Development of Pyridine-Boron Trifluoride Electrolyte Additives for Lithium-Ion Batteries

Mengyun Nie, Jian Xia,* and J. R. Dahn**,*

Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia B3H4R2, Canada

A series of novel electrolyte additives based on Lewis acid/base adducts has been designed and successfully synthesized. The synthesis is very simple: a pyridine derivative is mixed with boron trifluoride dissolved in diethyl ether to yield a solid crystalline product. The effect of Pyridine-Boron Trifluoride (PBF) and its derivatives has been thoroughly evaluated in Li[Li0.13Mn0.52Co0.33]O2/graphite and Li[Ni0.5Mn0.42Co0.08]O2/graphite pouch cells. Evaluation experiments, including high voltage storage, gas production, electrolyte decomposition, and interfacial impedance spectroscopy measurements, were performed to determine the effect of these additives on the stability and performance of these cells. The results were compared to baseline experiments on cells containing the novel additives. The results of these experiments showed that the PBF additives improve the capacity retention and maintain low impedance during high voltage cycling, in contrast to cells containing VC. The PBF additives are competitive with other known additives and can be used in high-voltage/high-temperature lithium-ion battery applications.

© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI:10.1149/2.0271507jes] All rights reserved.

Manuscript submitted February 25, 2015; revised manuscript received March 19, 2015. Published March 31, 2015.

Li-ion batteries (LIBs) are widely used in applications from portable consumer electronics to electric vehicles (EVs). In order to further increase energy density and improve battery performance, high-voltage electrode materials and electrolytes have been developed during the past two decades. However, there are big challenges which have prevented commercialization of these materials: 1) transition metal dissolution from positive electrode materials at high potential and; 2) electrolyte (salts and solvents) decomposition at high potential and elevated temperature.

The transition metal dissolution problem, more specifically manganese dissolution from spinel-type positive electrode materials such as LMO and LNMO, causes rapid capacity loss during charge-discharge cycling in Li-ion cells using these materials. Based on the proposed mechanisms of Mn dissolution, soluble manganese ions reach the graphite negative electrode and perturb the SEI layer on the graphite surface. Several methods have been reported to suppress manganese dissolution and hence improve battery performance. Among these methods, incorporating additives in the electrolyte is easy and can also be effective.

Vinyl pyridines reported by Komaba et al. for carbon/LiMn2O4 cells and Schiff bases patented by ATL company for graphite/NMC cells appeared to be effective for suppressing manganese dissolution. Both of these basic compounds, can trap dissolved transition metal ions in the electrolyte by forming coordinated complexes, thus inhibiting the reductive deposition of these metal ions onto negative electrode surface. Also, as Lewis bases, they have the potential to neutralize acidic gaseous compounds like PF5, HFn, and CO2 generated by electrolyte (LiPF6, and organic carbonates) decomposition, thus reducing gas generated during cycling.

Electrolyte decomposition is caused by electrochemical reactions (reduction or oxidation) within Li-ion cells, especially at elevated temperature and/or high voltage, causes gas generation, impedance growth and can consume active Li. Zuo et al. reported, by adding 1.0 - 2.0 wt% of LiBF4 into LiPF6-based electrolyte, significant improvements in capacity retention and interfacial impedance of graphite/Li[Ni0.5Mn0.42Co0.08]O2 pouch cells cycl aged between 3.0 and 4.5 V. They state in their conclusion: “On the other hand, in the presence of LiPF6, LiBF4 decomposes to BF3, which is believed to take part in the formation of a passivation film on the Li[Ni0.5Mn0.42Co0.08]O2 cathode during high voltage operation.” In addition, BF3, like many other electron deficient borates or boranes, is a typical Lewis-acid that could function as an anion receptor to help dissolve one of the LiPF6 decomposition products—LiF, from the electrolyte/electrode interface. The use of BF3 and some BF3 organic carbonate complexes as electrolyte additives have been patented by F-One Moli Energy and Toyota.

