Understanding the Role of Commercial Separators and Their Reactivity toward LiPF₆ on the Failure Mechanism of High-Voltage NCM523 || Graphite Lithium Ion Cells

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NCM523 || graphite lithium ion cells operated at 4.5 V are prone to an early “rollover” failure, due to electrode cross-talk, that is, transition metal (TM = Mn, Ni, and Co) dissolution from NCM523 and deposition at graphite, subsequent formation of Li metal dendrites, and, in the worst case, generation of (micro-)short-circuits by dendrites growing to the cathode. Here, the impact of different separators on the high-voltage performance of NCM523 || graphite cells is elucidated focusing on the separators’ structural properties (e.g., membrane vs fiber) and their reactivity toward LiPF₆ (e.g., ceramic-coated separators). First, the separator architecture has a major impact on cycle life. Fiber-structured separators can prevent the “rollover” failure by a more homogeneous deposition of TMs and formation of Li metal dendrites, thus, hindering penetration of dendrites to the cathode. In contrast, porous membrane-structured separators cannot prevent the cell failure due to inhomogeneous TM deposits/Li metal dendrites. Second, it is demonstrated that different types of ceramic-coated separators (Boehmite (γ-AlO(OH)) vs α-Al₂O₃) exhibit different reactivities toward LiPF₆. While α-Al₂O₃ shows a minor reactivity toward LiPF₆, the γ-AlO(OH) coating leads to in situ formation of the beneficial difluorophosphate anion in high amounts due to high reactivity toward LiPF₆ decomposition, which significantly improves cycle life.

1. Introduction

Lithium ion batteries (LIBs) are currently the state-of-the-art (SOTA) battery technology and dominate the field of high-energy applications such as mobile electronic devices, power tools, and electro-mobility due to their high energy density, long cycle life, and low self-discharge rate, among other beneficial factors.[1] However, especially for electric vehicles, it is necessary to further increase the LIB’s energy density to overcome limitations in terms of driving range.[2]

Besides the development of advanced LIB cell chemistries, including novel negative (anode) and positive (cathode) active materials with higher specific capacities, one common strategy is the increase of the cell voltage. This approach can be realized by the increase of the upper cut-off voltage, resulting in a higher delithiation degree of the cathode material and, thus, in a higher energy density.[3] SOTA cathode materials for LIB cells are the LiM₀₂-type layered transition metal (TM) oxides (M = Ni, Co, Mn, etc.), such as LiNi₀.5Co₀.2Mn₀.3O₂ (NCM523), due to their high theoretical capacities of up to ≈280 mAh g⁻¹.[2,4,5] For example, NCM523 can deliver a specific capacity of ≈170 mAh g⁻¹ in NCM23 || graphite cells in a cell voltage range of 2.8 to 4.3 V (20 °C, 1 C = 170 mA g⁻¹).[5]

However, the operation at elevated cell voltages (e.g., above 4.3 V) is highly challenging and known to result in severe capacity fading, which originates from several degradation mechanisms, such as Li⁺/Ni²⁺ cation mixing and associated NCM phase transformation, supposed oxidative electrolyte decomposition as well as cathode electrolyte interphase (CEI) growth and subsequent impedance rise.[1,4,6,6] A major degradation mechanism for LIB cells operated at high-voltage arises from electrode cross-talk phenomena, initiated by the dissolution of TMs from the cathode (e.g., Co³⁺, Ni²⁺, and Mn²⁺) into the electrolyte.[7] The dissolved TMs can migrate via the electrolyte and deposit at the anode, leading to a deterioration and degradation of the solid electrolyte interphase (SEI),
which results in significant SEI growth, subsequent impedance rise and higher irreversible capacities.\cite{7b,c,8} In this context, we previously demonstrated that the high-voltage operation (4.5 V) of capacity-balanced NCM523 || graphite full-cells (N:P ratio of 1.15:1) resulted in a high accumulation of deposited TMs at the graphite anode surface.\cite{5,9} We observed significant SEI growth at graphite, which then resulted in the formation of Li metal dendrites, subsequently leading to severe capacity fading, known recently as “rollover” failure or before that as “sudden death” phenomenon. This “rollover” failure for operation of NCM-based cathodes at cell voltages ≥ 4.4 V has also been observed by several groups.\cite{8c,10} We demonstrated that this dramatic cell failure mechanism is caused by penetration of Li metal dendrites through the separator to the cathode, leading to the formation of (micro-)short-circuits.\cite{5,9,11}

The role of the separator in this failure mechanism is not clearly understood so far. Separators can be roughly categorized into i) microporous membranes, ii) non-woven mats (fiber structure) and iii) ceramic-coated separators, besides solid electrolytes (inorganics, gel-polymers). Due to performance and cost advantages, most commercially used separators for LIBs are microporous polyolefin (polypropylene (PP), polyethylene (PE)) membranes having different architectures, such as single- or multi-layer designs, which can be combined with ceramic coatings.\cite{2b,12} When using a SOTA PP membrane separator (thickness =25 µm), a “rollover” failure of NCM523 || graphite cells was noted after ~50 cycles for operation at 4.5 V,\cite{5a} which was indicated by remarkable charge fluctuations and cell voltage “noise” within the cycles of cell-failure, thus, hinting to generation of (micro-)short-circuits.\cite{13} Moreover, we demonstrated that the “rollover” failure is suppressed within the first 100 cycles by substituting the relatively thin PP separator with a thicker glass fiber separator (thickness =680 µm, not compressed).\cite{5a} In this context, Markevich et al. demonstrated that an early induced “rollover” failure of NCM622 || Li metal cells (at 4.3 V) could be suppressed by using a SiO2-filled PE separator, due to the inhibition of cross-talk phenomena between cathode and anode.\cite{14} Furthermore, they showed that the SiO2-modified separator displayed a significant reactivity toward LiPF6, which may result in the beneficial in situ formation of additives such as lithium difluorophosphate (LiPO2F2).\cite{14} Additionally, Yan et al. reported on the beneficial effect of Li1.5Al0.5Ti1.5(PO4)3-coated PE separators in view of suppressing TM deposition at anodes in LiCoO2 || SiO/graphite cells and LiMn2O4 || SiO/graphite cells.\cite{15}

The separator can play a key role with respect to the suppression or reduction of detrimental cross-talk phenomena, which is of utmost importance to enable high-voltage operated LIB cells with long cycle life and high safety characteristics. In this work, we investigate various commercial separators in view of the cross-talk-induced “rollover” failure, especially regarding the formation of Li metal dendrites at the graphite anode in NCM523 || graphite cells operated at 4.5 V. We evaluate membrane- and fiber-based separators, as well as the impact of ceramic coatings in terms of their reactivity toward the LiPF6 salt and the subsequent impact on the electrochemical performance.

