Li-ion batteries (LIBs) are widely used in applications from portable consumer electronics to electric vehicles (EVs). Incorporating electrolyte additives into the electrolyte is the most effective method for extending lifetime of LIBs. In a previous study, pyridine boron trifluoride (PBF) showed clear benefits as an additive for NMC-based lithium ion cells. The two major functional groups pyridine (organic base) and BF₃ were combined together to try to solve issues in lithium-ion cells, including: 1) transition metal dissolution from the positive electrode material at high potential; 2) electrolyte (salts and solvents) decomposition at high potential and elevated temperature; and 3) impedance growth during high potential and long-term cycling. However, the mechanism by which PBF-type additives function is not understood.

When PBF-type additives are used there is a 1:1 addition of the pyridine derivative and BF₃. This may not be the optimum ratio. Zuo et al. reported that LiBF₄ added as an additive could reduce impedance during high potential cycling and that the beneficial effects of LiBF₄ arise from the single BF₄⁻ ion. It is important to know which functional group, pyridine or BF₃, has a greater impact in PBF-type additives and which functional group is more beneficial to Li-ion cell lifetime. By using the same simple synthesis method, one, two or three BF₃ molecules can easily be added to pyridine, pyrazine or triazine, respectively, to learn about the impact of this series of additives with increased BF₃ content.

In this work, additives with different amounts of BF₃ were successfully synthesized with 1:1 to 1:3 mole ratio of Lewis base:BF₃. These additives were used to study the benefits of BF₃ as a functional group and to optimize the BF₃ content in these additives.

Synthesis of Pyrazine-BF₃ and Triazine-BF₃ Compounds

The synthesis is similar to the synthesis of pyridine boron trifluoride. To a dry Nalgene bottle (used as a reaction flask) in an inert atmosphere (N₂, He or Ar), 3.550 mL BF₃/diethyl ether (boron trifluoride diethyl etherate, 4.082 g, 0.0283 mole) was added. Then 1.000 g Pyrazine (0.0124 mole) in 2 mL chloroform (boron trifluoride diethyl etherate, 4.082 g) was added slowly. The reaction was highly exothermic so the reaction bottle was kept near room temperature by the slow addition of the reagents. White or colorless crystals normally precipitated out immediately, but if no precipitate was observed then the reaction mixtures were transferred to a −20 °C freezer and crystals then formed. The solid products were then rinsed by chloroform twice and collected by filtration. The wet product was transferred to a vacuum oven and vacuum dried overnight at 45−50 °C. The reaction follows a 2:1 stoichiometric ratio and a slight excess of boron trifluoride etherate could be easily removed by vacuum drying. The purity of the synthesized samples after vacuum drying was checked by NMR (H, ¹⁹F, ¹¹B) and no peaks of the initial reactants were observed in the NMR spectra. NMR spectra are available in Figures S1 and S2 (supporting information). The melting point and boiling point of the synthesized additives were measured using an Electrothermal IA 9100 digital melting point apparatus and a differential scanning calorimeter (DSC Q1000, TA Instruments). Table I gives the melting points (M.P.) and boiling points (B.P.) and estimates of the purity of the synthesized materials used in this work based on the NMR spectra. Figure 1a shows a schematic of the synthesis procedure followed. The same procedure was used for the 1,3,5-triazine to make triazine(BF₃)₃ except that a 3:1 stoichiometric ratio of boron trifluoride etherate to triazine was used. All synthesized additives were stored in an Ar-filled glovebox to avoid moisture.

Pouch Cells and Electrolyte Preparation

1 M LiPF₆ EC/EMC (3:7 wt. % ratio, BASF) was used as the control electrolyte in the studies reported here. To this electrolyte, various synthesized electrolyte additives, listed in Table I, were added. Additive components were added at specified weight percentages to the electrolyte. Other standard electrolyte additives were also used for comparison. These included vinylene carbonate (VC, BASF, 99.97%) and prop-1-ene,1,3-sultone (PES, Lianchuang Medicinal Chemistry Co., 98.20%). PBF-type additives were synthesized at Dalhousie University as previously described and the molecular formulas are shown in Figure 1b.