In this work, a series of novel additives, intended to solve the two problems mentioned above, are presented. The additives combine two major useful functional groups including an organic base and BF3. These additives are easily made at low cost compared to many common additives. Thorough battery performance evaluation data (thermal storage, impedance, long-term cycling, etc.) is reported to demonstrate that these additives impart significant benefits to graphite/NMC cells.

Experimental

Synthesis of pyridine-BF3 and derivative compounds.— To a dry Nalgene bottle (reaction flask) in an inert atmosphere, (N2, He or Ar) 2.0 mL BF3/diethyl ether (boron trifluoride diethyl etherate, 2.30 g, ≥ 46.5% BF3, Sigma-Aldrich) was added. Then 1.5 ml pyridine (1.47 g Sigma-Aldrich, 99.8%) was added slowly. The reaction was highly exothermic, so the reaction system was allowed to cool down before further pyridine was added. White or colorless crystals precipitated immediately. Once no further precipitate was observed, the reaction mixture in the sealed Nalgene bottle was transferred to a -20 °C freezer to grow crystals. The solid products were collected and transferred to a vacuum oven and vacuum dried overnight at 45 °C. The reaction follows a 1:1 stoichiometric ratio, and any slight excess of either reactant could be easily removed by vacuum drying. The purity of synthesized samples after vacuum drying was checked by NMR (H, 19F, 11B) and no peaks of remaining reactants and/or impurities like BF3; ether were observed in the NMR spectra (see supporting information). Figure 1a shows a schematic of the synthesis procedure followed. Syntheses following the same procedure were made for the pyridine derivatives listed in Figure 1b and Table I to make the desired electrolyte additives.

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 either singly or in combination with other additives. Additive components were added at specified weight percentages in the electrolyte. Other standard electrolyte additives were also used for comparison. These included vinylene carbonate (VC), prop-1-ene,1,3-sultone (PES), methane methylenedisulfone (MMDS), tris-(trimethyl-silyl)-phosphite (TTPS), and triaryl phosphate (TAP). The PBF additives are competitive with other known additives and can be used in high-voltage/high-temperature lithium-ion battery applications.
Dry Li[Ni_{0.42}Mn_{0.42}Co_{0.16}]O_{2} (NMC442)/graphite pouch cells (240 mAh) balanced for 4.7 V operation or Li[Ni_{0.42}Mn_{0.42}Co_{0.16}]O_{2} (NMC111)/graphite pouch cells (220 mAh) balanced for 4.4 V operation were obtained without electrolyte from Li-Fun Technology (Zhuzhou City, Hunan Province, PRC, 412000, China). All pouch cells were vacuum sealed without electrolyte in China and then shipped to Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Hangzhou, Hangzhou, China. 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.

**Figure 1.** (a) Synthesis procedure and structure of Pyridine Boron Trifluoride (PBF). (b) Molecular formula and abbreviation for the novel PBF-series additives.

**Table 1.** Pyridine derivatives used to make electrolyte additives and the solubility in typical electrolyte.

| Reagent                  | Product (electrolyte additive)                                                                 | Short name | Solubility in 1 M LiPF_{6} EC:EMC 3:7 |
|-------------------------|------------------------------------------------------------------------------------------------|------------|----------------------------------------|
| pyridine                | Pyridine boron trifluoride                                                                      | PBF        | > 2%                                   |
| 3-fluoropyridine        | 3-fluoro pyridine boron trifluoride                                                              | 3F-PBF     | > 2%                                   |
| 2-fluoropyridine        | 2-fluoro pyridine boron trifluoride                                                              | 2F-PBF     | Approx. 2%                             |
| 3,4-Lutidine            | 3,4-lutidine pyridine boron trifluoride                                                          | LUTID      | > 2%                                   |
| 3-pyridine carbonitrile | 3-pyridine carbonitrile pyridine boron trifluoride                                               | PCN        | > 2%                                   |
| 4-vinyl pyridine        | 4-vinylpyridine boron trifluoride                                                                | VPBF       | Approx. 2%                             |
| 4-trifluoromethyl pyridine | 4-trifluoromethylpyridine boron trifluoride                                                   | TRIFM      | > 2%                                   |

**Electrochemical impedance spectroscopy.**—Electrochemical impedance spectroscopy (EIS) measurements were conducted on NMC/Graphite pouch cells before and after storage and also after cycling on the ultra high precision charger (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 mV at 10. ± 0.1 °C. A Biologic VMP-3 was used to collect this data.

