Elimination of Fluorination: The Influence of Fluorine-Free Electrolytes on the Performance of $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ /Silicon–Graphite Li-Ion Battery Cells

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ABSTRACT: In the quest for environmentally friendly and safe batteries, moving from fluorinated electrolytes that are toxic and release corrosive compounds, such as HF, is a necessary step. Here, the effects of electrolyte fluorination are investigated for full cells combining silicon–graphite composite electrodes with $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC111) cathodes, a viable cell chemistry for a range of potential battery applications, by means of electrochemical testing and postmortem surface analysis. A fluorine-free electrolyte based on lithium bis(oxalato)borate (LiBOB) and vinylene carbonate (VC) is able to provide higher discharge capacity ($147 \text{ mAh g}_{\text{NMC}}^{-1}$) and longer cycle life at C/10 (84.4% capacity retention after 200 cycles) than a cell with a highly fluorinated electrolyte containing LiPF_6 , fluoroethylene carbonate (FEC) and VC. The cell with the fluorine-free electrolyte is able to form a stable solid electrolyte interphase (SEI) layer, has low overpotential, and shows a slow increase in cell resistance that leads to improved electrochemical performance. Although the power capability is limiting the performance of the fluorine-free electrolyte due to higher interfacial resistance, it is still able to provide long cycle life at C/2 and outperforms the highly fluorinated electrolyte at 40°C . X-ray photoelectron spectroscopy (XPS) results showed a F-rich SEI with the highly fluorinated electrolyte, while the fluorine-free electrolyte formed an O-rich SEI. Although their composition is different, the electrochemical results show that both the highly fluorinated and fluorine-free electrolytes are able to stabilize the silicon-based anode and support stable cycling in full cells. While these results demonstrate the possibility to use a nonfluorinated electrolyte in high-energy-density full cells, they also address new challenges toward environmentally friendly and nontoxic electrolytes.

KEYWORDS: fluorine free, lithium-ion batteries full cell, silicon–graphite, solid electrolyte interphase, lithium bis(oxalato)borate

INTRODUCTION

Despite the tremendous increase in battery production due to the electrification of transportation as well as demands from grid storage, making batteries safer, sustainable, and easy to recycle still presents some challenges and concerns that need to be considered.^{1,2} While electrode materials that partially fulfill these requirements have been successfully established,^{3,4} it is generally not the case for the electrolyte, which typically remains highly toxic, introducing complications to battery recycling.^{5,6} State-of-the-art electrolytes contain the fluorinated electrolyte salt LiPF_6 , susceptible to undergo defluorination reactions forming toxic and corrosive compounds, such as HF and PF_5 , a process that is accelerated at higher temperatures.^{7–9} Furthermore, these degradation reactions are known to be detrimental for battery performance.^{10,11} Yet, fluorine-containing electrolytes are often considered necessary for optimal battery performance.¹²

Alternative fluorine-free salts, have been studied in recent decades to replace LiPF_6 . One of the most promising

candidates for lithium-ion batteries is lithium bis(oxalato)borate (LiBOB).^{13–15} Although its solubility and conductivity in carbonate-based solvents are lower (0.8 M and $8\text{--}9 \text{ mS cm}^{-1}$, respectively) than the counterpart LiPF_6 ($>1 \text{ M}$ and $>10 \text{ mS cm}^{-1}$), its higher thermal stability (stable up to 302°C) and low chemical activity and toxicity of its decomposition products (B_2O_3 and CO_2) help surpass these shortcomings.^{16,17} In addition, LiBOB has been classified as readily biodegradable by the European Chemicals Agency,¹⁸ meaning it will rapidly and completely biodegrade in aquatic environments under aerobic conditions according to the Organisation for Economic Cooperation and Development (OECD)

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Guidelines.¹⁹ Regarding battery safety, Jiang and Dahn have shown that the reactivity of the LiBOB electrolyte in lithiated graphite is lower than that of LiPF₆.²⁰ In contrast, the opposite behavior was observed for charged high-voltage cathodes, such as LiCoO₂.²¹ As the clear advantage of this fluorine-free salt is seen on the anode side, its electrochemical performance has mostly been investigated in cells containing graphite.^{14,16,20,22,23} These results showed that LiBOB is able to form a stable solid electrolyte interphase (SEI) on the graphite negative electrode, composed mostly of oxalates, semicarbonates (ROCO₂Li), and polyether-like species.^{24–28} Furthermore, Täubert et al. have compared the behavior of LiBOB, LiPF₆, and a mixture of both in graphite half-cells and full cells with LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA), concluding that all of the cells behaved similarly with good reversible capacity and stability.²⁹ Still, conventional batteries rely heavily on a fluorinated LiPF₆ electrolyte, although several authors have reported the use of LiBOB as an electrolyte additive, to take advantage of characteristics from both salts.^{11,21,29–31}