Table I. Physical properties of PBF, PRZ and TRIZIN used as additives in electrolytes.

| Product (electrolyte additive) | Short name | Purity (based on NMR) | Melting point (M.P., °C) | Boiling point (B.P., °C) |
|--------------------------------|------------|-----------------------|-------------------------|------------------------|
| Pyridine boron trifluoride     | PBF        | > 99%                 | 45°                     | 300°                   |
| Pyrazine boron trifluoride     | PRZ        | > 99%                 | 251°                    | N/A                    |
| 1,3,5-Triazine boron trifluoride | TRIZIN     | > 99%                 | 151°                    | 233°                   |

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Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000, China). All pouch cells were vacuum sealed without electrolyte in the assembly dry-room in China and then shipped to our laboratory in Canada. Before electrolyte filling, the cells were cut just below the heat seal and dried at 80°C under vacuum for 14 h to remove any residual water. Then the cells were transferred immediately to an argon-filled glove box for filling and vacuum sealing. The NMC/graphite pouch cells were filled with 0.9 g of electrolyte. After filling, cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.). First, cells were placed in a temperature box at 40.±0.1°C where they were held at 1.5 V for 24 hours, to allow for the completion of wetting. Then cells were charged at 11 mA (C/20) to 3.5 V. After this step, cells were transferred and moved into the glove box, cut open to release gas generated and then vacuum sealed again. After degassing, impedance spectra of the cells were measured at 3.8 V as described below. The NMC/graphite pouch cells destined for 4.5 V operation were degassed a second time at 4.5 V.

The amounts of gas created during formation to 3.5 V and between 3.5 V and 4.5 V were measured and recorded.

**Electrochemical Impedance Spectroscopy**

Electrochemical impedance spectroscopy (EIS) measurements were conducted on NMC/Graphite pouch cells before and after cycling on the UHPC. Cells were charged or discharged to 3.80 V before they were moved to a 10.±0.1°C temperature box. AC impedance spectra were collected with ten points per decade from 100 kHz to 10 mHz with a signal amplitude of 10.±0.1°C. A Biologic VMP-3 was used to collect this data.

**Ultrahigh Precision Cycling and Long-Term Cycling**

The cells were cycled using the Ultra High Precision Charger (UHPC) at Dalhousie University between 2.8 and 4.2, 4.4 or 4.5 V at 40.±0.1°C. For 4.2 V and 4.5 V UHPC cycling, a continuous charge and discharge protocol was used with a current corresponding to C/20. For cells tested to 4.4 V, in order to put the cells in an extended period at high potential, the cells were first charged to 4.2 V using currents corresponding to C/20 and then continued charging between 4.2 and 4.4 V using a current corresponding to C/60. The discharge protocol was the opposite of the charging protocol. This special protocol was named “barn” cycling and is shown by the black curve in Figure 2.

Long term cycling was conducted at 4.3 V and 4.5 V at different temperatures. The cells, after the 4.2 V continuous UHPC test, were charged and discharged at 80 mA between 2.8 and 4.3 V at 55.±0.1°C using a Neware (Shenzhen, China) charger system. The cells, after the 4.4 V “barn” UHPC cycling, were charged and discharged at 100 mA between 2.8–4.5 V at 40.±0.1°C on a Neware (Shenzhen, China) charger system.

**Determination of Gas Evolution in Pouch Cells**

Ex-situ (static) gas measurements were used to measure gas evolution during cycling. Measurements were made using Archimedes’ principle with cells suspended from a balance while submerged in liquid. The changes in the weight of the cell suspended in fluid, before, during and after testing are directly related to the volume changes by the change in the buoyant force. The change in mass of a cell, Δm (note that a balance reports mass, but actually measures weight and

![Figure 2](https://example.com/figure2.png)
Figure 3. (a) The cell terminal voltage as a function of capacity during the initial charge (formation cycle) to the first degassing point (3.5 V) and (b) differential capacity (dQ/dV) versus voltage (V) during the same formation process for NMC442/graphite pouch cells containing different concentrations of PBF, PRZ and TRIZIN.

divides the weight by the acceleration due to gravity, \( g \), to get the mass, \( m \), suspended in a fluid of density, \( \rho \), is related to the change in cell volume, \( \Delta V \), by

\[
\Delta V = -\Delta m / \rho \quad [1]
\]

Ex situ measurements were made by suspending pouch cells from a fine wire “hook” attached under a Shimadzu balance (AUW200D). The pouch cells were immersed in a beaker of de-ionized “nanopure” water (18 MΩ) that was at 20 ± 1°C for measurement. Before weighing, all cells were charged or discharged to 3.80 V.