**Ultrahigh precision cycling and storage experiments.**—The cells were cycled using the Ultra High Precision Charger (UHPC) at Dalhousie University between 2.8 and 4.2 V or 4.4 V at 40 ± 0.1 °C using currents corresponding to C/20 for 16 cycles where comparisons were made. Some cells were stored before UHPC cycling to mature their negative electrode SEI before testing.

The cycling/storage procedure used in these tests is described as follows. Cells were first charged to 4.2, 4.4 or 4.5 V and discharged to 2.8 V two times. Then the cells were charged to 4.2, 4.4 or 4.5 V at a current of C/20 (11 mA) and then held at 4.2, 4.4 or 4.5 V until the measured current decreased to C/1000. A Maccor series 4000 cycler was used for the preparation of the cells prior to storage. After the pre-cycling process, cells were carefully moved to the storage system which monitored their open circuit voltage every 6 hours for a total storage time of 500 h. Storage experiments were made at 40 ± 0.1 °C.

Long term cycling was conducted at 4.2 V and 4.4 V. The cells were charged and discharged at 80 mA between 2.8 and 4.2 V or between 2.8 and 4.4 V at 55 ± 0.1 °C using a Neware (Shenzhen, China) charger system.

**Top of charge hold cycle experiments and frequency response analysis.**—Some cells were tested extremely aggressively at 40 ± 0.1 °C to really push the limits of the electrolyte. These cells were subjected to two test protocols:

Type 1 - The cells were charged and discharged at 80 mA current (C/3) between 2.8 and 4.4 V and held at 4.4 V for 20 hours at 40 ± 0.1 °C before discharging again on a Maccor series 4000 cycler;

Type 2 - the cells were charged and discharged at 44 mA (C/5) between 2.8 and 4.4 V and held at 4.4 V for 20 hours every cycle. Automated impedance spectroscopy measurements were made after every three charge-hold-discharge cycles using a frequency response analyzer (FRA)/cycler system built at Dalhousie University. During FRA measurements, the cells were charged and discharged at 12 mA and AC impedance spectra were collected every 0.1 V.
Figure 2. (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.

Determination of gas evolution in pouch cells.—Ex-situ (static) gas measurements were used to measure gas evolution during formation and during cycling.22 The 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 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, suspended in a fluid of density, ρ, is related to the change in cell volume, Δv, by

\[
Δv = \frac{Δm}{ρ}
\]  

[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 (18.2 MΩ·cm) that was at 20 ± 1 °C for measurement.

Results and Discussion

Figure 2 shows the cell terminal voltage as a 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 concentrations of the additive, PBF. Figure 2a shows a plateau appeared at 2.3 V in PBF-containing cells (negative electrode potential ≈ 1.2 V vs Li/Li⁺) and the capacity of the plateau increased with PBF content. The peak in dQ/dV vs. V in Figure 2b corresponding to the plateau at 2.3 V is associated with the reduction of PBF at the graphite surface. Figure 2b indicates that PBF is reduced before EC. Figure 2b shows a second set of peaks corresponding to the reduction of EC at 2.9 V (≈ 0.8 V vs Li/Li⁺) appeared in all the cells. The intensity of the EC reduction peaks did not show significant changes when the concentration of the PBF additive was varied.

Figure 3 plots the capacity of the plateau at 2.3 V from Figure 2a versus the concentration of PBF added to the electrolyte. Most

similar to that which occurs during the reduction of pyridinium.23 For every radical anion in solution, one Li⁺ originating from the NMC, would also have to be in solution to maintain electrical neutrality in solution. However, further research is required to determine the mechanism of the reduction of PBF.