![Figure 1](image_url)

**Figure 1.** a,b) SEM images of the PP membrane separator and c) comparison of the charge/discharge cycling performance of NCM523 || graphite cells (coin cells, two-electrode configuration) at cell voltage ranges of 2.8–4.3 V (N/P ratio: 1:1.00) and 2.8–4.5 V (N/P ratio: 1.35/1.00) using the PP membrane separator. d,e) SEM images of the PP fiber separator and f) comparison of the charge/discharge cycling performance of NCM523 || graphite cells at 2.8–4.5 V (N/P ratio: of 1.35/1.00) using PP fiber and PP membrane separators.
performance in high-voltage LIB cells. Our results point out the importance to thoroughly evaluate the impact of the separator on cell performance, especially when it comes to comparison of electrochemical data within the scientific community.

2. Results and Discussion

2.1. Impact of PP Membrane and PP Fiber Separators with Different Thicknesses on the “Rollover” Failure

The electrochemical performance of NCM523||graphite full-cells using the thin “PP membrane” separator (Figure 1a,b) is evaluated at an upper charge voltage of 4.3 V and for comparing high-voltage operation also at 4.5 V (Figure 1c). At 4.3 V, the NCM523||graphite cells show an excellent cycling performance over 100 cycles with a specific discharge capacity of \( \approx 160 \text{ mAh g}^{-1} \) (at 1 C charge/discharge rate). In contrast, the cells operated at 4.5 V show an increased discharge capacity of \( \approx 180 \text{ mAh g}^{-1} \) (at 1 C) in the beginning of cycling, however, suffer from rapid capacity fading and an early “rollover” (=“sudden death”) failure after \( \approx 50 \) cycles (Figure 1c). The underlying mechanism has been discussed in previous works, particularly including the TM-induced formation of high surface area lithium\(^{[36]}\) in the form of Li metal dendrites at/on graphite and the subsequent generation of (micro-)short-circuits by dendrites growing to the cathode.\(^{[5,9a,11]}\) In this context, it should be noted that the N:P ratio for NCM523||graphite cells at 4.5 V was intentionally set to 1.35:1.00 compared to an N:P ratio of 1.15:1.00 for cells operated at 4.3 V, which should prevent Li metal plating at the anode considering the used operation conditions (charge/discharge rate), as an increased N:P ratio results in a shift to higher anode potentials.\(^{[17]}\) However, due to the TM-induced cross-talk between the cathode and anode, Li metal plating could not be prevented at 20 °C (see Figure 2), which was also shown in previous works.\(^{[5]}\)

By exchanging the PP membrane separator by a “PP fiber” separator (Figure 1d,e), the early “rollover” failure of NCM523||graphite cells is suppressed, while the capacity fading is nearly identical within the first 50 cycles (Figure 1f). This observation is a hint that the PP fiber separator itself will not significantly impact high-voltage-induced degradation mechanisms. Nevertheless, to examine the underlying reason for suppression of the early “rollover” failure using the PP fiber separator, the graphite anodes from both NCM523||graphite cells (Figure 1f) were collected after 100 cycles and analyzed by SEM and EDX.

![Figure 2. SEM images and EDX elemental mappings of graphite anodes after 100 charge/discharge cycles in NCM523||graphite full-cells (see Figure 1f) using a–h) the PP membrane separator or i–p) the PP fiber separator. SEM images (PP membrane separator) (a–d) and corresponding EDX elemental mappings (e–h) of Ni, Co, Mn, and F of the SEM image in (a). i–l) SEM images (PP fiber separator) and m–p) EDX elemental mappings of Ni, Co, Mn, and F of the SEM image in (k).](image-url)
The SEM images of the cycled graphite anodes from cells using the PP membrane separator are depicted in Figure 2a–d, showing various spots of thick “island-like” Li metal dendrites, and in particular at these spots and their surroundings a high accumulation of the three TMs (Ni, Co, and Mn) is noted (Figure 2e–g). In addition, a high content of fluorine was found at the Li metal spots, indicating an increased decomposition of the LiPF₆ salt at the Li metal surface (Figure 2h). These observations have been reported in our previous works, and solid-state ⁷Li NMR studies could also prove Li metal at the graphite surface.[⁵a] In comparison, the graphite anodes from cells using the PP fiber separator show a less explicit degradation, as illustrated in Figure 2i–l. Thereby, the anode surface can be classified in two areas, that is, a “bright grey” and a “dark grey” area (Figure 2i). The dark grey areas refer to formed Li metal dendrites, however, these dendrites are much more homogeneously distributed and less pronounced (Figure 2k,l) than the “island-like” Li metal dendrite spots using the PP membrane separator (Figure 2a–d). In contrast, the bright grey areas refer to highly covered graphite particles consisting of small spherically shaped nucleation points for the formation of Li metal dendrites. Similar examples are shown in Figure 5 and our previous work,[⁵a] where it is clear to see how these spherical nucleation points grow more and more together, so that needle-like Li metal dendrites are extruded from the anode surface. Nevertheless, similar to cells using the PP membrane separator, a high accumulation of the three TMs (Ni, Co, and Mn) is detected at the aged anode surface via EDX analysis (Figure 2m–p), indicating that the improved cycling performance and the prevention of the “rollover” failure (Figure 1f) is not the result of the suppression of the cross-talk phenomena. However, despite the severe TM deposition, it seems that both the TMs and Li metal dendrites are more homogeneously distributed at the graphite anode when using the fiber separator, which in turn can be beneficial regarding rollover suppression.