**Results and Discussion**

Figure 3 shows the cell potential as the function of capacity during the first charge to the first degassing point (3.5 V) along with the differential capacity versus voltage for NMC442/graphite cells with different electrolytes: 1% and 2% PBF, 0.5% PRZ, 1% TRIZIN and control electrolyte. Figure 3a shows that a plateau appeared at 2.3 V in PBF-containing cells (negative electrode potential approximately 1.2 V vs Li/Li⁺) and that the intensity of the corresponding peak in dQ/dV vs. V at 2.3 V increases with PBF content from 1 wt. % to 2 wt. % (Figure 3b). The cell with 1% TRIZIN has much shorter plateau at the same voltage compared to PBF-containing cells and the cell with 0.5% PRZ has the same voltage-capacity curve as control cells with only an EC reduction peak at about 2.9 V (≈ 0.8 V vs Li/Li⁺). (Note: Only 0.5% PRZ is soluble in the control electrolyte as shown in Table II.)

Table II indicates the amount of BF₂ included in each pouch cell when 1% PBF, 2% PBF, 0.5% PRZ or 1% TRIZIN was added. Table II also shows the solubility of the additive in wt. %, \( \mu \)mol of Lewis base added to a pouch cell, \( \mu \)mol of BF₂ added to a pouch cell, the capacity (mAh) for a one electron reaction with the Lewis base in a pouch cell, the capacity (mAh) for a one electron reaction with the BF₂ in a pouch cell and the measured capacity between 2 and 2.4 V during the formation cycle from Figure 3. Table II demonstrates that there may be a two electron reduction with the Lewis base in PBF and, perhaps, in TRIZIN. The reader is asked to notice the x-axis values in Figure 3 of reference 3 were improperly calculated which led to a spurious conclusion of one electron reduction in that paper. However, there is virtually no extra capacity at low potential indicative of additive reduction in the case of PRZ. The reader should note that this does not mean that PRZ is not reduced, but that it is not reduced at low potential.

Cells containing the additives PBF, PRZ and TRIZIN were tested using the Ultra High Precision Charger to three different upper cutoff potentials, 4.2 V, 4.4 V or 4.5 V. Figure 4 shows the UHPC cycling data for NMC111/graphite pouch cells cycled between 2.8 and 4.2 V using a constant current corresponding to C/20 at 40. ± 0.1°C. Cells contained 1% PBF, 2% PBF, 0.5% PRZ, 1% TRIZIN, 2% VC or control electrolyte. Figures 4a and 4e show the columbic efficiency, Figure 4b shows the discharge capacity, Figure 4c shows \( \Delta V \) (the difference between the average charge and discharge potentials) and Figure 4d shows the charge capacity all plotted versus cycle number. Figures 4a and 4e show that cells with 2% VC have the best CE, followed by cells with PBF then PRZ and finally TRIZIN, which are all substantially better than cells with control electrolyte. Figure 4b shows that, as is typical, discharge capacity versus cycle number in the early cycles cannot distinguish between the cells, even though accurate CE measurements can. Figure 4c shows that all cells, except control cells, have well-behaved polarization that does not increase during these early cycles. Cells with 2% PBF have a slowly decreasing \( \Delta V \). Figure 4d shows that the cells with 2% VC and 1% PBF have similar charge slippage. Cells with 2% PBF showed a smaller charge endpoint capacity slippage than cells with 1% PBF and the cell with 0.5% PRZ has the smallest charge endpoint capacity slippage. Cells with 1% TRIZIN showed the worst charge endpoint capacity slippage of all the additive-containing cells. Cells with 2% PBF and with 1% TRIZIN contain more BF₂ than the other cells, but cells with TRIZIN perform much worse than cells with PBF.