As energy density requirements for batteries continue to increase, graphite (with a rather limited practical capacity of 360 mAh g⁻¹) falls short. Therefore, research has been focused on developing other anode materials with higher energy density, such as lithium metal (3860 mAh g⁻¹) or silicon (3579 mAh g⁻¹). The latter is the perhaps the most promising material as it can be readily incorporated in a graphite matrix in different ratios, avoiding changing the battery manufacturing process. However, silicon electrodes suffer severe volume changes, resulting in low cycling stability.^{32,33} This drawback can be mitigated by incorporating additives that are able to form a robust SEI layer, such as fluoroethylene carbonate (FEC) and vinylene carbonate (VC).^{34–38} Of course, the use of FEC introduces yet another fluorinated compound, which additionally acts as a source of HF and has been reported to accelerate the degradation of LiPF₆-based electrolytes.^{39,40}

Identifying a fluorine-free electrolyte with acceptable performance is of great interest for the environmental and sustainability reasons already mentioned, but only very few studies have addressed this challenge for silicon-based anodes.^{24,41} Herein, we demonstrate the effect of reducing fluorination in LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC111)/silicon-graphite full cells by comparing LiBOB- and LiPF₆-based electrolytes. We present a thorough investigation encompassing cycling stability, resistance measurements, morphology analysis, and surface chemical composition and demonstrate the feasibility of using fluorine-free electrolyte alternatives for high-energy-density cells. These results are encouraging to continue the research toward safer and more environmentally friendly electrolytes for lithium-ion batteries.

MATERIALS AND METHODS

Materials. LP57 electrolyte (SelectiLyte BASF, 1 M LiPF₆, ethylene carbonate (EC)/ethyl methyl carbonate (EMC) 3:7 vol %), EC (SelectiLyte BASF), EMC (SelectiLyte BASF), vinylene carbonate (VC, SelectiLyte BASF), and fluoroethylene carbonate (FEC, Gotion) were battery-grade and used as received. LiPF₆ (Ferro Corp.) and lithium bis(oxalato)borate (LiBOB, Chemetall) were dried at 120 °C for 12 h under vacuum prior to electrolyte preparation.

Electrode Preparation and Battery Assembly. Silicon-graphite and NMC111 electrodes were kindly provided by VARTA Micro Innovation GmbH. The anode was composed of silicon alloy (L-20772, provided by 3 M), graphite (BTR 918), super-P carbon black, and lithium polyacrylate (LiPAA, 450 K) binder in a mass ratio

of 25:66:2:7 and had an areal capacity of 2.4 mAh cm⁻². The composition and morphology of the silicon alloy have been recently published by Berhaut et al.⁴² The cathode consisted of LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂ (NMC111), super-P carbon black, and poly(vinylidene difluoride) binder in a mass ratio of 94:3:3 and had an active mass loading of 13.7 mg cm⁻², equivalent to an areal capacity of 2.0 mAh cm⁻² (corresponding to a nominal capacity of 146 mAh g⁻¹). The Ø13 mm electrodes were punched out and dried at 120 °C under vacuum for 12 h prior to battery assembly. Coin cells were assembled in an argon glovebox adding 50 µL of electrolyte and using Celgard 2325 as the separator. The cells rested for 6 h before cycling was initiated. Apart from the conventional LP57 electrolyte from BASF, the other electrolytes were prepared in-house using the solvent mixture EC/EMC 3:7 v/v and incorporating different salts and additives (see Table 1).

Table 1. Electrolyte Composition and Nomenclature Used in This Work Using the EC/EMC 3:7 v/v Mixture as the Solvent

electrolyte	nomenclature
1 M LiPF ₆	LP57
0.7 M LiBOB	LiBOB
1 M LiPF ₆ + FEC 10 vol % + VC 2 vol %	LP57 + FEC + VC
0.38 M LiPF ₆ + 0.5 M LiBOB + FEC 10 vol % + VC 2 vol %	LiPF ₆ + LiBOB + FEC + VC
0.7 M LiBOB + VC 2 vol %	LiBOB + VC

Battery Testing. Galvanostatic cycling of NMC/Si-graphite full cells was performed using an Arbin BT-2043 battery testing system at room temperature. The cells were precycled twice at a constant current of C/20 between 3.0 and 4.2 V with a constant voltage step applied at the end of the charge until the current was below C/50. Thereafter, the cells were cycled at C/2 and a constant voltage step was applied after charge until the current dropped to C/20. The C-rate was based on the cathode's reversible capacity of 2.0 mAh cm⁻² (146 mAh g_{NMC}⁻¹). The Coulombic efficiency of full cells was calculated from the discharge capacity divided by the charge capacity in each cycle. The internal resistance was measured using the intermittent current interruption (ICI) method consisting of 1 s rest at 2 min intervals and following the analysis procedure reported by Lacey.⁴³ Electrochemical impedance spectroscopy (EIS) measurements were performed on the full cells using a Bio-Logic MPG2 potentiostat with a 10 mV amplitude and a frequency range of 20 kHz to 10 mHz. The cells for X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) analyses were cycled following the previous constant current–constant voltage conditions: two precycles at C/20 followed by three cycles at C/2, ending with the silicon-graphite anode in the delithiated state.