To further verify and visualize the assumption of a more homogeneous TM distribution and Li metal dendrite formation using the PP fiber separator compared to the PP membrane separator, laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analyses of de-lithiated graphite anodes after 100 cycles were performed, according to the method developed by Harte et al.,[¹⁸] allowing an elemental mapping of the whole graphite anode (Ø15 mm discs). Therefore, graphite anodes from NCM523 || graphite cells operated at 4.5 V using the PP membrane separator[⁵b] (Figure 3a–d) or the PP fiber separator (Figure 3e–h) were compared.

In particular, the elements Li, Ni, Co, and Mn were detected by this method and the intensity of each element can be identified via the color code, that is, from low intensity to high intensity: violet (lowest intensity), blue, green, yellow, and red (highest intensity). The graphite anode from cells based on the PP membrane separator shows a high accumulation of lithium, mostly “island-like” agglomerated spots, indicated by the highest intensity (red) at the graphite surface (Figure 3a). These “island-like” deposits were identified as Li metal dendrites, as also seen in Figure 2 and as reported previously.[⁵,⁹a,¹¹] Especially at the positions of the Li metal dendrite islands and their surroundings, a high accumulation of the three TMs was found by LA-ICP-MS analysis (Figure 3b–d). Thereby, Mn shows a more broad distribution and an overall higher intensity over the whole anode surface compared to Ni and Co deposits, which indicates that Mn has a greater impact on the aging of the anode and significantly participates in SEI alteration and growth as well as subsequent Li metal formation.[⁵a,⁷b] Jung et al. also reported that manganese shows a higher activity toward SEI degradation and cell failure of NCM622 || graphite...
cells compared Ni and Co, when adding the corresponding bis(trifluoromethane)sulfonylimide salts of Mn, Ni, and Co to the electrolyte.[8b]

In contrast, the graphite anode from the cells using the PP fiber separator does not display any formation of thick “island-like” lithium deposits at the electrode surface (Figure 3e–h), even though a certain amount of Li metal dendrites could be detected in the SEM images (Figure 2k,l). A very homogeneous distribution of lithium and all three TMs is observed by LA-ICP-MS analysis and fits quite well with the observations from SEM and EDX. It is also obvious here that manganese displays a higher intensity (Figure 3g) at the aged anode surface compared to Ni and Co (Figure 3f,h).

Finally, even though the degradation at the graphite anode seems less severe and rapid cell failure is suppressed (Figure 1f), TM deposition and formation of Li metal dendrites cannot be prevented by using the PP fiber separator in NCM523 | graphite cells operated at 4.5 V. By comparing the charge and discharge cell voltage profiles of both, the PP membrane- and PP fiber-based cells (Figure 4d), a nearly identical behavior can be recognized, that is, overlapping charge/discharge profiles with similar voltage drops within the first 50 cycles, resulting in a similar capacity fading rate (Figure 4a). This observation indicates that the separator itself has no significant impact on capacity loss and electrode degradation at the beginning of cycling.

However, the NCM523 | graphite cells using the two different separators show a completely different behavior between cycle numbers 50 to 100: The PP membrane-based cells show an “rollover” failure after ≈50 cycles (Figure 4a), which is accompanied by charge capacity fluctuations (Figure 4b) and voltage “noise” (Figure 4e) indicating the penetration of Li metal dendrites through the separator and the subsequent formation of (micro-)short-circuits.[35] In contrast, cell failure is prevented when using the PP fiber separator, which is also demonstrated by the fact that charge fluctuations (Figure 4c) and voltage “noise” (Figure 4f) cannot be observed within cycles 50 to 100. In summary, we suggest that these differences are the result of the above described more homogeneous distribution of the TM depositions and subsequently more homogeneous formation of Li metal dendrites for the PP fiber separator-based cells, which eventually suppresses the penetration of the Li metal dendrites through the separator at these cycle numbers and, thus, an early “rollover” failure at this cycling stage.

2.2. Impact of Ceramic-Coated PET and PE Separators on the “Rollover” Failure

Although the PP fiber separator can prevent severe cell failure of NCM523 | graphite cells operated at 4.5 V, with a thickness ≈230 µm in a not compressed state, it is significantly thicker

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**Figure 4.** a) Comparison of the charge/discharge cycling performance of NCM523 | graphite cells (coin cells, two-electrode configuration) at a cell voltage range of 2.8–4.5 V (N/P ratio: 1.35/1.00) using PP membrane and PP fiber separators. b) Charge and discharge capacities of cells using the PP membrane separator showing fluctuations of the charge capacity. c) Charge and discharge capacities of cells using the PP fiber separator. d) Cell voltage profiles of cells using PP membrane or PP fiber separators in the 1st, 4th, and 50th cycle. e) Cell voltage profiles of cells using the PP membrane separator in the 75th and 100th cycle showing voltage “noise”. f) Cell voltage profiles of cells using the PP fiber separator in the 75th and 100th cycle (without voltage “noise”).
than the PP membrane separator, which possesses a thickness of $\approx 25 \mu m$; that is, the separator thickness may have a major impact on electrode cross-talk. Even though such thick separators do not have any practical relevance for commercial high-energy LIB cells, these kinds of fiber separators are still commonly used in the battery research field. Therefore, it must be kept in mind that thickness and architecture of the separator (porosity, pore size distribution, etc.) can significantly influence the cycle life when comparing the electrochemical performance data here with that of other reports using different separators.

