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Spatially and Chemically Resolved Degradation of Fluorine-Free Electrolyte on Silicon/Graphite Surfaces

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Implementation of fluorine-free electrolytes that are safer and more sustainable than the state-of-the-art highly fluorinated electrolytes requires a thorough understanding of the interphase formation process. This work investigates the effects of LiPF6 and lithium bis(oxalato)borate (LiBOB)-based electrolytes on the electrochemical performance and surface chemistry of graphite, silicon, and silicon-graphite composite electrodes. The LiBOB-based electrolyte degrades more with the presence of silicon in the electrode, and tends to form a thicker solid electrolyte interphase (SEI) layer compared to the LiPF6-based electrolyte. Different degradation distributions were also found in the graphite-silicon composite electrode: The LiPF6 degradation products tend to form on silicon, while the LiBOB degradation products preferentially form on carbon species. These results provide insights into the relationship between electrolytes and electrodes in terms of electrochemical performance, as well as SEI composition and morphology.

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Lithium-ion batteries (LIBs) are in continuous development to improve energy density and cycling life. While these are the main performance metrics, many other challenges should be improved without compromising them, such as safety, recyclability, and sustainability.1,2 While lithium metal and silicon have higher theoretical capacity, 3860 mAh g−1 and 3579 mAh g−1, respectively, than the conventional graphite anode (372 mAh g−1), their implementation in commercial batteries is hindered due to their high reactivity and short cycling life. Therefore, the approach chosen to increase the capacity without compromising the electrochemical performance is to combine graphite with a small amount of silicon. This has been achieved with the conventional fluorinated electrolytes based on LiPF6 and fluorinated additives such as fluoroethylene carbonate (FEC). However, they lack in improving the sustainability aspect and ease of recycling. Therefore, alternative electrolytes ought to be found and optimized for silicon-based electrodes.

Fluorine-free electrolytes would avoid the formation of toxic and corrosive compounds, such as HF and PF5, that are usually released with LiPF6-based electrolytes under thermal dissociation or in contact with moisture. These compounds degrade components in the batteries during cycling, such as SEI, electrolytes, and electrodes, leading to performance decay.4,5 Besides the challenges inside the battery and during its operation, these compounds are also detrimental for the recycling process of batteries as their toxicity is an additional safety hazard, they corrode the reactors and often remain as impurities in the recycled material.3,6 In addition, they are released if a battery catches fire, even if it is only in small amounts they can harm the environment and the people around.7,8 As an alternative, the most well-studied fluorine-free salt is lithium bis(oxalato)borate (LiBOB), which has shown good electrochemical performance with graphite electrodes but very little is known about its effects on silicon-based electrodes.4,9

Thin-film silicon electrodes have shown better capacity retention with LiBOB-based electrolyte compared to LiPF6-based electrolyte thanks to its ability to form a stable solid electrolyte interphase (SEI) layer. In the fluorine-free system, the SEI layer contained reduction products of BOB anion while in the fluorinated electrolyte it was mostly composed of reduction products of ethylene carbonate (EC) solvent.10–12 When analysed in a powder-based electrode composed of silicon, graphite and disordered carbon, although LiBOB was shown to create a high-resistance layer, it provided good capacity retention. In contrast, LiPF6 led to low capacity retention but higher specific capacity. In addition, a mixed electrolyte containing both salts was seen to improve the overall electrochemical performance.13 Recently, promising performance with a fluorine-free electrolyte based on a combination of LiBOB and vinylene carbonate (VC) additive was shown in LiNi1/3Mn1/3Co1/3O2/Si-graphite full cells. However, the limitation of the electrolyte occurred when cycling at high current rates (C/2). In addition, it was noticed that the degradation of LiBOB was different on the two active materials, graphite and silicon, but it was not investigated further.9 While the role of LiBOB-based fluorine-free electrolytes on the SEI has been investigated for each active material separately,10–12,14,15 further investigation is still required to understand the impact when both are combined. As commercial electrodes tend to increase the amount of silicon, understanding the role of the electrolyte and its degradation mechanism on different active materials in the same electrode is crucial. Especially with novel fluorine-free electrolytes that have the potential to improve battery safety and sustainability.