X-ray Photoelectron Spectroscopy (XPS). Prior to analysis, cells were disassembled in an argon glovebox at the home laboratory, and the electrodes were removed and washed by slowly dripping 2 mL of dimethyl carbonate (DMC) over them to remove excess liquid electrolyte. The samples were transported to the synchrotron facility in vacuum-sealed packages. The samples were transferred to the beamline end-station via an argon glovebox using an especially designed transfer vessel to avoid exposing the samples to air. X-ray photoelectron spectroscopy (XPS) experiments were performed using the HIKE instrument (KMC-1 beamline)⁴⁴ at the BESSY II synchrotron at Helmholtz-Zentrum Berlin (HZB). Photons were monochromatized by a Si(111) double-crystal monochromator. Excitation energies of 2005 eV and the third-order light of 6015 eV were used for all samples. No charge neutralizer was used during the measurements. The area of analysis is estimated to correspond to approximately 50 µm × 100 µm. The spectra were recorded using a hemispherical VG Scienta R4000 analyzer set to a pass energy of 500 eV. Approximate probing depths of 17 and 43 nm were estimated for the energies of 2005 and 6015 eV, respectively, according to three times the inelastic mean free path (IMFP) of electrons. IMFP values

were derived for polyethylene,⁴⁵ as a representative material of the SEI formed on the anode electrode, from the NIST database.⁴⁶ While the estimated probing depths are a representative of the low-density surface layer, smaller probing depths would be expected for the denser inorganic material forming the bulk of the electrode.⁴⁷ The software package CasaXPS was used for the analysis of photoelectron spectroscopy data, and the Gaussian/Lorentzian peak shape GL(30) was used throughout the fitting. The spectra presented in this work were all energy-calibrated against the hydrocarbon C–C peak (284.8 eV) in the C 1s spectra.

Scanning Electron Microscopy (SEM). Prior to analysis, cells were disassembled in an argon glovebox, and the electrodes were removed and washed by slowly dripping 2 mL of dimethyl carbonate (DMC) over them to remove excess liquid electrolyte prior to analysis. The samples were transported to the SEM in a vacuum-sealed transfer chamber to avoid exposing the samples to air. The morphology of the electrodes was studied 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 energy-dispersive X-ray spectroscopy (EDS).

RESULTS AND DISCUSSION

Electrochemical Performance of NMC111/Si–Graphite Full Cells. The influence of electrolyte fluorination on silicon–graphite composite anodes and the potential use of fluorine-free electrolytes in commercial batteries, particularly full cells containing NMC111 as the cathode, were investigated using different electrolyte formulations (Table 1). Galvanostatic charge–discharge cycling combined with intermittent current interruption (ICI) experiments were carried out to determine the electrochemical performance as well as the internal resistance (approximately the sum of Ohmic electronic and ionic resistances in the electrodes and electrolytes and charge-transfer (kinetic) resistances).⁴³ Upon the first charge at C/20, the differential capacity (dQ/dV) profiles, which provide information about irreversible electrolyte reduction processes, are very different among the electrolytes (Figure S1). Electrolytes containing the LiBOB salt present a substantial peak at 1.8 V (for the full cell) corresponding to the reduction of the BOB anion forming an SEI layer on the anode's surface.^{11,23} The presence of this layer prevents the reduction of EC, which occurs afterward at higher voltages; 3.1 V for the full cell containing the LP57 electrolyte.³⁹ However, when incorporating FEC and VC additives in the LP57 electrolyte, a small peak appears at 2.5 V corresponding to the reduction of these additives and the peak from EC reduction also disappears.³⁹

Despite the presence of EC in all electrolytes, its reduction is prevented in the cells containing LiBOB, FEC, and/or VC due to their ability to form an SEI layer prior to the reduction of EC. These reactions occurring in the first charge determine the difference in the initial Coulombic efficiency (and in the initial irreversible capacity) of the full cells. The Coulombic efficiency of the first cycle for the cells containing LP57 and LP57 + FEC + VC was 81.6 and 81.4%, respectively. The cells containing the LiBOB salt showed slightly lower Coulombic efficiencies, being 80.4% for $\text{LiPF}_6 + \text{LiBOB} + \text{FEC} + \text{VC}$ and 80.2% for $\text{LiBOB} + \text{VC}$, due to the irreversible reduction of LiBOB salt on the anode. Despite the small changes in the irreversible capacity values, the voltage profiles of the four cells are similar without significant variations in polarization (Figure 1). However, differences can be seen in the internal resistance at the beginning of the first charge (Figure 1a). Cells containing the LiBOB salt show an initial sharp peak in resistance

Figure 1. Voltage and resistance profiles of NMC111/Si-graphite cells at C/20 for (a) first and (b) second cycles with different electrolytes: LP57 (black), LP57 + FEC + VC (red), $\text{LiPF}_6 + \text{LiBOB} + \text{FEC} + \text{VC}$ (yellow), and $\text{LiBOB} + \text{VC}$ (blue). The capacity of the different cells has been normalized for easier comparison, and the resistance has been calculated with the ICI method. Note that the scales of both axes are different in (a) and (b).

generated by the reduction of the BOB anion, which is also in agreement with the peak observed in the dQ/dV profiles (Figure S1). Nevertheless, the peak disappears in the second cycle (Figure 1b). Besides this initial peak in resistance with LiBOB, all cells followed a similar trend in resistance. At the beginning of charging, when NMC is fully lithiated (discharged) and Si-graphite delithiated, the cell resistance is high and decreases upon charging. As the NMC does not reach a fully charged (delithiated) state, not all of the lithium ions are extracted from the cathode and the resistance remains low.⁴⁸ The opposite behavior is observed during the discharge of the cell; the resistance is low at the beginning but increases toward the end when fully lithiated NMC is obtained (Figure 1). These results indicate that the highest resistance is observed when the cell is fully discharged, while the lowest is achieved at the fully charged state. Despite the similar trend among the

cells with different electrolytes, the resistance of the cells containing LiBOB is slightly higher in the initial cycles compared to the cells containing LiPF₆. Although the conductivity of the LiBOB + VC electrolyte is lower and, thus, its resistance is higher than LP57 + FEC + VC (Table S1), the value is insignificant compared to the bulk cell resistance measured with the ICI method. This means that the higher resistance of the cells containing LiBOB in the electrolyte is not due to its lower conductivity.