A thin commercial ceramic-coated (aluminum oxide) PE terephthalate (PET) fiber separator ("C-PET"); thickness: 30 $\mu m$; Figure 5b,c) was examined with respect to its ability to prevent the "rollover" failure of NCM523 | graphite cells at 4.5 V. The PET fiber side of the separator was placed to the graphite anode, while the ceramic-coated side was placed to the NCM523 cathode. Ceramic-coated separators can typically improve the thermal stability and therefore the safety performance of high-energy LIB cells. Like for the cells based on the thick PP fiber separator, the use of the C-PET separator results in the prevention of the early induced cell failure, as shown in Figure 5a. Both, the cells based on the PP fiber separator (Figure 1f) and using the C-PET separator, result in a similar capacity retention of $\approx 80\%$ after 100 cycles. Even though rapid cell failure is prevented, the use of the C-PET separator cannot hinder cross-talk phenomena in NCM523 | graphite cells. Like for the cycled graphite anode from the PP fiber separator-based cells (Figure 2i–p), the anode collected from cells using the C-PET separator after 100 cycles can be classified in two major areas, that is, "dark grey" and "bright grey" areas at the graphite surface, as shown in Figure 5d–i. The dark areas refer to agglomerated and more compact Li metal dendrites, which are very similar to those observed for the anode from the PP fiber-based cells (Figure 2i–p). Thereby, it is obvious that the C-PET fiber structure is highly pressed onto the anode surface within the cell, as the fiber structure influences the appearance of the formed Li metal dendrites (Figure 5f). In turn, this construction can impact the growth of Li metal dendrites and may prevent dendrite needles growing into the separator. The bright grey parts in the SEM images refer to the highly covered graphite particles (Figure 5g,h), with spherically-shaped spots indicating Li metal nucleation points, which grow more and more together with ongoing cycling and, thus, result in the formation of the needle-like dendrites as depicted in Figure 5g–i.

Figure 5. a) Comparison of the charge/discharge cycling performance of NCM523 | graphite cells (coin cells, two-electrode configuration) at a cell voltage range of 2.8–4.5 V (N/P ratio: 1.35/1.00) using the C-PET and PP membrane separators. SEM images of the C-PET separator with b) the fiber side placed to the graphite anode and c) the ceramic-coated side placed to the NCM523 cathode. d–i) SEM images of the graphite anodes after 100 charge/discharge cycles. j–l) Corresponding EDX elemental mappings of Mn, Ni, and Co from the SEM image in (e).
According to the EDX elemental mapping of Ni, Co, and Mn, it is evident that the cross-talk between the cathode and anode cannot be prevented (Figure 5j–l), despite the suppression of the early induced “rollover” failure. In summary, NCM523 \parallel graphite cells using the thin C-PET separator show a very similar cycling performance compared to the cells using the relatively thick PP fiber separator. For both cells, the deposition of TMs and Li metal dendrite formation occur more homogeneous compared to the PP membrane separator-based cells, thus, preventing the rapid cell failure. We suggest that the fiber structure (PP fiber and C-PET separators) is beneficial in terms of improved high-voltage cell performance because of an improved anode | separator interface (e.g., by an increased pressure), which results in the formation of more compact and more homogeneously distributed Li metal dendrites. However, further studies are needed to validate the above proposed mechanism. Next, we evaluated the impact of the C-PET separator on the performance NCM523 \parallel graphite cells (4.5 V), while the ceramic-coated side was placed to the graphite anode. We also found that severe rollover failure can be avoided, which is again the result of a more homogeneous Li metal dendrite formation than in the cells using “PP membrane” separators. The underlying reasons will be discussed in the following.

An additional parameter which can impact the cycling performance of high-voltage NCM523 \parallel graphite cells is the ceramic layer of the C-PET separator and its reactivity toward the electrolyte. In this context, Hall et al. examined the chemical reactivity of ceramic-coated NCM622 particles toward LiPF₆ decomposition, and they found out that an Al₂O₃ coating undergoes a chemical reaction with LiPF₆ according to Equation (1).

\[
2\text{Al}_2\text{O}_3(\text{s}) + x\text{PF}_6^- \rightarrow 2\text{Al}_2\text{O}_3(\text{s})_x + x\text{PO}_4\text{F}_2(\text{sub})
\]  

(1)

In this reaction, a difluorophosphate (DFP) anion is formed, which is a well-known electrolyte additive and can have a huge impact in high-voltage operated full-cells, as it can suppress the cross-talk between anode and cathode.\(^{[6a,5b,9b,21]}\) In previous works, we showed that the use of LiDFP as electrolyte additive can prevent the rapid capacity fading of NCM523 \parallel graphite cells operated at 4.5 V.\(^{[5a,9a]}\) Therefore, another commercial ceramic-coated separator was examined in NCM523 \parallel graphite cells at 4.5 V to explore whether a ceramic coating on the separator can guarantee an improved cycling performance by preventing the rapid cell failure. To demonstrate the wide diversity of commercially used separators and considering that different kinds of separators are used by different research groups in terms of benchmarking, another ceramic-coated (aluminum oxide) PE membrane separator (“C-PE”; thickness: 30 μm) was evaluated. As shown in Figure 6b, the PE membrane composition of one side of the C-PE is comparable to that of a pure PP membrane separator (Figure 1a,b), whereby the other side is coated by a ceramic (Figure 6c). However, the C-PE membrane separator cannot prevent the early cell failure of NCM523 \parallel graphite cells as it was the case for the ceramic-coated C-PET separator (Figure 6a). According to SEM images (Figure 6d–f), the use of C-PE results in a similar degradation of the graphite anode (“island-like” deposits) as observed for the pure PP membrane (Figure 2). A high amount of Li metal dendrites was removed during cell disassembly and separation of anode/separator, as the dendrites at the anode stuck strongly to the separator (Figure 6f; 1: dendrites; 2: detached dendrites after removal of the separator). Like previous observations for the other separators, a high accumulation of the three TMs was found on the graphite surface after 100 cycles (Figure 6g–i). These results further indicate that there is a significant difference between fiber-structured separators and membrane-based separators, as both fiber-structured separators can prevent the “rollover” cell failure, while both membrane-based separators cannot hinder the rapid capacity fading. However, as it is known that alumina-based ceramics (e.g., Al₂O₃ cathode coatings) are reactive toward LiPF₆\(^{[20,22]}\) which can lead to in situ formation of DFP,\(^{[20]}\) it might be possible that the C-PET separator shows a higher reactivity toward the electrolyte compared to the C-PE separator. In turn, the ceramics of both separators might lead to in situ formation of different amounts of DFP, which in turn can influence cell performance.