Cells containing the same electrolytes were also tested to higher potential. Figure 5 shows the UHPC cycling data for NMC442/graphite pouch cells cycled at 40. ± 0.1°C between 2.8 and 4.4 V using the “barn” cycling protocol (See Figure 2) which forces cells to remain at higher potential for greater fractions of time. All these cells were cycled without clamps. Figure 5a shows the CE versus cycle number. Different from the 4.2 V cycling, control electrolyte shows a

| Additive | Solubility | Wt. % in electrolyte | Lewis base in pouch cell (µmol) | BF₂ in pouch cell (µmol) | mAh (one electron reaction) Lewis base | mAh (one electron reaction) BF₂ | Capacity between 2 and 2.4 V (mAh) |
|----------|------------|----------------------|-------------------------------|--------------------------|----------------------------------|----------------------------|----------------------------------|
| 1% PBF   | >2%        | 1%                   | 61                            | 61                       | 1.6                              | 1.6                        | 5.2                              |
| 2% PBF   | >2%        | 2%                   | 122                           | 122                      | 3.2                              | 3.2                        | 2.7                              |
| 0.5% PRZ | ~0.5%      | 0.5%                 | 21                            | 42                       | 0.56                             | 1.1                        | 0.2                              |
| 1% TRIZIN| >2%        | 1%                   | 32                            | 95                       | 0.85                             | 2.5                        | 1.2                              |
gradually increasing CE with a similar behavior as the additive-containing cells, but the CE is much lower than the other cells. As earlier work demonstrated that VC is not suitable in NMC cells tested above 4.3 V, 2% PES was used as a comparative electrolyte additive for the cells tested to 4.4 V. For cells with PBF-type additives, similar trends as found for the 4.2 V UHPC cycling were observed. Cells with 2% PBF still showed better CE than cells with 1% PBF, 0.5% PRZ or 2% PES. Cells with 1% TRIZIN have similar CE to control cells and much lower CE than cells with other PBF-type additives. Figure 5d shows the charge endpoint capacity of the cells during cycling. Cells with 1% PBF, 2% PBF and 0.5% PRZ have similar charge endpoint capacity slippages. Cells with 1% TRIZIN do not show a significant improvement in charge endpoint capacity slippage compared to control cells.

Cells with the same electrolyte additives considered in Figures 4 and 5 have been tested to even higher potential. Figure 6a shows the CE versus cycle number of the cells continuously cycled at C/20 between 2.8 and 4.5 V at 40. ± 0.1°C. The CE values in Figure 6 (4.5 V continuous cycling) are much lower than those for cells with the same additives shown in Figures 4 (4.2 V continuous) and 5 (4.4 V “barn”) indicating severe electrolyte oxidation at high potential. Cells with PBF showed a higher CE than cells with PRZ or TRIZIN. At 4.5 V, cells with 0.5% PRZ cells have similar CE to cells with 2% PES. Figure 6c shows that ΔV for all cells increases with cycling indicating an overall impedance growth during charge-discharge testing to 4.5 V. Figure 6d shows the charge endpoint capacity of the cells. Figure 6d shows that when the upper cutoff increases to 4.5 V, the fractional benefit of the additives is much smaller than at 4.2 or 4.4 V.

After the cycling tests at 4.2, 4.4 and 4.5 V using the UHPC, EIS spectra of the cells described in Figure 7 were measured at 3.8 V and 10. ± 0.1°C. Figures 7a and 7b show the Nyquist plots of the impedance spectra of the pouch cells described by Figure 4. The impedance (Rct) of the cells containing control electrolyte increased after cycling, while those with 2% PBF decreased after cycling, which is consistent with the ΔV data shown in Figure 4c. The impedance spectra of the other cells with additives were virtually unchanged before and after cycling for 16 cycles at 40°C to 4.2 V at C/20. Figures 7c and 7d show the Nyquist plots of the impedance spectra of the pouch cells described by Figure 5 before and after 4.4 V “barn” UHPC cycling at 40°C. The diameter of the semi-circle in the impedance spectrum represents the sum of the resistive parts of the charge transfer impedance and the transfer of ions through the SEI layers for both electrodes. The cells with control electrolyte showed significant impedance growth after cycling and the semicircle distorted.