Electrochemical impedance spectroscopy (EIS) was carried out to determine the origin of these differences in resistance. The Nyquist plot of the impedance at the end of the first charge (delithiation of NMC) and its equivalent circuit model are shown in Figure S2. The fitting of the Nyquist plots shows that the depressed semicircle observed in Figure S2 is the combination of two semicircles at low and mid frequencies and is assigned to the interfacial resistance in the cell. The intersection of the semicircle at low frequencies corresponds to the solution resistance and the Warburg straight line to the solid-state Li⁺ diffusion in the anode. The main difference among the electrolytes is the interfacial resistance, the lowest value given by the cell with LP57 (17.7 Ω), followed by LP57 + FEC + VC (21.1 Ω), LiPF₆ + LiBOB + FEC + VC (38.5 Ω) and, finally, LiBOB + VC (35.8 Ω). The resistance values obtained with EIS are in agreement with those from ICI (Table S1), confirming the reliability of the latter technique. Incorporation of FEC and VC to the electrolytes led to a higher interfacial resistance due to the formation of an SEI layer already in the first charge. The fact that the LiBOB-containing electrolytes featured a slightly larger semicircle indicates that, besides the additive, this salt also forms an SEI on the anode that contributes to the slightly higher resistance after the first charge.

To compare the changes in cell resistance and the electrochemical stability upon cycling of the different electrolytes, the cycles following after precycling were performed at C/10 using the ICI method (Figure 2). A low current density is preferable in these experiments to be able to assume that the charge-transfer resistance is Ohmic.⁴⁹ The cell containing the conventional fluorinated LP57 electrolyte delivered high discharge capacity and high Coulombic efficiency for the first 50 cycles, while the cell resistance was low. However, this electrolyte is not able to form a stable SEI layer, which results in a continuous degradation of the electrolyte.^{50,51} Therefore, after 50 cycles, the cell resistance grows rapidly, worsening the electrochemical performance.

It is understood that improved cycling stability can be achieved by incorporating SEI-forming additives, such as FEC and VC, in the electrolyte formulation. While FEC forms mainly a fluorinated and inorganic SEI, VC forms an organic SEI, but both are beneficial for silicon-based anodes.^{8,37,38,52–56} As can be seen in Figure 2a,b, all cells containing additives in their electrolyte formulation featured longer cycle life and higher Coulombic efficiency compared to the reference LP57 electrolyte. Particularly, the cell with the fluorine-free electrolyte (LiBOB + VC) delivered the highest discharge capacity (147 mAh g_{NMC}⁻¹), capacity retention (84.4% after 200 cycles), and Coulombic efficiency (99.51% after 200 cycles), compared to the fluorinated electrolytes. The lower capacity retention of the cells with fluorinated electrolytes, 78.46% for LiPF₆ + LiBOB + FEC + VC and 76.5% for LP57 + FEC + VC after 200 cycles, is accompanied with an increase in overpotential (Figure S3), as the cutoff voltage is

Figure 2. Electrochemical performance of NMC111/Si-graphite cells cycled with the intermittent current interruption technique at C/10 between 3.0 and 4.2 V with electrolytes LP57 (black), LP57 + FEC + VC (red), LiPF₆ + LiBOB + FEC + VC (yellow), and LiBOB + VC (blue). (a) Discharge capacity, (b) Coulombic efficiency, and (c) median resistance during discharge.

reached before all Li⁺ ions are intercalated/deintercalated in NMC.⁵⁷ It can be observed in Figure 2 that there is no direct correlation between Coulombic efficiency and capacity fade for any of the cells regardless of the salt or additive used. This lack of correlation may indicate that the electrolyte oxidation in these cells has a greater impact on the capacity counting than other side reactions, e.g., SEI formation and degradation of the positive electrode.^{58–60}

The median of cell resistance of the cells in each cycle follows the same trend (Figure 2c). High resistances are observed in the first cycle due to the initial formation of the SEI and the degradation products of the electrolyte, which

Figure 3. Electrochemical performance of NMC111/Si-graphite full cells cycled at C/2 between 3.0 and 4.2 V with different electrolytes. (a) Discharge capacity and (b) Coulombic efficiency of LP57 (black diamonds) and 0.7 M LiBOB (green inverse triangles). (c) Discharge capacity and (d) Coulombic efficiency of LP57 + FEC + VC (red squares), LiPF₆ + LiBOB + FEC + VC (yellow circles), and LiBOB + VC (blue triangles).