Figure 4a shows the cell terminal voltage versus capacity during the first charge to the first degassing point (3.5 V) for NMC442/graphite pouch cells containing 2 wt% of the additives in Figure 1. Most

radical anions with the electron delocalized on the pyridine ring

Figure 3. Capacity of the plateau at 2.3 V vs. the concentration of PBF added to the electrolyte.

Figure 4. (a) The cell terminal voltage versus capacity during the first charge to the first degassing process and (b) differential capacity (dQ/dV) versus voltage (V) during the same formation process for NMC442/graphite pouch cells containing novel PBD derivatives.
interesting about Figure 4a is that the cells containing PBF, LUTID and PCN all show extended plateaus of about the same length near 2.3 to 2.5 V suggesting all the additive in the cells undergoes a one-electron reduction as discussed above. The results for cells with the other additives are very different. 2F-PBF shows no obvious feature associated with electron transfer to the pyridine ring. By contrast, 3F-PBF shows an apparent reduction plateau near 2.1 V but it does not appear to have enough capacity to correspond to a one-electron reduction of ALL the 3-PBF. Experiments as a function of additive concentration, as in Figure 2, would be useful for all these additives, but these have not yet been made. Rather than speculate further, we suggest that experiments in Li/graphite half cells as a function of additive concentration and careful cyclic voltammetry studies of these additives are required to help elucidate mechanisms. Figure 4b shows the differential capacity (dQ/dV) vs. V curves of the same cells described by Figure 4a. The addition of the various electron withdrawing or electron donating groups on the pyridine ring change the dQ/dV curves dramatically. It is not certain from these results, however, whether reaction products from the BF₃-containing additives are incorporated in the negative electrode SEI or not after a first partial charge to 3.5 V. Based on the results in Figures 2–4, it is believed that products from PBF, LUTID, VPBF and TRIFM do not seem to be incorporated and it is possible that products from 3F-PBF, 2F-PBF, and PCN may be incorporated. A significant amount of surface science studies would be required to determine the fate of these additives. Instead, the focus of this paper is on how these additives affect Li-ion cell performance.

Figures 5a and 5b show the open circuit voltage (OCV) versus time during storage for NMC111/graphite pouch cells at 4.2 V and NMC442/graphite pouch cells at 4.5 V (40 °C). The cells described by Figure 5 contain different electrolyte additives. Figure 5a shows that cells with 1% PBF have a smaller voltage drop after 500 hours compared to cells with 2% VC and that those cells are much better than cells with control electrolyte only. When 1% PBF is combined with 2% VC, the new combination (1% PBF + 2% VC) shows an even smaller voltage variation, less than a 50 mV loss from 4.2 V. This is an extremely small voltage drop, smaller than provided by any of the 110 additives or additive combinations studied in the extensive work of Wang et al. on NMC111/graphite cells (see Figure S1 and Table II in the supplemental material of reference 24). Figure 5a suggests that PBF helps limit electrolyte oxidation, transition metal dissolution and/or shuttle type reactions on the positive electrode surface. Figure 5b shows that NMC442/graphite cells containing 0.5% or 1% PBF perform much better than those with control electrolyte at 4.5 V. Unfortunately, data for cells with 2% VC is not available for cells stored at 4.5 V. Figure 6 shows a summary of the storage testing performed on NMC111/graphite cells at 4.2 V and on NMC442/graphite cells at 4.4 and at 4.5 V. All testing was done at 40 °C. Figure 6 shows that cells with PBF derivatives show smaller self-discharge than control cells during storage at 4.2 V, comparable self-discharge to cells with 2% VC at 4.4 V and smaller self-discharge than cells with control electrolyte at 4.5 V. Figure 6 also shows the benefit of adding more PBF additive. Figure 6b shows that increasing the PBF content from 1% to 1.5% improves self-discharge and Figure 6c shows a similar improvement when the PBF content is increased from 0.5 to 1.0%. Thus higher concentrations were explored in further experiments.