In this paper, we investigate the effect of LiBOB-based electrolyte on graphite and silicon separately as well as on a silicon-graphite composite electrode, and compare it to a LiPF6-based electrolyte. This study encompasses electrochemical performance, along with a thorough analysis of the morphology and composition of the SEI using surface-sensitive techniques. The SEI is studied after the first lithiation and the fifth delithiation cycles, which gives insights to the SEI formation at different stages. The results show the differences in electrolyte degradation distribution and SEI thickness with the different active materials in the electrodes.

Experimental

Materials.—Si powder (Alfa Aesar, crystalline, APS <50 nm, 98%, laser synthesized from vapor phase, surface area 70100 m2 g−1), graphite powder (Timcal Timrex, SLP90, particle size <30 μm), carbon black Super C65 (Timcal C-Nergy, particle size 150 nm), Na-CMC (Dow, Walocel CRT 2000 Pa, DS: 0.89), SBR (Targray, PSBR100, dispersed in water, 15 ± 0.5% solid content), citric acid (99.5% Sigma-Aldrich), potassium hydroxide (KOH, 90%), and lithium bis(oxalato) borate (LiBOB), which has shown good electrochemical performance with graphite electrodes but very little is known about its effects on silicon-based electrodes.4,9

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Electrode preparation.—A buffer solution of citric acid (3.3 g) and KOH (0.41 g) in water (100 g) was prepared with pH 3, which is seen to improve the cycling performance of silicon-based electrodes.\textsuperscript{16,17} Active material, binders, buffer solution and water (13% total solid content) were mixed in a MM 400 mixer mill (Retsch) for 30 min at 25 Hz. The obtained slurry was coated on a carbon-coated copper foil with a doctor blade with coating gap of 100 μm. Afterwards, the coating was dried at ambient temperature for 24 h, 13 mm electrode discs were punched out and nally dried at 120 °C in vacuum for 12 h. The mass ratio of the components in the graphite electrode were 87.25% graphite, 2.35% Na-CMC, 2.35% SBR, 1.88% carbon black, 6.18% buffer. The silicon-graphite composite with a ratio of 20% Si and 80% graphite was composed of 69.44% graphite, 17.24% Si, 2.33% Na-CMC, 2.33% SBR, 1.86% carbon black, 6.79% buffer. The silicon electrode composition was 61% Si, 4% Na-CMC, 4% SBR, 8% carbon black, 23% buffer.

The theoretical capacity of each electrode was 372 mAh g\textsuperscript{-1} for graphite electrodes, 1013 mAh g\textsuperscript{-1} for silicon-graphite composite electrodes, and 3579 mAh g\textsuperscript{-1} for silicon electrodes. The active material mass loading was c.a. 4.5 mg cm\textsuperscript{-2} for graphite electrodes, 3.8 mg cm\textsuperscript{-2} for silicon-graphite electrodes, and 1.0 mg cm\textsuperscript{-2} for silicon electrodes.

Cell assembly.—Coin cells were assembled in an argon glove box with the prepared electrodes, Celgard 2325 separator soaked with 50 μL of electrolyte and lithium metal discs with 15 mm diameter. Two electrolytes were prepared: a fluorinated based on LP57 (LiPF\textsubscript{6} in EC:EMC 3:7 vol%) with 10 vol% FEC and 2 vol% VC. The cells rested for 6 h before cycling was initiated.

Battery testing.—Galvanostatic cycling of half-cells was performed using Arbin BT-2043 and Neware BTS4000 battery testing systems at room temperature. Two different cycling protocols were used to investigate the cells after the half-cycle and after 5 cycles. For the first half-cycle (Hc) the cells were lithiated at C/20 until 0.01 V vs Li\textsuperscript{+}/Li followed by a constant voltage step (CCCV) until the current decreased to C/40. For 5 cycles (5c) the cells were cycled between 0.01–1.5 V vs Li\textsuperscript{+}/Li at C/20 with a CCCV step during lithiation until C/40 for two cycles; the remaining three cycles were done at C/5 until C/10 for graphite and silicon-graphite cells and until C/20 for silicon cells. The cells were stopped at the lithiated state after the first half-cycle and at the delithiated state after 5 cycles. The cells were disassembled for further surface analysis in an argon glove box. The electrodes were washed by slowly dripping 2 ml of dimethyl carbonate (DMC) over them to remove excess liquid electrolyte.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX).—The cycled electrodes were transferred to the SEM in a vacuum-sealed transfer chamber to avoid exposure to air. The morphology of the electrodes was investigated with a field-emission scanning electron microscope (Merlin, Carl Zeiss, Germany) with an acceleration voltage of 3 kV and a beam current of 100 pA. The elemental composition of the electrodes was examined by EDX with an acceleration voltage of 10 kV and a beam current of 1 nA.