2.3. Understanding the Reactivity of Ceramic-Coated Separators toward LiPF₆ with Respect to Fluoride and Difluorophosphate Formation

The C-PET fiber separator as well as the C-PE membrane separator were investigated regarding their reactivity toward LiPF₆ decomposition, whereby the focus was on the formation of the DFP anion. For this experiment, the C-PET and C-PE separators were separately placed into a pouch bag, soaked with the standard (STD) electrolyte, and stored at 20 °C for 3 days (see also Experimental Section). Afterward, the separators were centrifuged and the collected electrolyte was filtered and analyzed by ion chromatography (IC) to quantify the amount of in situ formed DFP. In addition, we studied the impact of the separators regarding their ability to scavenge fluoride anions from the electrolyte, as HF as is typically present in small amounts in the electrolyte.\(^{[23]}\) As shown in Figure 7a, compared to the pure STD electrolyte (25 ppm fluoride), the fluoride concentration drops below the limit of quantification when stored with the separators at 20 °C, which confirms that these kind of ceramic-coated separators can scavenge HF from the electrolyte. An even more interesting aspect for high-voltage NCM523 \parallel graphite cells is the concentration of formed DFP at 20 °C, which is ≈117 ppm for the C-PE and ≈726 ppm for the C-PET separator (Figure 7c).

The C-PE separator shows a reduced tendency to react with the electrolyte compared to C-PET, as C-PE results in a similar amount of DFP as observed for the STD electrolyte (=68 ppm). The mechanism for the formation of DFP anions in SOTA carbonate-based electrolytes has been described in literature.\(^{[24]}\) As the C-PET separator shows already a significantly increased amount of DFP at 20 °C compared to the C-PE or the STD electrolyte, it can also have a beneficial impact on the high-voltage operation of LIB full-cells. Therefore, besides the beneficial fiber structure another beneficial effect of the C-PET separator results from its enhanced reactivity toward LiPF₆ and, thus, the formation of DFP as electrolyte additive.

It is also very common that LIB full-cells are evaluated at elevated temperature (e.g., at 40 °C), therefore, the experiment was repeated at 40 °C, to examine the temperature effect regarding the ongoing LiPF₆ decomposition caused by the ceramic-coated separator.
separators. While both separators resulted in a decreased fluorine content compared to the pure STD electrolyte at 20 °C (Figure 7a), this effect is no longer obvious at 40 °C, as the fluorine content of both samples strongly increased (Figure 7b). It can also be noted that the fluorine content of the C-PET sample is around three times higher compared to the C-PE separator, and indicates that the C-PET separator shows a higher reactivity toward the electrolyte components both at 20 and 40 °C. The highly increased DFP concentrations at 40 °C (Figure 7d) also show that the temperature remarkably promotes the reaction between LiPF₆ and the separators. Even though the C-PE separator only showed a minor reactivity toward the electrolyte at 20 °C, the DFP content increased from ≈117 to ≈648 ppm at 40 °C. However, the C-PET separator shows again a higher reactivity as the formed DFP content increased from ≈726 ppm at 20 °C to ≈1293 ppm at 40 °C (Figure 7d). At this stage, the question raises why the C-PET fiber separator shows a much higher reactivity toward the LiPF₆ decomposition than the C-PE membrane separator.

For further understanding, the separators were analyzed by means of X-ray diffraction (XRD) to identify the bulk structure of the ceramic coating. The ceramic coating of the C-PE separator was identified as α-Al₂O₃ (Figure 8b). According to the XRD analysis, the coating of the C-PET separator either corresponds to α-AlOOH (Diaspore) or γ-AlOOH (Boehmite), as shown in Figure 8a. However, additional Raman spectroscopy measurements confirmed the Boehmite structure of the coating (Figure S1, Supporting Information).[25] Therefore, it must be considered that even if both separators are coated with aluminum-based ceramics, their structure is completely
different and might have an impact on the reactivity toward the electrolyte. γ-AlOOH exhibits a high amount of hydroxyl-groups at the surface and these hydroxyl-groups can, for example, act as base or acid.\[26\] In this context, Reshma et al. demonstrated that Boehmite can act as acid-base bi-functional catalyst in aldol condensation reactions.\[26b\] They proposed that γ-AlOOH has the ability to abstract a proton from acetone, and the resulting carbanion can then further react with an aldehyde. In contrast to that, the ceramic coating of the C-PE separator consists of α-Al2O3, which can be synthesized from Boehmite at high temperatures (\(\approx 1100–1200 \, ^\circ\text{C}\)) over a dehydration, as shown in Figure 8c. In the first step the γ-Al2O3 phase is formed by heat-treatment of Boehmite (at \(\approx 450–600 \, ^\circ\text{C}\)), which still exhibits residual hydroxyl-groups at the surface and is closely related to the Boehmite structure.\[27\] However, at high temperatures these residual hydroxyl-groups are further eliminated which then results in the formation of α-Al2O3.\[28\]

As the C-PET separator shows a much higher reactivity toward LiPF6 decomposition than the C-PE separator (Figure 7), especially at 20 °C, we propose that the hydroxyl-groups at the surface of the ceramic-coated separators play a key role in view of the decomposition of LiPF6 and the formation of the beneficial DFP additive. We suggest that the high reactivity of Boehmite-coated separators results in the mechanism proposed in Figure 8d. In the first step, \(\text{H}^+\) (e.g., from HF) undergoes a neutralization reaction by the hydroxyl-groups at the surface of Boehmite. Additionally, a strong interaction occurs between the Lewis acid (Al\(^{3+}\)) and the Lewis base fluoride (F\(^-\)), which results in the formation of aluminum oxyfluoride (Al\(_x\)O\(_y\)F\(_z\)).

Due to the neutralization reaction of HF with Boehmite, the released \(\text{H}_2\text{O}\) can promote the decomposition reaction of LiPF6 due to the hydrolysis of, for example, PF\(_6^-\).\[29\] Subsequently, this hydrolysis reaction results in the formation of POF\(_3^-\), or in a next step into PO\(_2\)F\(_2^-\). In both cases, HF is continuously generated and can further react with Boehmite to produce even more \(\text{H}_2\text{O}\) and, thus, more DFP will be formed. The postulated mechanism can explain why the C-PET separator shows a significantly higher reactivity toward LiPF6 decomposition compared to the C-PE separator, as α-Al2O3 (for C-PE) should have only a limited number of hydroxyl-groups at the surface.