Figure 4. UHPC data for NMC111/graphite pouch cells with PBF-type additives, 2%VC and control electrolyte. The cells were tested at 40°C with an upper cutoff of 4.2 V. (a and e) coulombic efficiency (CE), (b) discharge capacity, (c) ΔV, the difference between average charge and discharge potentials and (d) charge endpoint capacity. All are plotted versus cycle number.
Figure 5. UHPC data for NMC442/graphite pouch cells with PBF-type additives, 2%PES and control electrolyte. The cells were tested at 40 °C with an upper cutoff of 4.4 V using the “barn” cycling protocol described in Figure 2. (a and e) columbic efficiency (CE), (b) discharge capacity, (c) \( \Delta V \), the difference between average charge and discharge potentials and (d) charge endpoint capacity. All are plotted versus cycle number.

significantly into two semicircles. The increase of the low frequency semicircle is due to an increase of the charge transfer resistance of the positive electrode, consistent with the previous report of Ma et al.6 The cell with 2% PES showed a decrease in \( R_{\text{ct}} \) after these 16 cycles which is also consistent with Ma et al.6 All cells containing PBF, PRZ or TRIZIN showed little change to their impedance spectra before and after cycling. Again, Figures 7e and 7f show the Nyquist plots of the impedance spectra of the pouch cells described by Figure 6 before and after 4.5 V continuous UHPC cycling at 40 °C. The impedance spectra of all the cells were distorted from one semicircle to two distinguishable semicircles suggesting the growth of the cathode charge transfer impedance during high voltage cycling. The impedance of all cells, except those with 2% PES and 0.5%PRZ, increased significantly after the cycling to 4.5 V, consistent with the growth of \( \Delta V \) during the cycling.

Figure 8 shows a summary of the gas evolution of the cells after UHPC cycling to the three different upper cutoff potentials (Figures 4, 5 and 6). The gas generated in all cells was quite small, less than 5% of the initial pouch cell volume (2.2 mL). In fact, cells cycled to 4.2 V showed virtually no expansion at all. To put the amount of gas generated into perspective, Figure S3 shows a freshly vacuum-sealed pouch cell and a pouch cell that has expanded by 0.1 mL (5%). There is no visible difference.

Smith et al. consider how coulombic efficiency, charge end point capacity slippage and capacity fade are related.15 Equations 11–14 in that paper can be rewritten (in the case where there is no positive electrode damage and no reduction of salt concentration in the electrolyte) as:

\[
1 - CE = \frac{f}{Q} + \frac{\Delta c}{Q}
\]

where \( f \) is the capacity loss per cycle (in mAh/cycle), \( \Delta c \) is the charge end point capacity slippage per cycle (in mAh/cycle) and \( Q \) is the cell capacity (in mAh). Table III compares 1- CE, \( f/Q \) and \( \Delta c/Q \) for the UHPC measurements on all cells with the various additives tested to upper cutoff potentials of 4.2 V (Figure 4), 4.4 V (Figure 5) and 4.5 V (Figure 6). The measurements of \( f/Q \) in Table III were taken from the slopes of the last 5 data points in Figures 4b, 5b and 6b. The measurements of \( \Delta c/Q \) in Table III were taken from the slopes of the last 5 data points in Figures 4d, 5d and 6d. The measured values of 1 – CE in Table III were taken by averaging the last 3 data points in Figures 4e, 5e and 6e. The calculated values of 1-CE in Table III were obtained using Equation 2.

