Lithium-ion cells are the energy storage devices of choice for portable consumer electronics and electric vehicles, due to their superior volumetric energy density and cycle life. The energy density and cycle life of many lithium-ion cells are limited by the stability of their electrolyte solutions at the positive electrode. Electolyte reactions cause capacity loss and impedance growth as a result of the consumption of active lithium and the formation of solid-electrolyte interphases (SEI) on the surface of both electrodes. Electrolyte reactions can also result in gaseous decomposition products, causing pouch-type lithium-ion cells to swell or burst, possibly resulting destruction of the cell and the device it powers. The stability of the electrolyte salt plays a role in the reactivity of electrolyte solutions. LiPF₆, the most common salt in lithium-ion electrolytes, can decompose into LiF, PF₅ and P₂F₅ at elevated temperatures. This reaction leads to a cascade of unwanted reactions, and also decreases the conductivity of the electrolyte solution. PF₅ is a highly reactive Lewis acid, known to catalytically decompose organic carbonate solvent molecules into gaseous decomposition products. LiPF₆ can also react with protic impurities to form HF, which in turn can dissolve transition metals from the positive electrode.

In an effort to stabilize electrolyte solutions, LiBF₄ has often been studied as a replacement for LiPF₆. The BF₄⁻ anion has stronger inter and intra molecular forces than its phosphorous-based analogue. The B-F bond in LiBF₄ is less labile than the P-F bond in LiPF₆, resulting in improved hydrolytic and thermal stability of electrolyte solutions when LiBF₄ is substituted for LiPF₆. The ionic association between Li⁺ and BF₄⁻ in electrolyte solutions is also stronger than the ionic association between Li⁺ and PF₆⁻, resulting in lower conductivity, lower transport number and poorer cation solvation. The poor conductivity of LiBF₄ solutions does not however impair the cycling performance of graphite/LiNiO₂ cells, cycled to 3.9 V, even at sub-zero temperatures, as LiBF₄ apparently lowers charge transfer resistance (Rct). This beneficial effect of LiBF₄ is most apparent at the positive electrode. The use of LiBF₄ electrolyte has been observed to reduce Rct of LiMn₂O₄ positive electrodes seven-fold compared to LiPF₆, when these electrodes were cycled up to 4.4 V in carbonate solvents. It has been shown that LiBF₄ improves the coulombic efficiency (CE) of positive electrode half cells and reduces the parasitic current due to aluminum current collector corrosion at high potentials. These reports suggest LiBF₄-based electrolytes could be a promising solution to electrolyte instability at the positive electrode at high potentials. The purpose of this study is to observe the effect of LiBF₄ on the stability of electrolyte solutions at high voltage (>4.4 V), when reactions of the electrolyte at the positive electrode are known to contribute strongly or even dominate cell failure. The compatibility of LiBF₄ with electrolyte additives successfully used to improve the negative electrode SEI in LiPF₆-based electrolytes–vinylene carbonate (VC), prop-1-ene-1,3-sultone (PES), pyridine boron trifluoride (PBF) and pyridine phosphorus pentfluoride (PPF)–is also discussed in this work. Assessment of LiBF₄ electrolyte stability and evaluation of additive performance in this work was done by a combination of high voltage coulometry (UHPC), electrochemical impedance spectroscopy (EIS) and gas evolution measurements on machine-made lithium-ion pouch cells, containing Li[Ni₀.₄Mn₀.₄Co₀.₂]O₂ positive electrodes capable of being cycled up to 4.7 V. Electrolytes that are stable up to this voltage could extend the lifetime and increase the energy density of current lithium-ion technology, and are of thus great interest for consumer electronics and electric vehicle applications.