2.4. The Broader Picture: Understanding the Role of Ceramic Coatings and the Reactivity of AlF\(_3\)/Al\(_2\)O\(_3\)/γ-AlOOH Species toward the Electrolyte

Besides the direct reaction of the ceramics with LiPF6 or HF and besides the reaction of released \(\text{H}_2\text{O}\) stemming from the reaction of, for example, HF with Boehmite, another possible element of LiPF6 decomposition can be the formation of AlF\(_3\), which is the end-product for the complete reaction of Al\(_2\)O\(_3\) with LiPF6/HF.\[20\] In this respect, Qiu et al. showed that a silica-oxygen-borate hybrid network on an Al\(_2\)O\(_3\)-coated PE separator results in AlF\(_3\) formation due to an HF scavenging effect.\[23a\] Further, Owen et al. already
observed that AlF₃, which was used as cathode active material, underwent an unwanted side reaction with LiPF₆/LiF to form Li₃AlF₆.\[30\]

Therefore, we decided to examine the role of anhydrous AlF₃ in view of the possible formation of the beneficial electrolyte additive DFP via IC measurements. As shown in Figure 9a, the presence of anhydrous AlF₃ in the STD electrolyte at 20 °C already resulted in a strong decomposition of LiPF₆, as the concentration of DFP increased from ≈68 (without AlF₃) to ≈3000 ppm (with AlF₃). We postulate that AlF₃ mainly reacts with LiF to form Li₃AlF₆, which in turn would result in an equilibrium shift of the reaction from LiPF₆ to PF₅/LiF (Figure 9d). Subsequently, higher amounts of PF₅ should be present in the electrolyte, which could easily react with H₂O residues to form PO₃F or—in a next step—the DFP additive (Figure 9d). However, the postulated mechanism cannot explain why such high quantities of DFP anions were generated, as it was the case in the presence of AlF₃ in the STD electrolyte (Figure 9a), considering the small quantities of H₂O which are typically present in battery-grade electrolytes (≤10 ppm; according to electrolyte manufacturers). There must be a source of oxygen to produce such high amounts of DFP to support the proposed mechanism (Figure 9d). One possible reason can be that additional amounts of H₂O are already present at the surface of the anhydrous AlF₃, which are not detectable by XRD analysis, as no clear AlF₃·[H₂O]ₓ phases were found (Figure 9b). Besides small amounts of adsorbed water at the surface of anhydrous AlF₃, a more important factor can be the production route of AlF₃,\[31\] which can be synthesized according to Equation (2):

\[
\text{Al}_2\text{O}_3 + 6\text{HF} \rightarrow 2\text{AlF}_3 + 3\text{H}_2\text{O}
\]
Therefore, another explanation for the high reactivity of AlF₃ toward LiPF₆ decomposition, besides small water contaminations, can be the presence of aluminum oxide phase impurities which are not detectable via XRD. In this way, AlF₃ shifts the “LiPF₆ equilibrium” to PF₅/LiF (Figure 9d) due to the formation of Li₃AlF₆, whereby PF₅ subsequently can easier undergo hydrolysis by H₂O impurities to form PO₃F⁻ and PO₂F⁻. The hydrolysis reaction results in the formation of newly generated HF, which can further react with the aluminum oxide impurities to generate more H₂O and, thus, more LiPF₆ decomposition products such as DFP. The proposed mechanism is depicted in Figure 9d. As it was not possible to identify any Al₂O₃ impurity phases by XRD analysis, the anhydrous AlF₃ was further analyzed by X-ray photoelectron spectroscopy (XPS) as it is more surface-sensitive. As shown in Figure 9c, the pure commercial anhydrous AlF₃ with a major peak at 76.3 eV also has a small shoulder at ≈75.4 eV, which confirms the presence of an aluminum oxide impurity phase[33] and therefore confirms the above proposed mechanism of AlF₃ toward LiPF₆ decomposition and the subsequent formation of DFP.

We suggest that these findings can be very helpful, especially in view of the beneficial effect of the well-known AlF₃ coating approach of cathode material particles.[16] Different synthesis routes are known for preparation of AlF₃-coated materials, such as the chemical precipitation route, where the active material powder is immersed in a solution of Al(NO₃)₃·9 H₂O in deionized water, followed by a slow addition of an NH₄F solution.[34,35] Afterward, the solvent is evaporated and the resulting powder is heat-treated at ≥400 °C under N₂ or Ar atmosphere to avoid the formation of Al₂O₃.[34,35] In this process, an incomplete reaction of Al(NO₃)₃·9 H₂O with NH₄F can result in the formation of γ-AlOOH (even in Ar atmosphere), as shown by Myronyuk et al.[36] In turn, the formation of γ-AlOOH could lead to the beneficial effect in terms of DFP formation when using AlF₃ (Figure 9), that is, a synergistic effect of AlF₃ and Al₂O₃/γ-AlOOH. Delong et al. demonstrated that AlF₃·3H₂O can result in Al₂O₃ formation at temperatures >380 °C. As the synthesis route of AlF₃ coatings is carried out in aqueous solution it is possible to form AlF₃·3H₂O and therefore to generate Al₂O₃ impurities.[37]

According to the chemical precipitation route in water, Zheng et al. evaluated an AlF₃ coating for Li₁.₂Ni₀.15Co₀.10Mn₀.55O₂ cathodes (2.0–4.8 V), which resulted in a remarkably improved cycling performance compared to the uncoated cathode.[13a] Interestingly, Yu et al. studied AlF₃ coatings on a similar cathode material (Li₁.₂Mn₀.5Co₀.13Ni₀.13O₂) in the same voltage range, but they observed that neither a pure Al₂O₃ nor a pure AlF₃ coating resulted in significant cycling performance improvements.[38] The main difference between the works of Zheng et al. and Yu et al. lied in the coating preparation method: While Zheng et al. used the chemical precipitation method in aqueous solution, where formation of Al₂O₃/γ-AlOOH is possible, Yu et al.
prepared the AlF$_3$ coating by atomic layer deposition, which should result in less side products.$^{[35a,38]}$ Yu et al. also combined the AlF$_3$ coating with an Al$_2$O$_3$ coating and observed a remarkably improved capacity retention,$^{[108]}$ which further confirms the here proposed mechanism of a synergistic effect of AlF$_3$ and Al$_2$O$_3$/γ-AlOOH (Figure 9d). In this work, we could confirm the in situ formation of the electrolyte additive DFP, which improved the cell performance by TM scavenging. A similar beneficial impact of AlF$_3$/Al$_2$O$_3$/γ-AlOOH can be expected for Li/ Mn-rich cathode materials, which also suffer from TM dissolution and cell capacity fading.$^{[18]}$