contribute to an increase in the viscosity of the electrolyte.^{61,62} In the first 30 cycles, however, there is a decrease in resistance. This could be due to a decrease in the viscosity of the electrolyte because there is less dissolution of the SEI components that are precipitating on the electrode's surface. As suggested by Kitz et al., it is also possible that in the first cycles the low SEI thickness could facilitate the charge transfer, for example, lowering the energy required for stripping the solvation shell off the Li ions.⁶² Cells containing LiBOB (LiBOB + VC and LiPF₆ + LiBOB + FEC + VC) show slightly higher resistance at the beginning (~40 Ω), compared to the highly fluorinated electrolyte (25 Ω), but it levels off in the following cycles to become comparable to the highly fluorinated electrolyte (~20 Ω for all cells containing additives in the electrolyte) (Figure 2c). After 50 cycles, the internal resistance of the cells increases slightly, probably due to the SEI built upon the anode and the decrease of the electrochemically active mass.⁵¹ The cell resistance increases slower with the fluorine-free electrolyte, resulting in better capacity retention. This behavior can also be seen in the resistance profiles in Figure S3. Therefore, even if the resistance is higher at the beginning, especially for the cell containing LiBOB +

VC, the resistance levels out at a lower value. This indicates that the anode is stabilized and the cycle life is prolonged. Overall, these results suggest the benefit of using fluorine-free alternatives with the additional advantages of being more environmentally friendly and less toxic.

The effect of fluorination has also been investigated at higher currents, as illustrated in Figure 3 for C/2. The cell with the conventional LP57 was compared with a fluorine-free LiBOB-based electrolyte, both without additives (Figure 3a,b). In both cases, there is a slight drop in the discharge capacity followed by an increase in the capacity over the first ~25 cycles. This feature was minor or even not observed at lower currents and is therefore assigned to slow stabilization of the cell when changing from a low C-rate during precycling (C/20) to a higher one (C/2) in the following cycles. The cell containing the conventional fluorinated LP57 electrolyte delivered higher discharge capacity than the fluorine-free electrolyte. However, the latter featured better cycling stability and Coulombic efficiency, which we attribute to a more stable SEI layer. Despite these differences, both electrolytes showed a continuous and rapid capacity fade. The same behavior has also been reported for silicon-based electrodes in half-cells,⁴¹

(a) Pristine

(b) LP57+FEC+VC

(c) LiBOB+VC

Figure 4. SEM images (first column) and elemental mapping images for Si alloy–graphite composite: (a) pristine, (b) delithiated state after five cycles in fluorinated LP57 + FEC + VC electrolyte, and (c) delithiated state after five cycles in the fluorine-free LiBOB + VC electrolyte.

suggesting the silicon–graphite anode as the source of this capacity fade.

As seen in the previous results, incorporating the SEI-forming additives in the electrolyte improves cycling stability. However, at higher currents, the highly fluorinated electrolyte (LP57 + FEC + VC) is the best-performing one, delivering up to 144 mAh g^{−1} initial discharge capacity, 78.5% capacity retention, and 99.76% Coulombic efficiency after 300 cycles. As the choice of additives is crucial for the cycling stability of silicon-based cells, many authors have developed new additives or thoroughly investigated the effect of FEC and VC separately. Combining both additives results in much higher capacity retention compared to other reported full cells containing silicon that feature between 60 and 70% capacity retention after 100 or 200 cycles.^{52,63–66} Thus, these results show that the combination of two well-known additives to the conventional LP57 electrolyte leads to an improved cycle life for high-energy full cells. Nevertheless, toward the challenge of developing fluorine-free electrolytes, a partly fluorinated electrolyte (LiPF₆ + LiBOB + FEC + VC) delivered slightly lower discharge capacity (125 mAh g^{−1}) but similar cycling stability, with 76.9% capacity retention after 300 cycles, compared to the highly fluorinated electrolyte. These comparable results suggest that moving toward low fluorine content in the electrolyte is still a viable option to consider. In the case of the cell with the fluorine-free electrolyte (LiBOB + VC), it delivers high initial discharge capacity (132 mAh g^{−1}) but lower cycling stability than the cells with fluorinated electrolytes (the capacity retention was 59.4% after 300 cycles). This behavior can be explained by an increase in overpotential upon cycling observed for the cell with the

fluorine-free electrolyte, as seen in the voltage profiles in Figure S4. Furthermore, ICI combined with impedance spectroscopy was used to monitor the resistance changes upon cycling at C/2. Figure S5 shows the cell resistance measured with ICI compared to the resistance obtained from EIS measured every 10 cycles. We note that both techniques give the same resistance values, and both experiments show that the cell resistance decreases during the first cycles and then stabilizes for all of the electrolytes, as seen also at lower currents with the ICI method. However, after long-term cycling at C/2, the resistance increases and the differences between the different electrolytes can be seen in EIS experiments (Figure S6). In the case of the conventional electrolyte (LP57), the semicircle and Warburg impedance increased rapidly, indicating a high charge-transfer resistance and diffusion resistance with this electrolyte. These results suggest the formation of a thicker SEI layer and explain the rapid capacity fade observed for the cell with the LP57 electrolyte. The cell with a highly fluorinated electrolyte (LP57 + FEC + VC) showed a slow increase in interfacial resistance upon cycling, in agreement with the slow decrease in discharge observed for this cell. The partly fluorinated electrolyte (LiPF₆ + LiBOB + FEC + VC) featured slightly higher resistance, due to the presence of LiBOB. In the case of the cell with a fluorine-free electrolyte (LiBOB + VC), the interfacial resistance increased more rapidly after 125 cycles, which is in agreement with the faster capacity decay observed for this cell. These results obtained at C/2 are contrary to the observations at low currents. As seen from the ICI experiments at C/10, the cell with the fluorine-free electrolyte featured lower cell resistance upon cycling, suggesting that the SEI buildup happens at a slower rate