X-ray Photoelectron Spectroscopy (XPS).—The samples were transported to the XPS with a vacuum-tight transfer chamber to avoid exposure to air and moisture. The experiments were carried out using a PHI 5500 hemispherical analyzer equipped with a monochromatized Al Kα radiation \((h\nu = 1486 eV)\) source. Survey scans of all samples were measured first to identify elements in the samples. The C 1s, F 1s, P 2p, and O 1s spectra were measured for all electrodes with fluorinated electrolyte. Only the C 1s, B 1s, and O 1s spectra were measured for all electrodes with non-fluorinated electrolyte since there are no P 2p signals and no very few F 1s signals compared to other core-level signals in the survey scan spectra. For electrodes with a kinetic energy between 800–1300 eV, the inelastic mean free path (IMFP) of inorganic compounds is generally between 2.3–3.3 nm.\textsuperscript{18} The analysis depth in this work is defined as 3 times the IMFP, as this depth includes about 95% of the signal information. In order to understand the contribution from each material, we have investigated three different electrode compositions containing only graphite (Gr), silicon (Si) or a silicon-graphite composite electrode (SiGr). Furthermore, we have investigated the SEI formed from two different electrolyte formulations: a highly fluorinated electrolyte based on LiPF\textsubscript{6} in EC:EMC with FEC and VC additives (called LiPF\textsubscript{6} electrolyte from now on) and a non-fluorinated electrolyte based on LiBOB in EC:EMC with VC additive (called LiBOB electrolyte).

Electrochemical performance.—The electrochemical performance of Gr, Si and SiGr electrodes was investigated in half-cells against lithium metal. The voltage proﬁle of the initial lithiation cycle is presented in Fig. S1 and the derivative curves (dQ/dV) in Figs. 1a–1c. The main difference between the two electrolytes can be seen at the beginning of the cycle. The cells with LiBOB electrolyte show a degradation onset at 1.8 V vs Li\textsuperscript{+}/Li (dot lines in Figs. 1a–1c) regardless of the electrode’s active material, in agreement with the values reported in literature accountable for LiBOB reduction.\textsuperscript{24,26} This indicates that the onset of LiBOB degradation is independent of the active material, graphite or silicon. However, the peak shape is different in each case. For graphite cells, the peak is narrow but there is a continuous degradation taking place as seen from the derivative curve not going back to the initial baseline and from the voltage profile in Fig. S1(a) with capacity increasing even before reaching the graphite redox potential. In the case of silicon-containing electrodes, the peak minimum shifts to lower potentials and the intensity increases when moving from Gr, to SiGr to Si. This suggests that LiBOB salt is more prone to degrade when silicon is present although it is important to note that the silicon is nanosized, and therefore the silicon-based electrodes have a larger surface area which could affect the electrolyte degradation and SEI formation. In the case of the cells with LiPF\textsubscript{6} electrolyte, they all show a small peak at 1.5 V vs Li\textsuperscript{+}/Li on all the electrodes, attributed to the decomposition of FEC and VC.\textsuperscript{25} For all the cells, regardless of the electrode or electrolyte, other degradation reactions occur between 1 and 0.5 V vs Li\textsuperscript{+}/Li. For the Gr electrode, this is very subtle but it is more pronounced with the presence of silicon, especially for the SiGr electrodes with LiBOB electrolyte but for both electrolytes with Si electrode. The source of this degradation reaction could be ethylene carbonate (EC) which is reduced in that potential range and is common for both electrolyte formulations.\textsuperscript{26,27} This could indicate
that the silicon surface is not protected, therefore leading to the reduction of EC.

