However, it can be noted that the \( I_m/I_{16} \) signals for all masses are very low (below 0.15). An order of magnitude larger mass signals are obtained with 0.5% TMB additive, and are shown in Figures 6c–6e (please note the 10-fold larger \( I_m/I_{16} \) scale compared to Figure 6b) in order to explain the decomposition mechanism of TMB (scheme 1(a)–1(e)). The strongest signal is mass 49, which initiates at ≈4.8 V (Figure 6c) and is attributed to BF₃ release, confirmed by the concomitant appearance of mass 48, which is the expected mass-spectrometric fragment of BF₃ gas at the correct intensity of 25% compared to mass 49. Thus, it seems that BF₃ is the major compound which is evolved during TMB decomposition. Mechanistically, BF₃ is most likely formed by the nucleophilic attack of PF₆⁻ anions on the boron anion receptor of the TMB molecule, as was described for analogous boron-based anion receptors and as was suggested for TMB by DFT calculations. This reaction is described in scheme 1(a), namely the reaction of TMB with PF₆⁻ to trifluoro boroxine (B₃H₃O₃), CH₃ carbamions and PF₃. In analogy to the known decomposition of boroxine (B₃H₃O₃) to BH₃ and B₂O₃, it is reasonable to assume that trifluoroboroxine will decompose to BF₃ and B₂O₃, as is shown in scheme 1(b). As a next step in the TMB decomposition, one might consider the work by Smolansoff et al., who showed that B₂O₃ reacts with HF, evolving BF₃ gas and H₂O (scheme 1(c)). The latter is known to react readily with both PF₆⁻ and PF₃ to HF and POF₃ (scheme 1(d)).

If schemes 1(a)–1(c) were correct, we would expect to see mass signals for POF₃, HF, and/or PF₃. As a matter of fact, Figure 6d shows the evolution of the 85 and 19 signals, attributed to POF₃ and HF, respectively (note that their intensity in the absence of TMB

### Table II. Fitting parameters from EIS spectra shown in Figure 4 at the end of 1st and 20th discharge in electrolyte containing 0%, 0.2% and 0.5% TMB. Fit 1 and fit 2 refer to numerical fits of the equivalent circuit model shown in Figure 5, using the same data set but different initial estimates for the numerical fit.

| \( \Omega \cdot \text{cm}^2 \) | \( R_{electrolyte} \) | \( R_{sei} \) | \( R_{ct} \) | \( (R_{sei} + R_{ct}) \) | \( R_{electrolyte} \) | \( R_{sei} \) | \( R_{ct} \) | \( (R_{sei} + R_{ct}) \) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| no TMB / 1st cycle | 3.0 | 1.5 | 6.7 | 8.2 | 3.0 | 3.5 | 7.0 | 10.5 |
| no TMB / 20th cycle | 4.5 | 2.3 | 9.4 | 11.7 | 4.5 | 3.2 | 11.4 | 14.6 |
| 0.2% TMB / 1st cycle | 0.8 | 1.1 | 7.9 | 9.0 | 0.8 | 8.0 | 7.4 | 16.0 |
| 0.2% TMB / 20th cycle | 0.8 | 1.5 | 9.5 | 11.0 | 0.8 | 11.0 | 3.5 | 14.5 |
| 0.5% TMB / 1st cycle | 4.5 | 36 | 93 | 129 | 4.5 | 109 | 3.1 | 112 |
| 0.5% TMB / 20th cycle | 4.5 | 381 | 2471 | 2852 | 4.5 | 2247 | 306 | 2253 |
is an order of magnitude lower as shown in Figure 6b. The production of POF₃ is confirmed by the concomitant evolution of the 69 signal, which is a fragment of POF₃ with an expected intensity of ~20% compared to mass 85. In summary, the balance equation of the above proposed TMB decomposition reactions (scheme 1(a)–1(d)) is presented in scheme 1 as the “in sum” reaction, suggesting that TMB reacts with PF₆⁻ anions to BF₃, POF₃, and CH₃⁻ carbanions. This is consistent with the observation of gaseous BF₃ and POF₃ as well as the absence of significant amounts of PF₅ (mass 88). It is noteworthy, that this balance equation would suggest that TMB can be decomposed completely into BF₃ and POF₃, as well as with the presence of significant amounts of PF₂₆ (mass 88). However, other relevant mass signals are evolved during the LSV experiment (Figure 6e), which have not been discussed yet. These are masses 44, 31, and 15, which have a very similar evolution pattern and thus seem to be related. The signal at mass 44 is likely due to CH₃⁻ carbanions; while mass 15 could derive from CH₂, this does not seem possible, since it would require an equally strong signal on mass 16; so that we currently cannot identify the species detected on mass 15. CO₂ (mass 44) and alcohol (mass 31) evolution could be explained by a mechanism analogous to the nucleophilic attack of CH₃⁻ carbanions on the carbon atom in ethylene oxide shown in scheme 1(e), analogous to the nucleophilic attack of OH⁻ anion on the carbon atom in EC described by Aurbach. Thus, we hypothesize that the carbanion produced by the TMB oxidation (scheme 1(a)) decomposes the carbonate solvents of the electrolyte through a similar mechanism, resulting in the formation of CO₂ and propanol (scheme 1(e)).