CB=Carbon Black; Gr= Graphite; PAA=Polyacrylic acid; SEI= Solid Electrolyte Interphase

Figure 5. X-ray photoelectron spectra (F 1s, O 1s, C 1s), measured at excitation energies of 2005 and 6015 eV in each case, for silicon-graphite composite electrodes after five cycles with different electrolyte formulations. (a) Pristine electrode, (b) LP57 + FEC + VC, (c) LiPF_6 + LiBOB + FEC + VC, and (d) LiBOB + VC.

compared to the fluorinated electrolytes and it is not limiting the electrochemical reaction. However, at C/2, the interfacial resistance for the fluorine-free electrolyte increases rapidly upon cycling (as seen in Figure S6), suggesting a faster SEI buildup. These results indicate that the SEI formed with this electrolyte is less ion-conducting and slows down the kinetics of the reaction, resulting in lower electrochemical performance. This also explains why this is only observed at higher currents because at relatively low currents the resistance of the SEI does not limit the electrochemical performance of the cell. To further confirm this, rate capability studies were performed for the highly fluorinated and fluorine-free electrolytes (Figure S7). Indeed, increasing the current was accompanied by a notable increase in overpotential for the cell with the fluorine-free electrolyte.

However, apart from the sustainability aspects, there is another important drawback in the use of highly fluorinated electrolytes, which is their limited thermal stability. It has been reported previously that the combination of LiPF_6 and FEC in the electrolyte leads to severe degradation both chemically and electrochemically at elevated temperatures.⁴⁰ Therefore, the

electrochemical performance of these electrolytes was investigated at the moderately elevated temperature of 40 °C. The NMC111/Si-graphite full cell with the LP57 + FEC + VC electrolyte exhibited a steady decrease in capacity during cycling with 49% capacity retention after 300 cycles. However, with the fluorine-free electrolyte, the capacity retention was improved up to 77% after 300 cycles (Figure S8). These results show another beneficial property of this fluorine-free electrolyte, i.e., the prolonged cycle life at 40 °C, which is not an unreasonable internal temperature for a battery pack during operation, especially during extreme fast charging.⁶⁷

To further understand the origin of the difference in electrochemical performance of the different electrolytes, surface analysis of the silicon-graphite anodes was performed to determine the chemical compositions and properties of the formed SEI layers.

Surface Analysis of Silicon-Graphite Anodes. The morphology of the anode's surface upon cycling is dependent on the electrolyte used and influences the electrochemical performance of the cells. Therefore, the morphology of the pristine anode after five cycles at C/2 of the highly fluorinated

and the fluorine-free electrolyte was studied by SEM and EDS. The electrodes are comprised of large graphite particles and smaller particles of the silicon alloy, identified through elemental mapping (Figure 4). This is also confirmed in the SEM images in Figure S9, where the dark and large particles correspond to graphite, while the bright and small particles correspond to the silicon alloy material. The silicon alloy particles are rather homogeneously distributed over the electrode; however, the particle size distribution is broad, ranging from 0.4 to 5.6 μm .

Compared to the pristine anode (Figure S9a–c), the surface morphology after five cycles differs significantly in the fluorinated (LP57 + FEC + VC) (Figure S9d–f) and fluorine-free (LiBOB + VC) electrolytes (Figure S9g–i). The electrode cycled with the fluorinated electrolyte was characterized by a bumpy surface on the graphite (Figure S9e), which is attributed mainly to LiF.⁶⁸ This is further confirmed with the elemental mapping of fluorine (Figure 4), covering the surface of the anode. Additionally, we observe a high correlation between F and Si, indicating that degradation reactions to form a fluorine-containing SEI mainly take place on the surface of silicon. However, there is not a clear change in the morphology from the SEM images (Figure S9f,i). In contrast, the fluorine-free electrolyte formed a smoother SEI, mostly covering the graphite flakes (Figure S9h). This SEI can be attributed to polymeric species formed by VC together with reduction products of the BOB anion.^{25,27,56} These results are in agreement with the elemental mapping of boron, which appears mostly on the graphite flakes. Considering this difference in SEI composition and coverage on the silicon alloy particles between the electrolytes, we attribute the decrease in cycling stability of the cell with the nonfluorinated electrolyte to the relative lack of an efficient SEI layer to stabilize the silicon alloy particles during cycling at high currents (Figure 1).