Figures 1d–If shows the specific capacity of the cells during cycling. Cells with graphite electrodes featured an initial lithiation capacity at C/20 of 360 mAh g$^{-1}$ for the LiPF$_6$ electrolyte and 525 mAh g$^{-1}$ for the LiBOB electrolyte, and a coulombic efficiency (C.E.) of 78% and 71%, respectively. When increasing the current density to C/5, the capacity dropped to 300 mAh g$^{-1}$ for the LiPF$_6$ electrolyte and to 180 mAh g$^{-1}$ for the LiBOB electrolyte. In the case of SiGr cells, the initial lithiation capacity and C.E. at C/20 was 1256 mAh g$^{-1}$ and 85% for the cells with LiPF$_6$ electrolyte, and 1238 mAh g$^{-1}$ and 79% for the cells with LiBOB electrolyte. The specific capacity dropped to 750 mAh g$^{-1}$ and 550 mAh g$^{-1}$ in the fifth cycle at C/5 for LiPF$_6$ and LiBOB electrolytes, respectively. Silicon cells with both electrolytes showed similar initial lithiation capacity of 4500 mAh g$^{-1}$ but different C.E.: 85% for LiPF$_6$-based cells and 79% for LiBOB-based cells. All the cells, especially those containing silicon, showed higher experimental lithiation capacity than the theoretical on the first cycle due to more side reactions taking place. The lower C.E. and capacities of the LiBOB-based cells compared to those of the LiPF$_6$-based cells, especially for higher current densities, suggest more side reactions and higher resistance in these cells. This difference is more pronounced for graphite electrodes despite the smaller degradation peak of the LiBOB electrolyte observed in the dQ/dV curve. It is worth mentioning that the composition and fabrication of the electrodes have not been optimized for the best electrochemical performance, as the aim of this project is to understand the contribution of each electrolyte to the SEI on different electrodes. Therefore, in order to understand the formation and composition of the SEI, the surfaces of the electrodes were analysed by means of SEM/EDX and XPS after the first lithiation (Hc) and after five cycles (5c) in the delithiated state.

Surface morphology and elemental distribution.—The morphology and elemental composition of the pristine and cycled electrodes with different electrolytes were investigated with SEM and EDX. After the first lithiation, the Gr electrode cycled in the LiPF$_6$ electrolyte presented a rough surface that is more noticeable after five cycles (left column of Fig. 2) with spherical nanoparticles typical of LiF, formed from the decomposition of LiPF$_6$ salt and FEC additive. These particles grow in number and size after five cycles, indicating there is more LiF formed also after the first cycle. In contrast, the Gr electrode cycled in the LiBOB electrolyte formed a smoother layer on graphite, most likely resulting from the reduction of VC additive and BOB anion. This layer seems to be covering the whole electrode after 5 cycles which could explain the lower performance observed for this electrolyte with the Gr electrode. Despite the electrodes being washed, crystals of LiBOB remained in the Gr electrode after 5 cycles.

The right column of Figs. 2 and S2 show the SEM images of the Si electrodes. In the case of the Si electrodes, the LiPF$_6$ electrolyte, the silicon particles remained spherical and distinguishable after half-cycle and 5 cycles, with a diameter of 180 nm. With the LiBOB electrolyte, the particles tend to adhere to each other, forming a smooth layer after half-cycle that disappears after 5 cycles in the delithiated state and spherical particles can be seen with diameter ranging from 200 to 300 nm, larger than with the LiPF$_6$ electrolyte.

Pristine SiGr electrodes presented a homogeneous distribution of both components with similar morphology as the electrodes with each of the active material (middle column of Fig. 2). It is important to note that the carbon black and silicon have similar particle sizes and therefore it is difficult to distinguish them. Cells cycled with the LiPF$_6$ electrolyte presented LiF nanospheres on top of graphite, typical of LiF, formed from the decomposition of LiPF$_6$ salt and FEC additive. These particles grow in number and size after five cycles, indicating there is more LiF formed also after the first cycle. In contrast, the SiGr electrode cycled in the LiBOB electrolyte formed a smoother layer on graphite, most likely resulting from the reduction of VC additive and BOB anion. This layer seems to be covering the whole electrode after 5 cycles which could explain the lower performance observed for this electrolyte with the Gr electrode. Despite the electrodes being washed, crystals of LiBOB remained in the Gr electrode after 5 cycles.
are present, which is more pronounced after 5 cycles. This could explain the poorer electrochemical performance of the graphite-based electrodes, especially when increasing the C-rate. In contrast, with Si electrodes, this continuous SEI layer disappears, suggesting a breathing mechanism of the SEI on Si electrodes cycled with LiBOB electrolyte.