The beneficial effects of coating layers of AlF$_3$ and an Al$_2$O$_3$ impurity phase go beyond the promotion of LiPF$_6$ decomposition and formation of high quantities of DFP. We suggest that such coating layers exhibit a synergistic effect to enhance the cycle life, that is, on the one hand the coating functions as physical protection and on the other hand promotes in situ formation of functional electrolyte additives. For the development of advanced cathode coatings (especially oxide/fluoride-based coatings), we recommend that such coatings should be studied in view of LiPF$_6$ decomposition products and should be compared with the LiDFP electrolyte additive. From our experience, LiDFP is one of the most effective electrolyte additives for TM scavenging in LIB cells operated at high-voltage. Future studies can focus on further fundamental understanding of the in situ generation of DFP or related species within LIB cells.

3. Conclusion

We evaluated the impact of the separator and its reactivity toward the electrolyte on the performance of high-voltage NCM523 || graphite cells focusing on PP membrane, PP fiber, and ceramic-coated separators. The use of an SOTA PP membrane showed excellent cycling performance at 4.3 V (1 C) with a capacity retention of ≈97% after 100 cycles. However, by increasing the upper cut-off voltage to 4.5 V, a dramatic cell failure appeared after ≈50 cycles, which originated from Li metal dendrite formation and growth caused by electrode cross-talk phenomena between the cathode and anode, that is, TM dissolution/deposition (Mn, Co, and Ni). These high-voltage-operation induced Li metal dendrites can penetrate trough the separator to the cathode surface, thereby generating (micro-)short-circuits as indicated by voltage “noise” and charge fluctuations within the cycles of rapid capacity decay. The substitution of the PP membrane by a PP fiber separator prevented early “rollover” failure of NCM523 || graphite cells at 4.5 V even though the electrode cross-talk could not be suppressed. Instead, the use of the fiber separator resulted in a significantly more homogeneous and more plane distributed formation of Li metal dendrites, which correlated with a more homogeneous TM deposition. Furthermore, we examined two different ceramic-coated, aluminum oxide-based separators, that is, C-PE and C-PET at 4.5 V. While the cells based on the C-PE separator showed an early rollover failure, the cells using the C-PET separator prevented severe capacity decay, even though electrode cross-talk was not completely suppressed. Instead, TM deposits and Li metal dendrites were found at the aged graphite anode, but less dominant and more homogeneously distributed compared to the cells using either PP membrane or C-PE separators. On the one hand, the fiber structure of the separator (facing the anode) seems to be beneficial compared to the membrane structure, in terms of homogeneity of Li metal formation and dendrite morphology. On the other hand, a very important role regarding an improved cycling performance of NCM523 || graphite cells by less dominated Li metal dendrite formation can be associated to the reactivity of the ceramic coating toward LiPF$_6$ decomposition. Here, we proved that this decomposition reaction results in in situ formation of the electrolyte additive DFP, which has been previously shown to have a beneficial impact on the cycling performance of high-voltage cells. We found that an α-Al$_2$O$_3$ coating (C-PE membrane separator), shows a minor reactivity toward LiPF$_6$ decompositions and less DFP formation, which also correlates with the observed rapid capacity decay. In contrast, an γ-AlOOH (Boehmite) coating (C-PET fiber separator) shows a much higher reactivity toward LiPF$_6$ decomposition (even at 20 °C), resulting in the formation of significantly higher amounts of DFP, a well-known electrolyte additive, which in turn also correlates very well with the improved cycling stability in the presence of these high DFP amounts. Overall, it is very important to identify the structure/chemistry of used ceramic separator coatings, as their characteristics, for example, the reactivity toward LiPF$_6$, can have a major impact in view of the in situ formation of the DFP electrolyte additive.

In addition, we evaluated the reactivity of AlF$_3$ toward the electrolyte, as AlF$_3$ is the end-product for a complete reaction of Al$_2$O$_3$ with LiPF$_6$/HF. We found that minor impurities of Al$_2$O$_3$/γ-AlOOH can result in generation of the DFP additive, which can subsequently influence cycling performance. As AlF$_3$ is typically applied as cathode active material coating, we also recommend that such coatings can in future be studied regarding their reactivity toward LiPF$_6$ decomposition and in situ formation of the LiDFP electrolyte additive or related electrolyte decomposition species with additive function. In summary, it is recommended to be kept in mind that ceramic coatings for separators and/or active materials will not only influence the cell performance by their (beneficial) mechanical properties, but also by their reactivity toward electrolyte components, which in turn can result in in situ formed novel components impacting CEI and SEI formation in the first cycles and alteration during long-term cycling. In future works, the impact of separators on the suggested failure mechanism should also be demonstrated in practical cells, for example, in multilayer pouch cells. Furthermore, it is highly recommended to evaluate the separator characteristics (e.g., pore size distribution, tortuosity, air permeability, wetting behavior, and electrolyte uptake) in more detail to obtain a better fundamental understanding on how its physical properties can enable a homogeneous TM deposition at the graphite anode.