In addition to the elemental mapping studied by EDS, the chemical composition of the surface was analyzed by X-ray photoelectron spectroscopy (XPS). The experiments were carried out at two different excitation energies (2005 and 6015 eV), corresponding to probing depths of 17 and 43 nm, respectively, for the silicon–graphite composite electrode cycled in fluorinated and fluorine-free electrolytes, for which the F 1s, O 1s, and C 1s core-level spectra were measured (Figure 5). After five cycles at C/2, it is expected that a significant SEI layer has built upon the electrodes, which allows for a fair comparison between different electrolytes. Measuring at multiple excitation energies, it is possible to build an understanding of the composition of the electrode in the near-surface region as well as deeper where the bulk electrode material may be detected.

By evaluating the intensity of the C=C peak corresponding to the graphite and carbon black particles in the electrode, we can make an assessment of the thickness of the SEI. In the more surface-sensitive measurements for each cycled electrode, which correspond to a probing depth of approximately 17 nm, we observe nearly no intensity for the C=C peak. This indicates that at a probing depth of 17 nm the signal is mostly coming from the SEI layer. The peak is of similar intensity for all cycled electrodes in the deeper measurements at the excitation energy of 6015 eV, which corresponds to a probing depth of up to 43 nm. Since we observe intensity for the particles buried beneath the SEI at this energy, we can say that the SEI thickness on the graphite and/or carbon black particles

is between 43 and 17 nm after five cycles for each of the electrolytes. With the kinetic energy of electrons from the Si 1s core level being lower than that for the C 1s core level at an excitation energy of 6015 eV, we expect a probing depth of approximately 33 nm when analyzing electrons from Si 1s. From the Si 1s spectra (Figure S10), we observe little intensity for the Si peak at ~ 1839 eV for both electrolytes containing LiBOB but a higher intensity for the highly fluorinated electrolyte. This indicates that a thicker SEI layer is formed by the LiBOB-containing electrolytes on silicon particles, likely up to ~ 30 nm, but a thinner SEI layer for the highly fluorinated electrolyte.

The pristine electrode is composed mainly of graphite particles, which is reflected in the C 1s spectrum at both probing depths (C=C, 283.7 eV). Another major component is the lithium polyacrylate (LiPAA) binder that gives an intense signal in the C 1s and O 1s spectra, in which SiO_2 is also detected, originating from the native oxide layer of the silicon particles. The Li 1s and Si 1s signals are also present for the binder and the active material, respectively (see Figures S11 and S10, Supporting Information). A very low fluorine signal is detected, showing that the electrode is indeed fluorine-free, with the negligible amount present attributable to contamination during sample preparation. The source of this fluorine contamination is most probably the glovebox atmosphere; XPS is so surface-sensitive that it is impossible to avoid any contamination at all.

With a highly fluorinated electrolyte, we observe some major variations in the composition after five cycles (Figure 5b). There is an apparent thick fluorinated layer present on the surface of the electrode, characterized by the high relative intensity of the F 1s signal. The predominant species is F^- from LiF, which is a well-known component of the SEI layer formed when employing FEC as an electrolyte additive.^{37,38,55,69} Some other electrolyte degradation products include PF_6^- or similar (see also P 2p spectra in Figure S12), C–O/C=O likely from the decomposition of carbonate solvents, and Li_2O detected at greater depths (close to the surface of the particles).⁷⁰ It can also be noticed that the C=C peak, detected at higher excitation energy, has shifted to lower binding energy, on account of a partially lithiated phase (Li_xC) or as a result of an electric potential gradient at a buried interface between the thick SEI layer and the electrode active materials, as has been previously reported.⁷¹

With the addition of LiBOB to the electrolyte (Figure 5c), the electrode surface is still highly fluorinated after five cycles, with LiF being a key component of the SEI. However, a high fraction of oxygen is additionally observed with C–O and C=O species, attributed to LiBOB (or the decomposition thereof), now making up a significant share of the surface layers. B 1s spectra (Figure S13) also confirm the presence of boron products on the surface.^{25,72} Again, Li_2O is found at greater depths as a product formed close to the particle surfaces.

Upon cycling in the fluorine-free electrolyte, the SEI is rich in oxygenated species, as can be deduced from the high relative intensity for the O 1s transition. Components including C–O, C=O, Li_2O , and OH^- are fitted for this electrolyte. A negligible fluorine signal observed is attributable to minor contamination. The B 1s spectrum (Figure S13) of the fluorine-free counterpart only shows the presence of B–O species (190–194 eV).⁷²

On both of the electrodes cycled in fluorinated electrolytes, fluorinated species are the main SEI components observed by the surface analysis, which is very typical as discussed in previous studies.^{37,38,55,69} LiF becomes the major species formed on the surface of these electrodes with some other contributions from P–F (electrolyte salt), C–O, and C=O, the latter two likely to have formed from polymerization of carbonate solvents and additives or from deposition or decomposition of the LiBOB salt when present in the electrolyte. The main difference between these electrodes is that the amount of oxygen and carbon species is very low when cycled in a highly fluorinated electrolyte. This is due to the presence of FEC that forms an SEI rich in fluorinated compounds, known to be beneficial for silicon electrodes, and a low amount of oxygen-containing species.^{38,55,73} However, when partly replacing LiPF₆ with LiBOB in the electrolyte, the oxygen species appear in the SEI from the decomposition products of the BOB anion.²⁵ Despite the change in the composition of the SEI, this electrolyte showed similar electrochemical performance to the highly fluorinated electrolyte, indicating that the oxygen species are not detrimental to the battery cycling. In fact, they are also able to contribute to forming a stable SEI layer, accommodating the volume changes of silicon, and delivering a long cycle life.