Figure 9 displays the results of Table III. Figures 9a and 9c show the fraction of capacity loss per cycle and the fraction of capacity lost per hour, respectively. This capacity loss represents Li atoms which accumulate in the thickening negative electrode SEI. Figures 9b and 9d show the fraction of capacity by which the charge endpoint slips each cycle and the fraction of capacity by which the charge end point slips each hour. This charge endpoint capacity slippage is primarily caused by electrolyte oxidation. Figures 9e and 9f show 1 - CE and \( (1 - CE)/(time \ of \ one \ cycle) \), respectively. The values in Figures 9a and
Figures 9a and 9c show that the fade term, $f/Q$, does not increase dramatically with potential, while, by contrast, Figures 9b and 9d show the $\Delta f/Q$ term increases dramatically with potential. For cells cycled to 4.5 V, $\Delta f/Q$ is an almost an order of magnitude larger than $f/Q$. Figures 9a and 9c show that the various additives do not impact $f/Q$ strongly at 4.2 V while Figures 9b and 9d show the additives have an enormous impact of limiting electrolyte oxidation compared to control cells at 4.2 V. At 4.2 V, since $f/Q$ of all the cells are similar, one can conclude that these additives have similar effects to control electrolyte on negative electrode SEI growth. By contrast, the charge endpoint capacity slippage of is strongly suppressed by the additives at 4.2 V. This is why the CE of cells containing the additives is greatly improved at 4.2 V. However, when the upper cutoff potential was increased to 4.4 V or 4.5 V, Figures 9b and 9d show that the charge endpoint capacity slippages show a similar increasing trend for all cells, with or without additives demonstrating the insidious impact of electrolyte oxidation.

At 4.4 V, additives can reduce the charge endpoint capacity slippage by almost a factor of 2 compared to control electrolyte but at 4.5 V the benefit is only about a 20% reduction compared to control electrolyte.

Figure 9 conveys an extremely important message about electrode-electrode interactions in these cells. The fact that the $f/Q$ term does not increase (in fact, it may decrease) with upper cutoff potential indicates that any oxidized species produced at the positive electrode which then migrate to the negative electrode do not compromise the negative electrode SEI in these cells. The failure mechanism in the cells will be shown below to be mainly caused by impedance growth due to the electrolyte oxidation.

After the 4.2 V continuous UHPC cycling, the same cells were transferred to long-term cycling with 0.1 V increased voltage range: 2.8–4.3 V at 55°C using currents 80 mA ($\sim C/3$). Figure 10a shows the capacity versus cycle number for the NMC111/graphite cells. Cells with 1% PBF were shown to have good long-term cycling performance with 1% TRIZIN showed more dramatic capacity loss after 150 cycles and much worse capacity retention than cells with PBF of PRZ. Figure 10b shows the difference between average charge and discharge voltage ($\Delta V$) vs cycle number indicating the impedance is stable during cycling (no significant increase). Therefore, the same long-term cycling tests were carried out on cells with the PBF-type additives with increased BF$_3$ content. The cells were cycled without clamps. The cell containing 2% PBF has the best capacity of all the BF$_3$-containing cells. Cells with 1% TRIZIN showed more dramatic capacity loss after 150 cycles due to the electrolyte oxidation.

The changes of ($\Delta V$) are a good indicator of the impedance growth during cycling. The cells with PBF have the smallest increase of $\Delta V$ indicating the impedance is stable during cycling (no significant increase), which correlates well to their improved capacity retention. The other cells have large slopes in $\Delta V$ vs cycle number indicating the overall impedance grows rapidly which is consistent with the capacity fade during cycling. Figure 10b shows that impedance increase is a major factor for the degradation of these cells cycled to 4.3 V and 55°C.

After 4.4 V “Barn” UHPC cycling, the same cells were transferred to long-term cycling between 2.8 V and 4.5 V at 40.0°C using currents corresponding to C/2.5 (100 mA). Figure 10c shows the capacity fade during cycling. The other cells have large slopes in $\Delta V$ vs cycle number indicating the overall impedance grows rapidly which is consistent with the capacity fade during cycling.

### Table

| Cycle Number | Ch.EndCap.(mAh) | CE |
|--------------|----------------|----|
| 2            | 221            | 0.992 |
| 4            | 223            | 0.994 |
| 6            | 225            | 0.996 |
| 8            | 227            | 0.998 |
| 10           | 229            | 0.999 |

### Figure 6

UHPC data for NMC442/graphite pouch cells with PBF-type additives, 2%PES and control electrolyte. The cells were tested at 40°C with an upper cutoff of 4.5 V. (a and e) coulombic efficiency (CE), (b) discharge capacity, (c) $\Delta V$, the difference between average charge and discharge potentials and (d and f) charge endpoint capacity. All are plotted versus cycle number.