**Experimental**

**Electrolyte preparation.**—Electrolyte preparation was done in an Ar-filled glove box to ensure minimal exposure to moisture and oxygen. 1 M electrolyte solutions were prepared by dissolving LiPF₆ or LiBF₄ salts in a 3:7 weight ratio of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) solvents (BASF). The salt was weighed on an analytical balance and transferred to a Nalgene vial. The amount of solvent needed to make a 1 M solution was added to the vial using a micro pipette, with an accuracy of ±0.01 mL. The following additives were added to the electrolyte in amounts of 2 wt%: vinylene carbonate (VC, BASF, 99.97%), prop-1-ene-1,3-sultone (PES, Lianhuang Medicinal Chemistry Co., Ltd., China, 98.20%), pyridine boron trifluoride (PBF, 3 M Co.) and pyridine phosphorus pentfluoride (PPF, 3 M Co.). A ternary blend of additives, containing 2 wt% PES, 2 wt% 1,3-dioxothiolan-2,2-oxide (DTD, YaCoo, >98%), and 2 wt% (1-trimethylsilyl)phosphite (TTSpi, TCI, 95%), abbreviated henceforth as “PES222” was also used. Electrolyte without additives is referred to henceforth as “control”.

**Cell construction.**—Machine-made lithium-ion polymer cells were obtained without electrolyte from a reputable manufacturer (Li-Fun Technology, Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuhou City, Hunan Province, PRC, 412000). The negative electrode of these cells was 96% artificial graphite particles (15–30 μm), 2% carbon black conductive diluent and 2% sodium carboxymethylcellulose (NaCMC)/styrene butadiene rubber (SBR) binder. The positive electrode was 96% Li[Ni₀.₄Mn₀.₄Co₀.₂]O₂ (NMC442) particles (5–15 μm, obtained from Umicore, Korea), 2% carbon black conductive diluent and 2% polyvinylidene fluoride (PVDF) binder. The ratio of negative/positive electrode capacity allowed for cell voltages of 4.7 V to be reached, delivering a capacity of 250 mAh. Prior to filling with electrolyte, the cells were opened without additives is referred to henceforth as “control”.

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**Effect of Substituting LiBF₄ for LiPF₆ in High Voltage Lithium-Ion Cells Containing Electrolyte Additives**

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This work evaluates the performance of LiBF₄-containing electrolytes in lithium-ion cells charged to high voltages (>4.4 V) and explores the compatibility of LiBF₄ with additives known to improve the performance of LiPF₆-based electrolytes. It was found that the benefit imparted by LiBF₄ is lost when cells are charged beyond 4.4 V, at which point electrolyte oxidation causes gas evolution and impedance growth. In the case of LiBF₄, impedance growth is shown to be due to increased charge transfer resistance at the negative electrode, indicating poor passivation of the negative electrode. Of the additives tested, only those containing prop-1-ene-1,3-sultone benefit cells with LiBF₄ electrolyte at high voltage.

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and dried under vacuum at 80 °C for 14 hours, to remove residual moisture. The cells were then transferred to an Ar-filled glove box, without exposure to air. To each cell 0.8 mL of electrolyte was added. The aluminium-laminate cell casings were sealed by heat crimping at 150 °C, under a gauge pressure of ~90 kPa, using a (Model MSK-115 V from MTI Corp.) vacuum sealer.

Archimedes volume change measurements.—The volume of gas generated by cycling was quantified by subtracting the weight of the cells submerged under liquid before and after gas-forming reactions, according to Archimedes’ principle. Details of the Archimedes volume measurement instrument at Dalhousie University can be found in several publications.17–19 Archimedes volume measurements were taken before and after the first and second degas steps (described in the Cell formation sections below) for cells undergoing UHPC cycling and storage, to determine the amount of gas formed by reactions of the electrolyte with the anode and cathode, respectively.

In-situ Archimedes volume measurements were performed on cells that were cycled at 40.0 ± 0.1 °C, using a Newark (Shenzhen, China) charging system. Cells destined for in-situ volume measurements underwent wetting, cell formation to 3.5 V and the first degas, according to the standard protocol described below. After degrading, the cells were loaded into the in-situ Archimedes measurement system and cycled once between 2.8 and 4.5 V at a rate of C/20, followed by C/5 cycling, with 10 hour 4.5 V constant voltage holds following every charge cycle.