The elemental mapping of the electrodes was performed with EDX, which gives information on where the decomposition products appear within the electrode’s surface, as shown in Fig. 3 for SiGr electrodes after 5 cycles and S3-5 for the rest. The intensity of each element is color coded from black/blue (low concentration) to pink/white (high concentration). The results from the SiGr electrodes (Figs. 3 and S5) are the most interesting and relevant as they show the preferences of the decomposition products that form on different active materials. For the pristine SiGr electrode, the oxygen signal, which distributes both on silicon and graphite particles, could be contributed by the binders, buffer solution, and natural SiO2 on Si particles. When the cells were cycled with the LiPF6 electrolyte, the decomposition products (O, F and P) after 5 cycles mainly appear where silicon is present and very little concentration is observed on top of graphite particles. This indicates the preferential decomposition of the fluorinated electrolyte on silicon particles compared to graphite. Cells cycled with the LiBOB electrolyte showed boron decomposition products mainly on graphite particles, suggesting a preferential decomposition of LiBOB on graphite particles when it is present in the electrode. As seen from the electrochemical data, LiBOB decomposes on the three different electrodes at the same onset potential. These side reactions are more pronounced with Si electrodes as seen from the larger LiBOB degradation peak in the dQ/dV curve. These different results indicate that the LiBOB

Figure 2. SEM images of the graphite, silicon-graphite composite, and silicon electrodes. Pristine electrodes are shown on the top row, followed by the first lithiation (Hc) and after 5 cycles (5c) with the LiPF6-based electrolyte, and the first lithiation (Hc) and after 5 cycles (5c) with the LiBOB-based electrolyte.
electrolyte forms more degradation products on Si electrodes, due to the higher surface area, but it is more prone to degrade on graphite particles when both active materials are present. This could also explain the lower capacity observed for the graphite-containing electrodes (Gr and SiGr) with LiBOB electrolyte compared to LiPF₆ electrolyte. In the case of oxygen species, they are more spread out, although slightly higher concentrations can be observed in the silicon areas. Oxygen decomposition products can come from LiBOB salt but also the solvents and additives.

Figure S3 shows the EDX mapping images for Gr electrodes. With the LiPF₆ electrolyte, the SEI degradation products (O, F and P) are mainly observed on the carbon additive rather than on the graphite particles, which agrees with the observations from the SiGr electrode, with less SEI degradation products formed on graphite particles than on silicon nanoparticles. This could be due to the higher surface area of the carbon black where more side reactions can occur or a higher preference compared to graphite. With the LiBOB electrolyte, a different behavior can be observed. Boron signals are mainly found in the regions with greater carbon signals. Given that the surface of the Gr electrode is covered with a continuous SEI layer, as shown in the SEM images (Figs. 2 and S3), it is hard to distinguish carbon black from the graphite particles in these regions. Therefore, the boron species from LiBOB salt decomposition could form on graphite and/or carbon black. Oxygen species appear everywhere with slightly higher concentration in-between graphite particles, which could correspond to decomposition products on the carbon additive or binder components. These oxygen species might come from electrolyte additives and solvents, as it is similar in behavior to the LiPF₆ electrolyte. Although oxalate from LiBOB could be another source of oxygen, those oxalates would be expected to be on the regions where boron is present.

In the case of Si electrodes (Fig. S4), the silicon has similar particle size as the carbon black and therefore differences in the elemental mapping are not obvious. In fact, all Si electrodes show a homogeneous distribution of the degradation products throughout the surface, accompanied by a decrease in silicon amount upon cycling. However, the concentration of carbon species increases, which is not assigned to the carbon black, as that would also be covered by the SEI layer. Instead, carbon species are assigned to the degradation of additives and solvents which could also explain the high concentration of oxygen species observed with both electrolytes. The breathing behavior observed in Si electrodes using LiBOB electrolyte with SEM is also detected with EDX, showing a slightly lower concentration of boron and higher concentration of silicon after 5 cycles compared to half-cycle.

Surface composition.—To obtain further information about the SEI composition, XPS was used as it is a more surface-sensitive technique and provides information on the chemical environment. The electrodes sampled for XPS analysis were consistently sourced from the same electrodes used in SEM/EDX examinations. All spectra were calibrated using the hydrocarbon peak at 285 eV and normalized to the peak area (sum of peak area = 1) for each core level.