Figure 7 shows the amount of gas evolved during the storage periods at 4.2, 4.4 and 4.5 V for the cells described in Figure 6. All cells evolve less than 0.02 ml of gas which is less than 1% of the total cell volume (2.2 ml). Some of PBF-derivative containing cells actually shrank slightly suggesting gas generation is not problematic at these voltages and 40 °C. The results in Figures 5 and 6 suggest that the PBF additives are very useful and warrant further study. Figures 8a and 8b show the impedance spectra of NMC442/graphite pouch cells before and after storage at 4.5 V and 40 °C. All impedance measurements were made at 3.8 V and at 10. ± 0.1 °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. For simplicity of notation, the diameter of the semicircle is called Rct here. Figure 8a shows that the cells with 1% 2F-PBF had the largest Rct before storage and Rct for those cells decreased slightly after storage. On the contrary, cells with 1% LUTID showed no obvious change in Rct before and after storage suggesting LUTID might be useful for preventing impedance growth. Cells containing the other new additives showed an increase in Rct during storage but their impedance spectra were not significantly distorted. By contrast, the impedance spectra of the control cells changed from overlapping semicircles to a pair of distinct semicircles. This is caused by growth of impedance at the positive electrode side. Based on only the data in Figure 8, it is not clear if the additives PBF and VPBF are useful in preventing impedance growth.

Figure 9 shows ultra-high precision cycling data for NMC111/graphite pouch cells cycled at 40 °C between 2.8 and 4.2 V using a constant current corresponding to C/20. Figure 9 shows results for cells with control, 1% PBF, 2% VC and 1% PBF+2% VC. Figure 9a shows the coulombic efficiency, Figure 9b shows the discharge capacity and Figure 9c shows the charge end point capacity all plotted versus charge-discharge cycle number. Cells with 1% PBF and cells with 2% VC show similar CE versus cycle behavior and similar charge end point capacity slippage. Cells with 1% PBF + 2% VC show higher CE (better) and lower charge end point capacity slippage (better) then...
the cells with 1% PBF only or the cells with 2% VC only. Figure 5a shows that cells with 1% PBF + 2% VC show less potential drop during 4.2 V storage than cells with 2% VC only or cells with 1% PBF only. Therefore, the results in Figure 5a and in Figure 9c match our previous experience of the relationship between charge end point capacity slippage and V\text{drop} during storage.\textsuperscript{25,27}

After the cycling tests using the UHPC, the EIS spectra of the cells described in Figure 9 were measured at 3.8 V and 10.0 ± 0.1°C. Figure 10 shows that the impedance of the cells containing 1% PBF alone and 2% VC alone were virtually unchanged before and after cycling for 16 cycles at 40°C. By contrast the cells with 1% PBF + 2% VC had a dramatically larger initial impedance and which doubled after the charge-discharge cycling period. This suggests that VC and PBF interact together in an unwanted fashion and should probably not be combined together as co-additives. For this reason, cells containing PBF + VC were not prepared for long-term cycle tests.

Figure 11a shows the discharge capacity of NMC111/graphite cells vs. cycle number during extended testing (~7 months) at 55°C. In order to clearly compare the curves, the capacities of the cells were normalized to the same starting value - 210 mAh. The actual capacities were in the range of 205 to 217 mAh. The cells with control electrolyte lost more than 20% of their initial capacity in the first 225 cycles. Figure 11a compares the capacity retention of cells with 1% PBF to cells with other well-known additives.\textsuperscript{24,28} The performance of cells containing only 1% PBF is competitive to that of NMC111/graphite.

### Figure 6
Voltage drop during storage at 40°C of the NMC/graphite pouch cells with various PBF-series additives (a) 4.2 V (b) 4.4 V and (c) 4.5 V. Duplicate cells were used in these tests and the errors bars represent the standard deviation of the two measurements.