Cell formation—wetting.—After filling with electrolyte, the cells were held at 1.5 V for 24 hours. This allowed time for the electrolyte to permeate through the separator and electrodes. The voltage of 1.5 V was applied to prevent oxidation of the copper current collector, which occurs above 3.2 V vs Li/Li+.

Cell formation—first degas.—The cells were then transferred to a 40.0 ± 0.1 °C temperature controlled box, where they were cycled with a Maccor 4000 series charger. All pair cells in this study underwent the formation cycling in parallel, unless indicated others. The currents specified are the currents per cell (half the current applied per pair). The cycling procedure began with an 11 mA (C/10) charge to 3.5 V, followed by a 1 hour constant voltage hold at 3.5 V. During this step EC and other electrolyte components are reduced, forming the initial SEI on the negative electrode and creating gaseous by-products. If the volume of gas produced exceeded 0.2 mL, cells were transferred to an Ar-filled glove box, where they were “degassed” by opening and resealing the laminate cell casings under vacuum.

Cell formation—second degas.—The cells were returned to their temperature controlled box, where they were charged at 11 mA to their upper voltage limit, either 4.35 V, 4.4 V or 4.5 V. The voltage was held at this value for 1 hour, to equilibrate the cells at this potential. The cells were then discharged at 11 mA to 3.8 V and held at this potential for 1 hour. The cells were removed from the temperature controlled box for Archimedes volume measurements and degassed a second time if the volume of gas produced exceeded 0.2 mL.

Electrochemical impedance spectrometry (EIS).—EIS measurements were taken before and after cycling and storage tests. EIS measurements were performed at 10.0 ± 0.1 °C, using a BioLogic VMP3 potentiostat to induce a 10 mV bias at frequencies ranging from 10 mHz to 100 kHz. The magnitude of Rct was obtained by determining the diameter of the mid-frequency semicircle in the Nyquist plot.21–23

Ultra-High precision coulometry (UHPC) cycling.—After formation, cells destined for cycling were loaded into 40 ± 0.1 °C temperature controlled boxes and cycled with a UHPC system. The UHPC system was designed and built at Dalhousie University, as described in several publications.24,25 All cells were cycled, with clamps, using one of two cycling protocols: continuous and “barn” cycling. The continuous cycling test consisted of constant current cycling, at a rate of 10 mA, between 2.8 V and 4.4 V. The “barn” cycling test was designed to highlight the effects of electrolyte oxidation at high voltage.26 “Barn” cycling consisted of a 10 mA charge from 2.8 V to 4.2 V, followed by a slower, 4 mA charge from 4.2 V to 4.5 V. The same currents in the same potential ranges were used during discharge.

Storage.—After formation, the cells destined for storage were loaded into 40.0 ± 0.1 °C temperature controlled boxes and connected to a Maccor 4000 series charger for prep-storage cycling. The UHPC system was deemed unnecessary for these storage experiments, as changes in capacity between cycles were large. The cycling procedure was identical to that prescribed in the literature for analysis of capacity loss at high voltage, using the lithium inventory model.27 The pre-storage cycling procedure consisted of a full discharge/charge cycle at a rate of 10 mA, between 2.8 V and either 4.4 V or 4.5 V. After pre-storage the cells were left to rest, fully charged, for 500 hours. Cell voltage measurements were taken at hourly intervals. Following storage, the cells were discharged to 2.8 V and cycled once more at a rate of 10 mA, before being equilibrated at 3.8 V for final EIS and Archimedes volume measurements.