C 1s.—Figure 4 shows the C 1s spectra for the pristine electrodes and the electrodes with both LiPF₆ and LiBOB electrolytes after the first lithiation (Hc) and after five cycles (5c) in the delithiated state. All pristine samples show the characteristic peaks of graphite (except for the silicon electrodes) and carbon black, as well as the binder (Na-CMC and SBR) and the buffer solution (citric acid and K₂CO₃ from KOH), see binding energy in spectra.³²,³³

In all pristine electrodes, a peak in the lower binding energy region (GrCB) is attributed to the sp² hybridized carbon in graphite and carbon black. This feature can also be observed particularly in the Gr and SiGr electrodes cycled with the LiPF₆ electrolyte. Note that in these cycled electrodes, this peak could also stem from lithiated graphite and carbon black located beneath the SEI layer. This “bulk” peak exhibits a relative binding energy shift, which can be attributed to the potential gradient existing between the bulk and surface layer in these cycled electrodes.³⁴ No traces of the GrCB peak are detected in the electrodes with LiBOB electrolyte or in the Si electrode with LiPF₆ electrolyte, suggesting a thicker SEI layer on these samples compared to the Gr and SiGr electrodes cycled with LiPF₆ electrolyte. The graphite and carbon black in these electrodes are buried deeper beneath the thick SEI layer, leaving them outside the analysis depth of the XPS measurements.

The ether (C-O), carbonyl (C=O), and ester (O-C=O) peaks, originating from the binders and citric acid in the buffer solution, can be observed in the C 1s spectra of the pristine electrodes. An additional peak with a higher binding energy assigned to carbonates (CO₃²⁻) appeared in all cycled electrodes. This peak originates from the solvents and additives decomposition products. For both electrodes that show GrCB signals, the relative intensity of the CO₃²⁻ peak compared to the GrCB peak is higher for the SiGr electrodes than for Gr electrodes, as shown in Table I. This may be due to a lower concentration of carbon active material in the SiGr electrode compared to the graphite electrode or a thicker SEI layer on the electrode with the presence of silicon (SiGr) as suggested previously. Considering the difference of atomic concentration...
between pure graphite and silicon-graphite composite, the lower concentration of graphite in the SiGr electrode is not expected to be the primary reason for the increased CO\(^{3-}/\text{GrCB}\) ratio (see detailed discussion in Supporting Information). These results imply a more prominent solvent and additive decomposition when having silicon in the electrode with LiPF\(_6\) electrolyte. The CO\(^{3-}/\text{GrCB}\) ratio also increases after 5 cycles in both electrodes, suggesting a continuous SEI formation upon cycling.

For the electrodes cycled with the LiPF\(_6\) electrolyte, the C–C/ C–H peak generally dominates in the spectra, whereas the ester peak at ~289.7 eV is more pronounced in the electrodes cycled with the LiBOB electrolyte. The solvent and additives in both electrolytes serve as the sources for the esters, while in the case of LiBOB electrolyte, the BOB anion provides an additional source for ester (oxalate) species. In the LiBOB electrolyte cases, the carbonates can only originate from the solvent decomposition, but the esters can originate from both solvent and LiBOB residue/decomposition products. By presuming a consistent ratio of solvent decomposition into esters and carbonates among three electrodes, the intensity ratio of ester peak to carbonate peak can be seen as an indicator for understanding how the salt residue/decomposition is varied with different electrode active materials. As shown in Table I, after 5 cycles, the O=C–O/CO\(^{3-}\) ratio is lower for the SiGr and Si electrode compared to the Gr electrode. Also, this ratio increases after 5 cycles for the Gr electrode. As some crystals are seen in the SEM figure of the Gr electrode with LiBOB electrolyte after 5 cycles (Fig. 2), it is important to determine if LiBOB residue is the main source for the ester content. The B 1s and O 1s spectra, shown in Fig. S6, are

| Table I. The intensity ratios of carbonate to GrCB peak (CO\(^{3-}/\text{GrCB}\)), ester to carbonate peak (O=C–O/CO\(^{3-}\)), and LiF to Li\(_x\)PF\(_y\)/Li\(_x\)PF\(_y\)O peak (LiF/(LPF, LPFO)). |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
|                                | CO\(^{3-}/\text{GrCB}\) | O=C–O/CO\(^{3-}\) | LiF/(LPF, LPFO) |
|                                | Gr   | SiGr | Si   | Gr   | SiGr | Si   | Gr   | SiGr | Si   |
| LiPF\(_6\) Hc                  | 1.46 | 2.32 | —    | 1.23 | 2.05 | 6.19 | 0.59 | 1.07 | 1.37 |
| LiPF\(_6\) 5c                  | 1.75 | 2.53 | —    | 1.12 | 1.07 | 0.71 | 1.94 | 1.22 | 2.40 |
| LiBOB Hc                       | —    | —    | —    | 19.77| 23.20| 11.14| —    | —    | —    |
| LiBOB 5c                       | —    | —    | —    | 28.74| 9.67 | 9.70 | —    | —    | —    |