Figure 6. Current densities and OEMS signals obtained during a linear voltammetric scan (0.2 mVs⁻¹) on a carbon electrode in electrolyte electrolyte (1 M LiPF₆ in EC/DMC (1/1 g/g)) containing no TMB and containing 0.5% TMB: a) voltammetric current vs. potential; b) mass signals normalized to the ³⁶Ar isotope signal, I₇/I₃⁶, in electrolyte containing no TMB; c-e) mass signals in electrolyte containing 0.5% TMB. The corresponding species and the proposed reaction mechanism are shown in scheme 1(a)–1(e).

Discussion

The presented study suggests that TMB decomposes at ≥4.5 V by producing large amounts of BF₃, POF₃, and CO₂ as well as H₂O and H₂. These results would be in accordance with the study by Sharabi et al., in which it was shown by XPS that TMB additive leads to higher amounts of fluorophosphates (PₓOᵧFₓ or LiₓPₓOᵧFₓ) on the LCP surface while no boron surface species could be detected. The former would likely be created through the reaction of POF₃ with the LCP surface while the absence of boron surface species can be explained by the preferential formation of BF₃. Again, for the completion of the sequence of schemes 1(a)–1(d), only trace amounts of HF or water would be required.

The increased mass signal for water (mass 18) with increasing potential suggests that another factor, caused by the decomposition products of TMB, is responsible for water and/or HF production. In the Figure 6c, the signals corresponding to BF₃ (49 and 48) seem to decrease at the end of the LSV and the trend is confirmed since the experiment was made until 5.5 V (not shown). A significant decrease of the intensity I₇/I₃⁶ is correlated with a consumption of the produced gases. Gasselin demonstrated that boron trifluoride, which can be considered as a Lewis acid, is a highly reactive compound. Many reactions are described but, however, no clear conclusion can be made about the origin of water and/or HF during the TMB oxidation. The analysis of ICL and CV are suggested that an optimum amount of TMB is needed to passivate the electrode. An excess of TMB shows higher degradation currents and bigger ICL values. Probably, the high amount of the side reaction products from TMB decomposition (H₂O, HF and BF₃) could be responsible of the fading mechanism of LCP half-cell. Also, the interaction with the counter electrode cannot be neglected since H₂ coming from the reactivity of lithium metal with water is evolved.
The electrochemical and chemical decomposition of TMB was described. However, the improved electrochemical performance showed by Sharabi on LCP is still an open question. It was mentioned in the work by Reddy et al. that the first step of TMB decomposition allows the polymerization of carbonates in the electrolyte due to the catalytic effect of PF5. Moreover, Rokicki et al. showed that the reaction between oxiranes and carbonates, which leads to poly(ether-carbonate)s, is enhanced by the presence of the complex BF3-Et2O. The catalytic activity of BF3 and/or PF5 on the carbonates could coat faster the surface of LCP particles and avoid the degradation of the material that is responsible for the poor electrochemical performance. Also, it is not excluded that the formation of the propanol, found in the OEMS, is enhanced by the presence of the complex BF3-Et2O. The catalytic action between oxiranes and carbonates, which leads to poly(ether-carbonate)s, enhances the capacity retention of LCP.