Symmetric cells.—After UHPC “barn” cycling, control cells, equilibrated at 3.8 V, were dissected into an Ar-filled glove box. Disks with a 1 cm² diameter were punched from negative and positive electrodes and rinsed with EMC solvent to remove residual LiPF6 and EC. Symmetric cells were made by assembling two electrodes of the same type in 2325-type coin cells, using microporous polypropylene (Celgard 2301) and blown-microfiber (3 M Co) as separators and 1 M LiPF6 in 3.7 EC:EMC as electrolyte. EIS done on these symmetric cells allowed the determination of the Re of individual positive and negative electrodes.

Results and Discussion

Electrolyte reactions during formation.—Figure 1A shows dQ/dv versus V of cells with control electrolyte during the first formation step. The large peak at ~2.9 V is caused by the reduction of EC and the formation of a passivating graphite SEI. The area of this peak corresponds approximately to the number of electrons used in the reduction of EC and approximately to the amount of EC needed to passivate the graphite electrode. Figure 1B shows the number of electrons used for the reduction of EC and the additives PBF, PPF and PES222, determined by integrating the area under the reduction peak, after subtracting a linear background. The area of the VC reduction peak is not shown, as this peak was too small to clearly distinguish from the background. Figures 1A and 1B show that the number of electrons used in the reduction of EC increased as LiBF4 was substituted for LiPF6, suggesting that more EC is required to fully passivate the negative electrode in the presence of LiBF4. Figure 1B shows that the number of electrons in the reduction of PBF, PPF and PES222 additives also increased as LiBF4 was substituted for LiPF6, suggesting that LiBF4 promotes the reduction of these species as well.

Figure 1C shows the first cycle irreversible capacity loss, the difference between the first charge capacity and the first discharge capacity. Substitution of LiBF4 for LiPF6 resulted in more irreversible capacity loss, except with the use of PPF and PES222. The increase in irreversible capacity is likely due to the poor passivation of the graphite negative electrode in LiBF4 electrolytes. The red bars marked “control”, with error bars, in Figure 1C show results for cells that were formed individually (not in parallel with a pair cell), and which underwent a complete discharge to 2.8 V prior to the second degas. These cells portray a truer irreversible capacity, as the discharge cycle was uninterrupted, and measured on the same instrument.

Figure 2 shows the volume of gas formed during the first charge (formation cycle). Figure 2A shows the change in volume occurring between 1.5 V and 3.5 V, as the negative electrode SEI is formed. Figure 2A shows that more gas was evolved in electrolytes with LiBF4 salt, possibly due to the increased consumption of EC, as shown previously in Figure 1B. The reduction of EC in lithium-ion...
Figure 1. A) dQ/dV versus V of cells with control electrolyte during the first charge to 3.5 V, showing a prominent peak due to the reduction of EC. B) the integrated area of the reduction peaks for EC (black) and additives (red) and C) the first cycle irreversible capacity for cells cycled to 4.5 V (black) and 4.4 V (red).

Figure 2. A) volume change during the first charge to 3.5 V, before the first degas and B) volume change during the first charge from 3.5 V to 4.35 V (blue) 4.4 V (red) or 4.5 V (black), before the second degas.

The amount of gas produced prior to the first degas in cells with LiBF₄.

Figure 2B shows the gas formed above 3.5 V during the first charge, due to oxidation of electrolyte at the positive electrode. The red bars show the volume of gas produced by cells charged to 4.5 V. The black bars show the volume of gas produced in cells charged to 4.5 V. The large difference between the red and black bars indicates that the oxidative event which produced gas in cells with LiBF₄ occurred between 4.4 V and 4.5 V. In all cells, the substitution of LiBF₄ for LiPF₆ resulted in larger volumes of gas when cells were charged to 4.5 V. This is consistent with DFT calculations, which predict that the rates of solvent oxidation and gas evolution increase when solvents are coordinated to the BF₄⁻ anion, compared to PF₆⁻. All additives reduced the amount of gas formed at high voltage, relative to control, at high voltage in cells with either LiPF₆ or LiBF₄. The additives PBF and PPF were the most effective in reducing the amount of gas formed at high voltage in cells with both LiBF₄ and LiPF₆.