### Figure 9

UHPC data for NMC442/graphite pouch cells with PBF-type additives, 2%PES and control electrolyte. The cells were tested at 40°C with an upper cutoff of 4.5 V. (a and e) coulombic efficiency (CE), (b) discharge capacity, (c) $\Delta V$, the difference between average charge and discharge potentials and (d and f) charge endpoint capacity. All are plotted versus cycle number.
versus cycle number for the unclamped NMC442/graphite pouch cells with BFs-containing additives along with comparative cells including control and cells with 2% PES. The control cells have quite poor performance during this high voltage cycling. Cells with 2% PES start to show large capacity fade after 200 cycles. Cells with 1% PBF or 0.5% PRZ have better capacity retention than cells with 1% TRIZIN and reach 80% of initial capacity after about 400 cycles. Figure 10d shows the difference between average charge and discharge voltage (ΔV) vs. cycle number for the same cells shown in Figure 10c. The large ΔV changes indicate the impedance increase of the cells. There is rapid capacity fading during the 4.5 V cycling compared to the 4.3 V, 55°C cycling (Figure 10a).

From both the charge endpoint capacity slippage results for the cells as shown in Figure 9b and the changes in ΔV (overall impedance change) shown in Figures 10b and 10d, cells containing 2% PBF showed the smallest charge endpoint capacity slippage at different voltages implying less electrolyte oxidation at cathode surface up to 4.5 V and the slowest impedance growth during long-term cycling. It is our opinion that the electrolyte oxidation is the root cause of the impedance growth, so limiting charge endpoint capacity slippage leads to less impedance growth and better charge-discharge cycling performance.

Figures S4 and S5 show the impedance spectra (measured at 3.8 V and 10.0°C) and gas volume generated in the cells displayed in Figures 8 and 9.

**Figure 7.** Nyquist plots of the impedance spectra of the cells before and after UHPC at different voltages. (a) The cells described on Figure 4: before UHPC cycled at 4.2 V, and (b) after UHPC cycled at 4.2 V, (c) the cells described in Figure 5: before UHPC cycled at 4.4 V, (d) after UHPC cycled at 4.4 V, (e) the cells described in Figure 6: before UHPC cycled at 4.5 V, (f) after UHPC cycled at 4.5 V.

**Figure 8.** Summary of volume expansion of pouch cells after the UHPC cycling presented in Figures 4, 5 and 6. a) cells cycled to 4.2 V; b) cells cycled to 4.4 V; c) cells cycled to 4.4 V; d) cells cycled to 4.5 V.

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**Table III.** 1-CE, fraction of capacity loss/cycle (f/Q) and fraction of charge endpoint capacity slippage/cycle (Δc/Q) calculated from 4.2, 4.4 and 4.5 V UHPC data of the cells with different electrolytes.