Conclusions
The combination of CV, EIS and OEMS techniques allows the understanding of the additive decomposition at high voltage. It is shown that TMB decomposes at ≥4.5 V essentially to BF3, POF3 and carbanion. A complete mechanism is proposed. However, two questions cannot be answered and further investigations are needed. On the one hand, the origin of water and/or HF production during the decomposition of TMB cannot be explained. On the other hand, the reason for a better cycling stability of LCP in presence of TMB is not clear. It is suspected that TMB decomposition products (BF3 and/or POF3) can catalyze the polymerization of carbonates and subsequently, the formation of a protective layer which happens earlier in the LCP charge. Impedance results seem to correlate this assumption but a careful XPS study should bring more information.

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References
1. H. Ikeda, S. Uena, T. Saito, S. Nakaido, and H. Tamaru, Denki Kagaku, 45, 391 (1977).
2. M. S. Whittingham, J. Electrochem. Soc., 123, 315 (1976).
3. K. Ozawa, Solid State Ionics, 69, 212 (1994).
4. M. S. Whittingham, Chem. Rev., 104, 4271 (2004).
5. A. K. Padhi, K. S. Nanjundaswamy, and J. B. Goodenough, J. Electrochem. Soc., 144, 1188 (1997).
6. K. Zaghib, A. Guerfi, P. Hogving, A. Viji, M. Trudeau, and D. Lauterbach, Energy Environ. Sci., 4, 4978 (2011).
7. E. Markevich, R. Sharabi, H. Gottlieb, V. Borgel, K. Fridman, G. Salitra, D. Aurbach, G. Semrau, M. A. Schmidt, N. Shill, and C. Bruenig, Electrochem. Commun., 15, 22 (2013).
8. R. Sharabi, E. Markevich, V. Borgel, G. Gershinsky, G. Salitra, D. Aurbach, G. Semrau, M. A. Schmidt, N. Shill, and C. Stinner, J. Power Sources, 203, 109 (2012).
9. R. Sharabi, E. Markevich, K. Fridman, G. Gershinsky, G. Salitra, D. Aurbach, G. Semrau, M. A. Schmidt, N. Shill, and C. Bruenig, Electrochem. Commun., 28, 20 (2013).
10. N. Tsouvaras, S. Meini, I. Buchberger, and H. A. Gasteiger, J. Electrochem. Soc., 160, A471 (2013).
11. I. C. Jang, H. H. Lim, S. B. Lee, K. Karthikeyan, V. Aravindan, K. S. Kang, W. S. Yoon, W. I. Cho, and Y. S. Lee, Journal of Alloys and Compounds, 497, 321 (2010).
12. V. Petrcek, M. Dusek, and L. Palatinus, JANA 2006, Z. Kristallogr. 229, 345 (2014).
13. N. Brannik, K. Nikolowski, C. Haehnel, G. Brammik, and H. Ehrenberg, Chem. Mater., 19, 908 (2007).
14. R. E. Rogers, G. M. Clarke, O. N. Matthew, M. J. Ganter, O. N. Matthew, M. W. Forney, and B. J. Landi, J. Appl. Electrochem., 43, 271 (2013).
15. Y. M. Kang, Y. I. Kim, M. W. Oh, R. Z. Yin, Y. Lee, D. W. Han, H. S. Kwon, J. H. Kim, and G. Ramanath, Energy Environ. Sci., 4, 4978 (2011).
16. V. Petricek, M. Dusek, and L. Palatinus, JANA 2006, Z. Kristallogr. 229, 345 (2014).
17. N. Tsouvaras, S. Meini, I. Buchberger, and H. A. Gasteiger, J. Electrochem. Soc., 160, A471 (2013).
18. V. Petrcek, M. Dusek, and L. Palatinus, JANA 2006, Z. Kristallogr. 229, 345 (2014).
19. N. Brannik, K. Nikolowski, C. Haehnel, G. Brammik, and H. Ehrenberg, Chem. Mater., 19, 908 (2007).