Figure 3 shows the results of the in-situ Archimedes volume change experiment performed on cells with control electrolyte with LiPF₆ and LiBF₄. Figure 3A shows the voltage curves of the cells during the formation cycle, followed by repeated cycle-hold-rest testing. Figure 3A shows that the cells with LiBF₄ (shown in red) have the same capacity as the cells with LiPF₆ (shown in black) during the first cycle, but that the capacity of cells with LiBF₄ decreased over cycle time. Figure 3B shows the volume change vs cycle time of the cells with LiPF₆. During the second step of the formation cycle, the control cell containing LiPF₆ (shown in black) began producing gas at 3.8 V. After the first charge, the control cell with LiPF₆ electrolyte shrank over time, as gas was consumed, a phenomenon described by Self et al. The addition of VC and PES additives (shown in red and blue...
Electrolyte reactions during cycling.—Figure 4 shows the results of the UHPC cycling tests. Figures 4A–4E (top row) show CE as a function of cycle number. Figures 4A–4E (second row) show charge end-point capacity slippage per cycle (Δc) as a function of cycle number. Figures 4A–4E (third row) show the average voltage hysteresis (ΔV) as a function of cycle number. Figures 4A–4E (bottom row) show discharge capacity (Qd) as a function of cycle number. The first two columns, A and B, show UHPC data for cells with control electrolyte, cycled continuously to 4.35 V or 4.4 V. These figures show that addition of LiBF4 increases the CE, lowers the rate of Δc and lowers ΔV for control cells cycled up to 4.4 V. The best performance was achieved in cells that contained 0.5 M of both LiBF4 and LiPF6. This suggests that LiBF4 could be a useful additive to LiPF6-based control electrolyte cycled up to 4.4 V. The discharge capacity of cells with LiBF4 is lower than those with LiPF6, as a result of the increased capacity loss during the first cycle in LiBF4 electrolytes, as shown in Figure 1C (by the red bars marked with “∗”). The rightmost three columns in Figure 4 show UHPC data for control cells (C) and cells with the addition of 2% VC (D) and 2% PES (E), “barn” charged to 4.5 V. Figures 4C–4E show that when the voltage limit is increased to 4.5 V with control electrolyte, the benefit imparted by LiBF4 is lost by the 10th cycle. Figures 4D–4E show that the addition of 2% VC did not improve performance of cells with LiBF4 electrolyte cycled to 4.5 V, as shown by the decreased CE and increased Δc. The addition of 2% VC did however improve the passivation of the negative electrode in cells with LiBF4, as evidenced by discharge capacities which equalled that of cells with LiPF6 electrolyte. Figures 4E–4E show that the addition of 2% PES improved the CE and Δc of cells with both LiPF6 and LiBF4 based electrolytes equally. Figure 4Eiii shows that ΔV is larger for cells with LiBF4, compared to LiPF6, with 2% PES. This could be due to the increased consumption of EC and additives at the negative electrode during formation with LiBF4 electrolytes, as was previously shown in Figure 1B.

Figure 5 shows Rct measured after UHPC cycling (Figure 5A, top) and volume change of cells (Figure 5B, bottom) during UHPC cycling. Rct is taken to be the diameter of the mid frequency semi-circle in the Nyquist plot. Substitution of LiBF4 for LiPF6 resulted in lower Rct and small volume changes when cells were cycled to 4.4 V (red). When cells with control electrolyte were “barn” charged to 4.5 V (black), substitution of LiBF4 for LiPF6 resulted in increased Rct and large amounts of gas evolution. This suggests that the reaction which causes gas evolution and Rct growth in cells with LiBF4 occurs between voltages of 4.4 V and 4.5 V. The addition of 2% VC and 2% PES reduced the amount of gas evolved in cells with both LiPF6 and LiBF4 electrolyte during cycling. The addition of VC increased Rct of cells with LiPF6, but did not significantly affect Rct of cells with LiBF4. The addition of PES reduced Rct of cells with LiPF6 electrolyte but, similarly to the addition of VC, did not significantly affect Rct of cells with LiBF4.