4. Experimental Section

Electrode Preparation: NCM523-based cathodes and graphite-based anodes were prepared in large-scale at an in-house battery line. The cathodes consisted of 95 wt% NCM523 (pristine NCM523; Custom Cells Itzehoe GmbH), 3 wt% polyvinylidene difluoride binder (Solfel 5130, Solvay), and 2 wt% carbon black (Super C65, Imerys Graphite & Carbon) and were cast onto aluminum foil (15 µm; Nippon Foil). The solvent for
the cathode paste was N-methyl-2-pyrrolidone (Sigma Aldrich, purity: 99.5%). The cathode mass loading was 12.2 mg cm\(^{-2}\) and the cathode areal capacities were 2.0 mAh cm\(^{-2}\) at a cell voltage of 4.3 V and 2.2 mAh cm\(^{-2}\) at 4.5 V. The anodes consisted of 95 wt% graphite (SG3, synthetic graphite, SGL Carbon), 1.5 wt% styrene-butadiene-rubber (SBR; SB5521, LIPATON, Polymer Latex GmbH), 3 wt% Na-CMC (Walocel CRT 2000 PPA12; Dow Wolff Cellulosics), and 0.5 wt% carbon black (Super C65, Imerys Graphite & Carbon) and were cast onto copper foil (10 µm; Nippon Foil), using deionized water as solvent. The anode mass loading was either 8.8 mg cm\(^{-2}\) (3.0 mAh cm\(^{-2}\)) or 6.9 mg cm\(^{-2}\) (2.3 mAh cm\(^{-2}\)) to achieve suitable N:P ratios. After drying and calendaring of the electrode sheets (porosity: 30%), they were punched into circular Ø14 mm (cathode) and Ø15 mm (anode) discs. The electrodes were dried in a vacuum oven at 100 °C under reduced pressure. The electrode capacity balancing of anode and cathode (N:P ratio) was set to 1.13:1.00 (4.3 V; anode : cathode = 2.3 : 2.0 mAh cm\(^{-2}\)) and 1.35:1.00 (4.5 V; anode : cathode = 3.0 : 2.2 mAh cm\(^{-2}\)).

**Cell Assembly:** 2032-type coin cells (full-cell setup, two-electrode configuration) were assembled to investigate the cell performance and TM dissolution from the NCM523 cathode and TM deposition at the graphite anode in NCM523 graphite full-cells. The Ø15 mm anode disc was separated by the separator from the Ø14 mm cathode disc, which was soaked with 40 µL of the electrolyte. The standard electrolyte (STD) used in this work was 1 M LiPF\(_6\) in ethylene carbonate (EC):ethyl methyl carbonate (EMC) 3:7 (by weight; Solvionic; purity: battery grade). Four different separators were used: i) “PP membrane” separator (PP; Celgard 2500; Celgard); ii) “PP fiber” separator (PP; FS2190; Freudenberg); iii) “C-PET” separator (ceramic-coated PE terephthalate; Mitsubishi OZ 2500; Celgard); iv) “CP” separator (ceramic-coated PE membrane; collected from commercial pouch cells; Li-Fun technology). Further details can be found in Table S1, Supporting Information.

**Constant Current–Constant Voltage Charge/Discharge Cycling:** The electrochemical charge/discharge cycling performance of NCM523 graphite full-cells was studied via constant current (CC) charge/discharge cycling on a Maccor 4000 battery testing system in cell voltage ranges between 2.8–4.3 V and 2.8–4.5 V. The cell formation conditions consisted of one cycle at 0.1 C and one cycle at 0.2 C. Afterward, the cells were cycled with 1 C (1 C = 170 mA g\(^{-1}\) at 4.3 V; 1 C = 190 mA g\(^{-1}\) at 4.5 V). After each charge step, a constant voltage (CV) step was performed with the limiting conditions of either achieving a time limit of maximal 30 min or when the specific current reaches values below 0.05 C. All electrochemical studies were performed in climatic chambers at 20 °C. At least three cells were evaluated for each study to ensure a high reproducibility, which is indicated by error bars in the respective figures.

**SEM and EDX Investigations of Graphite Anodes after Cycling:** The investigation of the surface morphology of the cycled graphite anodes (after 100 cycles) was performed by a Zeiss Auriga electron microscope and EDX was carried out with an accelerating voltage of 20 kV with an energy-dispersive X-ray detector (X-MaxN 80 mm\(^2\), Oxford Instruments). Prior to analysis, the cells were disassembled in dry atmosphere (dry room) and the anode surfaces were rinsed with 1 mL of EMC. After a short drying period under reduced pressure, the electrodes were transferred into the SEM analysis chamber. XPS was measured using a monochromatic Al K\(_\alpha\) radiation (0.154 nm wavelength). The powder patterns were collected from commercial pouch cells Li-Fun technology. Further details can be found in Table S1, Supporting Information.

**Analysis of Ceramic-Coated Separators:** In order to evaluate the performance of ceramic-coated separators, the separators were washed with 40 mL of EMC. After a short drying period under reduced pressure, the separators were transferred into the SEM analysis chamber. XPS was measured using a monochromatic Al K\(_\alpha\) radiation (0.154 nm wavelength). The powder patterns were recorded in a 2θ range of 10°–80° with a step size of 0.021° and a measurement time of 1.5 s per step.

For XPS of anhydrous AlF\(_3\), the powder was mounted on a sample holder and transported to a glovebox connected to an Axis Ultra DLD XPS (Kratos Analytical). From here, the powder was moved into an ultra-high vacuum (10\(^{-8}\) mbar) chamber inside the device and was stored for at least 12 h to remove volatile species, before moving into the analysis chamber. XPS was measured using a monochromatic Al K\(_\alpha\) source (hv = 1486.6 eV) at an emission current of 10 mA and with an accelerating voltage of 12 kV. A charge neutralizer was used to suppress positive charging of the sample’s surface. The angle of emission was 0° and the hemispherical analyzer was set to a pass energy of 160 eV for survey spectra and 40 eV for core spectra. Core spectra were recorded in the following regions: F 1s, C 1s, and Al 2p.

For IC-CD analysis, 100 mg anhydrous AlF\(_3\) were dried at 100 °C for 2 days and then transferred into a pouch bag filled with 1 mL of the STD electrolyte. After 3 days of storage at 20 °C, the electrolyte was filtered and analyzed by IC-CD to quantify the amount of formed DFP anions.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.
Keywords

ceramic-coated separators, electrode cross-talk, LiPF₆ decomposition, rollover failure, transition metal dissolution, transition metal deposition

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