| Additives | 1%PBF | 2%PBF | 0.5%PRZ |
|-----------|-------|-------|---------|
|           | 1-CE_{Elec} | f/Q  | Δc/Q   | 1-CE_{Elec} | f/Q  | Δc/Q   | 1-CE_{Elec} | f/Q  | Δc/Q   |
| **1%PBF** |       |       |         |       |       |         |       |       |         |
| 4.2 V     | 0.0019 | 0.000727 | 0.001136 | 0.0018 | 0.000834 | 0.00095 | 0.0023 | 0.000854 | 0.001143 |
| 4.4 V     | 0.0032 | 0.000292 | 0.0002708| 0.0029 | 0.000245 | 0.0002781| 0.0042 | 0.000345 | 0.0003046|
| 4.5 V     | 0.0044 | 0.000455 | 0.004000| 0.0045 | 0.000386 | 0.004182| 0.0058 | 0.000459 | 0.0004582|
| **1%TRIZIN** |       |       |         |       |       |         |       |       |         |
| 4.2 V     | 0.0025 | 0.000854 | 0.00143 | 0.0055 | 0.00082 | 0.00467 | 0.0023 | 0.000854 | 0.004023 |
| 4.4 V     | 0.0042 | 0.000719 | 0.0003961| 0.0046 | 0.000854 | 0.00047 | 0.0037 | 0.000011 | 0.0003650|
| 4.5 V     | 0.0058 | 0.000847 | 0.005083 | 0.0058 | 0.000869 | 0.005068 | 0.0049 | 0.00025 | 0.0004718|
| **Control** |       |       |         |       |       |         |       |       |         |
| 4.2 V     | 0.0025 | 0.000854 | 0.00143 | 0.0055 | 0.00082 | 0.00467 | 0.0023 | 0.000854 | 0.004023 |
| 4.4 V     | 0.0042 | 0.000719 | 0.0003961| 0.0046 | 0.000854 | 0.00047 | 0.0037 | 0.000011 | 0.0003650|
| 4.5 V     | 0.0058 | 0.000847 | 0.005083 | 0.0058 | 0.000869 | 0.005068 | 0.0049 | 0.00025 | 0.0004718|
Figure 9. Summary of the (a) fraction of capacity fade/cycle, $F(\Delta C)/Q$; (b) fraction of capacity by which the charge endpoint slips each cycle, $\Delta V/Q$; (c) fraction of capacity fade/hour, $F(\Delta C)/Q \cdot t$; (d) fraction of capacity by which the charge end point slips each hour, $\Delta V/Q \cdot t$; (e) 1-CE and (f) 1-CE/time of a cycle of the cells tested in the different voltage ranges using the UHPC.

Figure 10. (a) Discharge capacity versus cycle number for NMC111/graphite pouch cells cycled without clamps at C/3 (0.08 A) at 55. ± 0.1°C between 2.8 and 4.3 V with different additives and control electrolyte, (b) difference between average charge and discharge voltage (delta V) of the same cells, all plotted versus cycle number, (c) discharge capacity versus cycle number for NMC442/graphite pouch cells cycled without clamps at C/2.5 (0.1 A) at 40. ± 0.1°C between 2.8 and 4.5 V with different additives and control electrolyte. A C/20 cycle was included every 50 cycles, (d) difference between average charge and discharge voltage (delta V) of the same cells, all plotted versus cycle number.
10c and 10d after 500 cycles. The cell with control electrolyte shows a significant gas production and impedance growth during cycling while the cells with other additives show much less gas evolution and impedance growth. This reduction in gas production, which helps maintain stack pressure on the electrodes in the cells, is why the cells with TRIZIN, which have similar charge endpoint capacity slippage and coulombic efficiency to control cells (see Figure 9) have much better capacity retention than control cells.

Conclusions

Pyridine-Boron Trifluoride, Pyrazine-(BF₃)₂ and Triazine-(BF₃)₃ are easily synthesized using similar synthesis reactions. The additives were evaluated using various experiments including UHPC, impedance, gas measurements and long-term cycling in different potential ranges. These additives suppress impedance growth. The comparisons between PBF, PRZ and TRIZIN indicate that cells with PBF had the highest CE and the smallest charge endpoint capacity slippage in every voltage range for both NMC111 and NMC442 type cells. 0.5% PRZ has comparable effects to 1% PBF. Cells with 1%TRIZIN cells showed quite low CE and large charge endpoint capacity slippage at every voltage so the effects of PBF-type additives are not simply improved by increasing the ratio of BF₃ in the molecules. Additionally, the type of Lewis base may also be very important. PBF, with the simplest structure, outperforms the other derivatives.

When the upper cutoff potential was increased, the charge endpoint capacity slippages (ΔQ/Q, the dominant term) showed a similar increasing trend for all cells suggesting the benefits of additives in suppressing electrolyte oxidation is limited at the highest voltages (4.4 V and 4.5 V). The similar electrolyte oxidation (with/ without additives) which occurs at 4.5 V on the cathode surface is caused by the oxidation of carbonate solvents. Although PBF performed as a very promising additive, alternative solvents may be required to significantly reduce the charge endpoint capacity slippage and improve the capacity retention during cycling to 4.5 V.

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