To investigate the cause of Rct growth in cells with LiBF4 salt at 4.5 V, EIS was done on graphite/graphite and NMC/NMC symmetric cells made from electrodes that had undergone “barn” cycling to 4.5 V. Figure 6A shows the Nyquist plots of graphite/graphite symmetric cells cycled with LiBF4 (red) and LiPF6 (black) electrolyte. Rct of the graphite electrode cycled in LiBF4 is roughly three times larger than that cycled in LiPF6 electrolyte. The reason for this is likely the poor passivation of the negative electrode and increased reactions of EC in cells with LiBF4, as shown previously by Figures 1B and 1C. Figure 6B shows the Nyquist plots of NMC/NMC symmetric cells cycled with LiBF4 (red) and LiPF6 (black). Rct of the NMC positive electrodes cycled in LiBF4 and LiPF6 electrolytes are more or less equivalent, except for an increase in the high frequency semi-circle (labelled with ∗), which is attributed to the contact resistance of the positive electrode with the Al current collector. Overall, Figure 6 indicates that the increased Rct of control cells with LiBF4 “barn” cycled to 4.5 V, is a result of increased graphite electrode Rct and increased contact resistance of the positive electrode with the aluminum current collector. This is in agreement with other
Figure 4. Results of UHPC cycling tests. Columns A and B show data for control cells continually cycled to 4.35 V and 4.4 V. Column C shows data for control cells “barn” cycled to 4.5 V. Columns D and E show data for cells with 2% VC and 2% PES. “barn” cycled to 4.5 V. Columns D and E show data for cells with 2% VC and 2% PES, “barn” cycled to 4.5 V. Ai–Ei (top row) show CE as a function of cycle number. Aii–Eii (second row) show ΔE versus cycle number. Aiii–Eiii show ΔV vs cycle number. Aiv–Eiv (bottom row) show discharge capacity vs cycle number.

Figure 5. Rct, (top, A) and volume change (bottom, B) after UHPC cycling to 4.4 V (red) and 4.5 V (black).

Figure 6. (A) CE, and (B) discharge capacity vs cycle number for control cells and cells with VC, PES, and LiBF4 electrolyte.

Figure 7A shows the voltage drop during the 500 hours of storage. Prior to storage, cells were equilibrated at either 4.4 V (red) or 4.5 V (black). Voltage drop during storage is caused by parasitic reactions of the electrolyte with the positive electrode, resulting in decreased positive electrode capacity and an increase in cell voltage. Substitution of LiBF4 for LiPF6 resulted in reduced self-discharge for cells with control electrolyte and the ternary blend PES222. Substitution of LiBF4 for LiPF6 resulted in increased self-discharge for cells with VC, PBF and PPF additives. The use of additives improved the self-discharge of all cells containing LiPF6.

Figure 7B shows the capacity lost reversibly (due to solvent oxidation) during the 500 hours spent at open-circuit voltage storage. These capacities were calculated by the method put forward by Sinha et al., using the lithium inventory model, by subtracting the capacity of the discharge cycle immediately following the storage experiment from the second discharge cycle after storage. Substitution of LiBF4 for LiPF6 resulted in smaller reversible capacity losses for electrolytes with PBF, PPF, PES222 and control electrolyte stored at 4.4 V. It is not clear why the cells with LiBF4 and the additives PBF and PPF had higher self-discharge and smaller reversible capacity losses, as these are both expected to be measures of electrolyte oxidation.

Figure 7C shows the capacity lost irreversibly (due to SEI growth) during the 500 hours spent at open-circuit voltage storage. The irreversible loss was calculated by subtracting the second discharge following the storage experiment from the discharge cycle prior to the storage experiment. In all cells, substitution of LiBF4 for LiPF6 resulted in greater amounts of irreversible capacity loss. This indicates that electrolytes with LiBF4 do not adequately passivate the negative electrode, leading to continued consumption of active lithium over time.