Figure 4. The C 1s spectra of the graphite, silicon-graphite composite, and silicon electrodes with fluorinated electrolyte (LiPF\(_6\)) and non-fluorinated electrolyte (LiBOB) after the first lithiation (Hc) and after 5 cycles (5c) in the delithiation state. All spectra are calibrated by using the hydrocarbon peak (yellow) at 285 eV and normalized to the peak area (sum of peak area = 1).
normalized to the background. If LiBOB residue were the main factor for the increased $\text{O}=$C-O/CO$_3^{2-}$ ratio, a higher intensity ratio of B 1s to O 1s would be expected. However, in cases that exhibit higher $\text{O}=$C-O/CO$_3^{2-}$ ratio, such as the Gr electrode (5c) and the SiGr electrode (Hc), this cannot be observed. Thus, this rules out the possibility that LiBOB residue contributes to the increased $\text{O}=$C-O/CO$_3^{2-}$ ratio. These findings suggest that there are more LiBOB salt degradation products forming in the SEI layer on the Gr electrode; and that this is more pronounced after 5 cycles.

F 1s and P 2p.—Only the electrodes cycled with LiPF$_6$ electrolyte are discussed here due to the absence of F and P in the LiBOB electrolyte. In the F 1s spectra (Fig. 5a), one feature is the broad peak at 687–688 eV, representing multiple overlapping components from Li$_x$PF$_y$ and Li$_x$PF$_y$O$_z$. The peak at ~685.2 eV is assigned to LiF, a typical decomposition product of LiPF$_6$ salt and FEC additive. The LiF peak shows the highest intensity in the spectra for all samples, except for the Gr electrode after the first lithiation. This exception suggests that LiF is not the dominating F-based decomposition product in the SEI layer of the Gr electrode after the first half-cycle. This can be supported by less LiF particles observed in the SEM image (Fig. 2) for the Gr electrode after the first lithiation.

Table I also shows the intensity ratios of LiF peak to Li$_x$PF$_y$/Li$_x$PF$_y$O$_z$ peak. After 5 cycles, this ratio increases for all cases. Since the Li$_x$PF$_y$ and Li$_x$PF$_y$O$_z$ compounds can be only formed from LiPF$_6$ salt decomposition and LiF can be sourced from both FEC additive and LiPF$_6$ salt decomposition, the increased ratio after 5 cycles suggests more FEC additive decomposed during cycling than LiPF$_6$ salt, especially for the Gr electrode. The small C–F peak at ~688.9 eV in the spectra of the graphite electrode after 5 cycles and the silicon electrode after the first lithiation can be attributed to the decomposition of FEC maintaining the C–F bond.

In the P 2p spectra (Fig. 5b), the green and blue peaks correspond to the Li$_x$PF$_y$ and Li$_x$PF$_y$O$_z$ peaks originating from the decomposition of LiPF$_6$. Compared to the other electrodes, the Si electrodes show a higher relative amount of Li$_x$PF$_y$O$_z$ in the spectra. Additionally, for the Si electrode, the intensity ratio of Li$_x$PF$_y$ peak to Li$_x$PF$_y$O$_z$ peak decreases after 5 cycles, suggesting that the O-rich degradation products from the LiPF$_6$ tend to form after the first lithiation. The Li$_x$PF$_y$O$_z$ observed here also contributes to the O-species that are detected in the EDX mappings.

The O 1s and B 1s spectra were measured (Figs. S6 and S7), and various O-species and B-species with small differences in binding energy contribute to a single broad spectral feature in these spectra, making it impossible to conclusively differentiate the contributions.