### Figure 7
Summary of gas evolved during storage at different voltages as indicated.

### Figure 8
Impedance spectra of NMC/graphite pouch cells with PBF-series additives stored at 40°C (a) before 4.5 V storage (b) after 4.5 V storage.

### Figure 9
UHPC data of NMC111/graphite pouch cells with 1% PBF, 2% VC or 1% PBF + 2% VC. The cells were tested at 40°C with an upper cutoff of 4.2 V. (a) Columbic efficiency (CE), (b) discharge capacity and (c) charge end point capacity. All are plotted versus cycle number.
Figure 10. Impedance spectra of NMC111/graphite pouch cells with 1% PBF, 2% VC or 1% PBF + 2% VC (a) before and (b) after UHPC cycling and (c) impedance spectra of the cells with 1% PBF, 2% VC and control electrolyte before and after UHPC cycling with and expanded scale.

Figure 11. (a) Discharge capacity versus cycle number for NMC111/graphite pouch cells containing PBF and other well-known additives as indicated. The cells were cycled with 80 mA between 2.8 - 4.2 V at 55°C. (b) Summary of gas evolved during 500 cycles between 2.8 - 4.2 V at 55°C. Error bars represent the standard deviation of the data.

Figure 12. UHPC data for NMC442/graphite pouch cells cycled between 2.8 - 4.4 V at 40°C with a series of new additives as indicated (a) CE (b) discharge capacity. The data are plotted versus cycle number.

cells containing the best additive blends reported previously. The cells were cycled without clamps, so gas evolution can affect the capacity retention. Figure 11b shows the amount of gas generated after 500 cycles for the cells in Figure 11a. Cells with 1% PBF generated less gas than cells with control electrolyte and comparable gas to cells with VC211 and 2% VC, but more than cells containing PES211. There is no doubt that PBF is a very interesting additive for NMC/graphite cells tested to 4.2 V and future studies should examine PBF in combination with other additives.

The new PBF-based additives were examined in cycling tests at higher voltage. Figure 12 shows UHPC data for NMC442/graphite pouch cells cycled at 40 ± 0.1°C between 2.8 and 4.4 V using currents corresponding to C/20. These cells had previously been stored at 4.4 V and 40°C for 500 h and are the same cells described by Figure 6b. The columbic efficiency (Figure 12a) and normalized discharge capacity...
The impedance of the NMC/graphite pouch cells was the highest CE. Cells with PBF-based additives, the cells with 1.5% PBF additive have equal to that of the cells containing VC. It appears that, among the cells with PBF-based additives, the cells with 1.5% PBF additive have the highest CE.

Figure 13 shows the evolution of impedance of the cells that were stored at 4.4 V (Figure 6b) and then cycled between 2.8 and 4.4 V (Figure 12). The impedance of the NMC/graphite pouch cells was measured at 3.8 V and 10. ± 0.1°C for all these cells. Figure 13a shows the impedance spectra immediately after formation, Figure 13b shows the results after the storage period and Figure 13c shows the results after the cycling period. Figures 13d and 13e focus on the behavior of the cells with 1% PBF or 1.5% PBF after formation (13d) and after UHPC cycling (13e). Figures 13a to 13c show that the impedance of the VC-containing cells increases dramatically during exposure to high potentials, consistent with the work of Ma et al., 26 while the impedance the cells with PBF and PBF derivatives increases less significantly. Figures 13d and 13e show that adding more PBF increases the initial impedance but slows impedance growth. The PBF-based additives appear to have significant value in controlling impedance increase.