Figure 8 shows Rct, (8A, top) and volume change of cells (8B, bottom) after 500 hours of storage at 4.4 V (red) and 4.5 V (black). In all cases, the substitution of LiBF4 for LiPF6 resulted in increased Rct and large amounts of gas evolution, with the exception of cells with PES222. The addition of PES222 caused cells with LiBF4 to shrink to a greater degree than cells with LiPF6.
Conclusions

Previous studies have indicated that LiBF₄ improves the performance of cells by reducing parasitic reactions and Rct at the positive electrode.\(^6,7,12\) This work confirms that LiBF₄ reduces parasitic reactions at the positive electrode in cells with control electrolyte (evidenced by reduced \(\Delta_2\) during cycling and reduced self-discharge during storage), but only up to cell voltages of 4.4 V. This work confirmed that the substitution of LiBF₄ for LiPF₆ resulted in reduced Rct when cells were cycled continuously up to 4.4 V. Prolonged exposures to voltages above 4.4 V, during the 4.5 V “barn” cycling experiment, caused increased gas evolution from electrolyte oxidation in cells with LiBF₄, as predicted by DFT calculations.\(^28\)

Electrolyte solutions of LiBF₄ produce undesirable effects at the negative electrode, as suggested by previous studies.\(^6,9\) This work improves the understanding of this phenomenon, by showing that the presence of LiBF₄ causes more EC to be reduced at the negative

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Figure 6. Nyquist plots for A) symmetric cells with negative electrodes and B) symmetric cells with positive electrodes, harvested from the cells with control electrolyte that underwent “barn” charging to 4.5 V.

Figure 7. A) voltage drop after 500 hours of open-circuit storage B) capacity lost reversibly, due to electrolyte oxidation and C) capacity lost irreversibly due to SEI growth. Control cells charged to 4.4 V are shown in red. Cells charged to 4.5 V are shown in black.

Figure 8. Rct, (top, A) and volume change (bottom, B) after 500 hours of open-circuit storage at 4.4 V (red) and 4.5 V (black).
electrode during the first charge. Cells with LiBF$_4$ have lower discharge capacities than those with LiPF$_6$, as a result of the loss of active lithium during the first cycle. With LiBF$_4$ electrolyte $R_{ct}$ at 3.8 V after UHPC cycling increased when the upper voltage limit increased from 4.4 V to 4.5 V. With LiPF$_6$ electrolyte, the change in upper voltage limit did not significantly affect $R_{ct}$, measured at 3.8 V after cycling. The cause of the larger $R_{ct}$ in cells with LiBF$_4$ was determined to be a three-fold increase in $R_{ct}$ at the negative electrode, and an increase in the contact resistance between the positive electrode and the Al current collector. The dramatic growth of $R_{ct}$ in cells with LiBF$_4$ when cycled above 4.4 V suggests that a reaction at the positive electrode at high potentials causes modification of the negative electrode SEI, as suggested by several others.$^{30,31}$

Several additives known to improve the negative electrode SEI, reduce gas evolution and control $R_{ct}$ growth in cells with LiPF$_6$ electrolytes were tested with LiBF$_4$. It was found that these additives were much less effective in cells with LiBF$_4$ electrolyte, when cycled above 4.4 V. The addition of VC to cells with LiBF improved the irreversible capacity loss, but increased the rate of charge end point capacity slippage, $\Delta U_{c}$, during cycling and the self-discharge during storage. The presence of VC actually worsened the performance of these cells at high voltage. This finding highlights the importance of solution structure to their efficacy.

Further work should be done to optimize the concentration of LiBF$_4$ and find additives that provide better passivation of the graphite negative electrode in LiBF$_4$ electrolyte. This work offers insight into the reaction mechanisms of common additives for LiPF$_6$ electrolytes, by highlighting the importance of solution structure to their efficacy.

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