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Figure 5. The (a) F 1s and (b) P 2p spectra of the graphite, silicon-graphite composite, and silicon electrodes with LiPF$_6$-based electrolyte after the first lithiation (Hc) and after 5 cycles (5c) in the delithiation state. Note that the lower signal-to-noise ratio in the P 2p spectra of the silicon electrode is due to fewer scanning iterations.
from individual species. However, in Fig. S6(a), a minor lithium oxide (Li$_2$O) feature next to the broad spectral feature can be observed in the O 1s spectra of Gr and SiGr electrodes cycled with LiPF$_6$ electrolyte after the first lithiation. It was reported that Li$_2$O generally forms in the inner part of the SEI layer on graphite electrode and is a common product from EC reduction. However, it has also been reported for EC-free LiBOB-based electrolytes. It is also one of the SEI components embedded within other organic species for silicon electrode, yet its concentration decreases upon delithiation due to the electrochemical reaction between it and silicon. This indicates that a thicker outer SEI layer is covering the inner SEI layer for the Si electrodes cycled with LiPF$_6$ electrolyte, which correlates with the absence of GrCB signal in the C 1s spectra for these electrodes. The Li$_2$O signal is, however, not found in the Gr and SiGr electrodes with LiPF$_6$ electrolyte after 5 cycles, in which the GrCB signals are still observable. There may be other side reactions that consume Li$_2$O during cycling or the GrCB cycles, in which the GrCB signals are still observable. The Li$_2$O signal is, however, not detected in the electrodes cycled with LiPF$_6$ electrolyte. Together these samples could be isolated carbon active materials in or on the SEI layer that have been exfoliated from the electrode. These speculations require more studies on the electrode and SEI during cycling to understand the electrodes surface together with the inner part of SEI layer.

The effect of LiPF$_6$ and LiBOB electrolytes on Gr, Si, and SiGr electrodes has been investigated with regard to the electrochemical properties, surface morphology and composition. In general, both electrolytes show more decomposition into ester, carbonate, and carbonyl species with the presence of silicon in the electrode, which is likely due to the higher surface area of silicon nanoparticles compared to the larger graphite flakes. For the LiPF$_6$ electrolyte, LiF, stemming from the LiPF$_6$ salt and FEC additive decomposition, forms earlier in the cycling process with Si compared to the Gr electrode, which explains why FEC is a good additive for silicon-based electrodes. On the graphite surface, LiF nanoparticles are clearly seen while they are indistinguishable on the silicon nanoparticles. In the case of the SiGr electrode, the degradation of LiBOB and LiF electrolytes shows different patterns: the fluorinated and phosphorus species from LiF are more concentrated on silicon, whereas the boron species from LiBOB preferentially form on carbon species. Traces of bulk electrode materials (graphite and carbon black) can be observed in the Gr and SiGr electrodes cycled with LiPF$_6$ electrolyte. Also, Li$_2$O, which tends to form closer to the electrode surface, is only seen in Gr and SiGr electrodes with LiPF$_6$ electrolyte after the first half-cycle. The above findings are not detected in the electrodes cycled with LiBOB electrolyte. Together this indicates that the LiBOB electrolyte tends to form a thicker SEI layer. In addition, by comparing the intensity ratio of ester to carbonate peak in the C 1s spectra, it is noticed that there are more LiBOB salt degradation products forming on the Gr electrode, which leads to larger resistance and lower coulombic efficiency and capacity of graphite-containing electrodes during cycling. The results from this project show that the behavior of LiBOB-based electrolyte is different when silicon and graphite are combined, with a preferential salt decomposition observed over graphite particles compared to silicon. This suggests that the LiBOB-based electrolyte forms a less effective SEI on silicon particles when graphite is also present in the electrode.

Conclusions

Fluorine-free electrolytes are considered a safer and more environmentally friendly alternative to the conventional LiPF$_6$-based electrolytes used in lithium-ion batteries. In order to realize this transition, further insights into the compatibility with the active material and the interphase formation processes are crucial. Herein, the degradation of electrolyte components and their effects on graphite and silicon-based electrodes have been explored during the initial half-cycle and subsequent cycling. The main conclusion from this study is the preferential degradation of LiBOB on graphite particles compared to silicon. Lower electrochemical performance of the LiBOB electrolyte compared to the LiPF$_6$ electrolyte was observed, particularly in graphite-containing electrodes compared to electrodes with only silicon as active material for the LiBOB-based cells. From EDX mapping, a higher concentration of boron species was found on graphite and not as much on silicon areas. This preferential degradation is confirmed by the C 1s spectra that show a higher intensity ratio of ester species (mainly coming from LiBOB) to carbonates (from solvents and additive) in the graphite electrode compared to the silicon electrode.

The lesson learned with the LiBOB electrolyte is that when designing new electrolyte formulations, it is important to consider at the same time the electrode formulation, particularly when active materials with varying sizes and surface chemistry are mixed in a composite electrode, to achieve improved SEI layers and cycling performance.

Supplemental Material

Further voltage profiles, SEM images, EDX mappings, and XPS spectra.

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