Figure 14 summarizes the results in Figure 12a and Figure 13c as well as additional data. Figure 14a shows the columbic inefficiency calculated as (1-CE)*100%. Figure 14b shows the charge end point capacity slippage measured during the UHPC cycling described by Figure 12. Figure 14c shows the amount of gas evolved during storage and the additional gas evolved during UHPC cycling. Finally, Figure 14d summarizes the impedance data shown in Figure 13c. Although the error bars are large, Figure 14a shows the cells with 2% VC had the largest CIE (bad) of all cells. Figure 14b shows that cells with 1% PBF, 1.5% PBF and 1% VPBF, have similar charge end point capacity slippage during 4.4 V cycling to cells containing 2% VC. Figure 14c shows that the volume change of the cells due to gas evolution was in the range of 0.02 - 0.06 mL, which is less than 1% of the pouch cell volume, and such a small change should not lead to loss of stack pressure during these measurements. Figure 14d shows the cells containing 2% VC had significantly larger Rct than cells with the PBF-based additives after the testing period. The new additives appear to be better than VC for use at 4.4 V.

Figure 15 shows the discharge capacity versus cycle number of NMC442/graphite pouch cells containing different additives under extremely aggressive conditions. The cells were cycled between 2.8 V and 4.4 V at 55°C with 80 mA current (∼ C/3). The cells were cycled without clamps, so generated gas would promote loss of stack pressure. After 500 cycles (more than 4 months), all of these cells retained less than 80% of their initial capacity but the cells with 2% PBF performed best. All the cells with PBF-based additives showed better capacity retention than the cells with PES211 or 2% triallyl phosphate (TAP). TAP has been reported to be a useful high voltage additive by Shi et al., 31 and hence it was selected for comparison. Cells with additives based on PBF and its derivatives showed promising long-term cycling results at high voltage (4.4 V) and high temperature (55°C).

Figure 16 summarizes the capacity retention (a), volume change (b) and impedance (c) of the cells described by Figure 15 after 500 cycles at 55°C. Figure 16a shows that 2% PBF appears to be best under these conditions and 2% TAP is worst. Figure 16b shows that all cells expand by about 0.2 mL during the cycling except for cells with 2% LUTID or 2% TAP. The large volume change in the cells with 2% TAP could be a factor in the poor capacity retention. Figure 16c shows the charge-transfer resistance of cells measured after long-term cycling and Figure S8 shows the detailed Nyquist plots of the same cells before and after long-term 55°C cycling. Cells with PBF-based additives, like PBF, LUTID, TRIFM and 3F-PBF had small impedance, similar to that of cells containing PES-211. Cells with 2% 2F-PBF, 2% VPBF and 2% PCN had larger impedance than those based on PBF and its derivatives in addition to those of PBF, LUTID, TRIFM and 3F-PBF but their impedances were still much smaller than that of cells with 2% TAP. These new additives...
Figure 15. Discharge capacity versus cycle number for NMC442/graphite pouch cells with PBF-based additives and comparison cells containing PES-211 or TAP. The cells were cycled between 2.8–4.4 V at 80 mA at a temperature of 55°C.

yielded improvements in controlling gas generation and impedance growth which are critical to long-term cycle performance (capacity retention, cycle life, etc.).

To explore further the effect of the PBF-based additives on NMC442/graphite cells operating at high potential, cycle-hold-cycle protocols, where cells were held at 4.4 V for 20 h before discharging, were used. The details of these protocols, called Type 1 and Type 2, were given in the Experimental section. During the potentiostatic hold for 20 h at 4.4 V, electrolyte oxidation occurs and can hopefully be mitigated by the electrolyte additives. Figure 17a shows the capacity versus cycle number curves for cells cycled with the Type 1 protocol at 40°C. Cells with 2% PBF performed best, in agreement with Figure 15. The new cycle protocols minimize, somewhat, the effect of impedance growth on capacity because the cells are given 20 h to fully charge. Therefore it is very useful to simultaneously monitor the impedance spectra versus potential and cycle number as is done in the Type 2 protocol. Figure 17b shows the capacity versus cycle number curves for cells cycled with the Type 2 protocol at 40°C. Cells with control electrolyte, 2% TRIFM and with 2% VC additive show dramatic capacity loss after 15, 20 and 45 cycles, respectively, while the other cells do not. Figure 18 shows that the diameter of the semicircle of the impedance spectrum, Rct, measured at 4.3 V plotted versus cycle number for the cells described by Figure 17b. It is clear that the cells with control electrolyte, 2% TRIFM and 2% VC show dramatic impedance growth with cycle number, while the other cells do not. Clamps were applied to the cells with 2% PCN, 2% 3F-PBF and 2% 2F-PBF to see the impact of clamping after 42 cycles in Figure 17b. The clamping increased the capacity somewhat but did not change Rct significantly (see the 42 cycle point in Figure 18), as expected. This suggests the capacity increase caused by clamping mitigated the stack pressure loss caused by gas generation due to extended periods at high potential and 40°C. Therefore, it is important to compare the amount of volume expansion in the cells.