The two electrolytes containing LiBOB present some differences, which may be important to understanding the electrochemical performance of the respective cells. For the fluorinated electrolyte containing LiBOB, the major oxygen components are rather the C–O-containing species, which we can conjecture are formed from the decomposition of FEC, EC, and VC, which are known to be consumed during SEI growth to form alkoxides and polyethers and from the decomposition of the LiBOB salt. During cycling, decarboxylation reactions of FEC and also the BOB anion lead to the formation of ether bonds.^{14,28,73} For the fluorine-free electrolyte, where the SEI contains no fluorine, the major components are C=O-containing species, likely products from the decomposition of LiBOB forming carbonyl-rich compounds²⁸ and other polymeric species, also coming from VC.³⁷ Less C–O-containing species are formed without LiPF₆ and FEC in the electrolyte, which indicates a decrease in decarboxylation reactions. We additionally notice higher amounts of OH[−] and Li₂O components formed in the fluorine-free electrolyte, compared to the highly fluorinated electrolyte due to the absence of HF that dissolves Li₂O in the latter electrolyte.^{74,75} These compounds additionally contribute to the SEI and presumably cause slightly increased resistance at the electrode interface, hence a lower rate performance than that for the fluorinated electrolytes (Figure 3).

Although the chemical composition of the SEI changes depending on the degree of fluorination of the electrolyte, it is notable that all cells showed good electrochemical performance, including the fully fluorine-free electrolyte. Over the last decades, fluorinated electrolytes and additives have been dominating in lithium-ion batteries due to their ability to form stable SEI layers that allow for long-term cycling. Alternatively, our results suggest that an oxygen-rich SEI is also able to stabilize the anode and provides comparatively good cycling stability in silicon-based cells.

Overall, electrolyte fluorination has a large influence on the electrochemical performance, particularly on the rate capability, morphology, and chemical composition of the SEI. While the best-performing electrolyte at high currents is still

the highly fluorinated one forming a LiF-rich SEI, at low currents it is the fluorine-free electrolyte with an SEI composed of oxygen-rich species that comes out on top. Therefore, these results indicate that fluorine-free alternatives are good candidates for high-energy-density full cells, opening up new possibilities toward safer, more sustainable, and less toxic batteries. As these results show, the key to accomplishing this is to explore fluorine-free electrolyte compositions that are able to match the high rate performance of state-of-the-art fluorinated electrolytes.

CONCLUSIONS

Aiming to reduce or eliminate fluorinated species in the electrolyte, such as LiPF₆ and FEC that release toxic compounds on degradation, developing fluorine-free alternatives is an urgent challenge for lithium-ion batteries. Herein, the influence of electrolyte fluorination on silicon–graphite composite anodes was investigated in full cells containing NMC111 cathodes. Comparing a cell with a conventional LiPF₆-based electrolyte to another with a fluorine-free alternative based on LiBOB, the latter featured higher cycling stability and Coulombic efficiency. However, both cells presented rapid capacity fade due to their inability to form a stable SEI on the surface of the silicon–graphite electrodes. Incorporating the SEI-forming additives FEC and VC in the fluorinated electrolyte and only VC in the fluorine-free alternative resulted in a clear improvement in cycling stability. At low currents (C/10), the fluorine-free electrolyte (LiBOB + VC) featured the highest discharge capacity (147 mAh g_{NMC}^{−1}) and capacity retention (84.4% after 200 cycles) due to the lower internal resistance and thus lower overpotential after 50 cycles. However, the fluorine-free electrolyte showed less useful rate capability with increasing overpotential at higher currents, potentially due to higher resistance in the SEI that limits the electron transfer and lithium-ion diffusion near the surface of the electrode. This was observed during long-term cycling at C/2, which led to a faster capacity fade for the fluorine-free electrolyte. Nevertheless, at elevated temperatures, this electrolyte featured improved cycling stability compared to the highly fluorinated electrolyte, thanks to its superior thermal stability.

Surface analysis by XPS, SEM, and EDS showed crucial differences between the electrolytes already after five cycles at C/2. The highly fluorinated electrolyte formed a fluorine-rich SEI, mostly composed of LiF and covering the silicon particles. In contrast, the fluorine-free electrolyte formed an oxygen-rich layer consisting of reduction products of the BOB anion and other organic species and predominantly covering the graphite particles. All in all, these results indicate that a fluorine-free electrolyte, with an oxygen-rich SEI, is able to provide good electrochemical performance in high-energy-density full cells (NMC111/Si–graphite). These results open up the possibility to replace LiPF₆, which generates toxic compounds, with other more environmentally friendly and less toxic alternatives, such as LiBOB. Further optimization of the fluorine-free additives able to form a more conducting SEI layer would overcome the rate-limiting performance of this fluorine-free electrolyte and provide improved electrochemical results at higher currents.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.0c01733>.

Additional electrochemical results, SEM images, and XPS spectra (PDF)

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Notes

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■ NOTE ADDED AFTER ASAP PUBLICATION

Figure 1 was replaced on June 29, 2020 to correct the units of the y-axis.