Figure 19 shows summaries of the testing using the Type 1 and Type 2 protocols. Figures 19a and 19b show the capacity loss in % after 30 cycles and 80 cycles, respectively, for cells tested using the
Type 1 (19a) and Type 2 (19b) protocols. Figures 19c and 19d show the volume expansion of the cells after the tests while Figures 19e and 19f show $R_{\text{ct}}$ measured after the displayed cycles in Figure 17 at 3.8 V.

The data in Figure 19e was measured at 10°C and 3.8 V for the cells cycled using the type 1 protocol and $R_{\text{ct}}$ of the cells measured using the FRA at 40°C and 3.8 V using the type 2 protocol. The values of $R_{\text{ct}}$ were measured at the end of the testing shown in Figure 17.

Summary

The results of the experiments on PBF-based electrolyte additives in NMC111/graphite and NMC442/graphite cells can be summarized as follows:

1. Cells with PBF-based additives generally performed much better in storage experiments than cells with control electrolyte and in a comparable manner to cells with 2% VC (Figs 5 and 6).
2. Gas evolution during storage for cells with PBF-based additives was similar to cells with 2% VC or control electrolyte (Figure 7).
3. UHPC cycling experiments to 4.2 V at 40°C showed that CE and charge end point capacity slippage was virtually identical for cells with 1% PBF or 2% VC (Figure 9) and that impedance changes during cycling were similar (Figure 10) suggesting 1% PBF could be a replacement for 2% VC.
4. Cells with 1% PBF outperformed cells with 2% VC or VC211 in cycling tests to 4.2 V at 55°C (Figure 11). Cells with 1% PBF performed virtually the same as cells with 2% PES + 1% MMD + 1% TTSPi (“PES-211”), an excellent electrolyte additive blend for NMC/graphite cells) in the same tests (Figure 11).
5. UHPC cycling experiments to 4.4 V at 40°C showed that CE and charge end point capacity slippage was very similar for cells with 1% PBF or 2% VC (Figures 12 and 14). Increasing the PBF content to 1.5% may improve performance. Impedance growth in cells during cycling to 4.4 V was much less for the PBF-based additives than for 2% VC (Figure 13).
6. Charge discharge cycling experiments at 55°C between 2.8 and 4.4 V showed that cells with PBF-based additives had better capacity retention than cells with PES-211 or 2% TAP (Figure 15). During these tests the impedance and gas production of the most cells with PBF-based additives remained comparable to PES-211 (Figure 16).
7. During aggressive charge-discharge cycling at 40°C with 20 h holds at 4.4 V, cells with PBF-based additives (except TRIFM) outperformed cells with 2% VC or control electrolyte in terms of capacity retention and impedance growth, (Figures 17–19)

However, there was more gas generation in the cells with the PBF-based additives.

Conclusions

PBF and its derivatives are easily synthesized in a one-step process. Thorough evaluation of these additives shows that they are as effective or more effective than VC in NMC/graphite cells. When PBF-based additives were used in cells charged to 4.4 V, they helped suppress impedance increase in high voltage cycling and storage (4.4 V and 4.5 V). The charge-discharge cycling tests at 55°C and up to 4.4 V showed that PBF-based additives may bring special advantages to the table for high energy density NMC-based cells that get exposed to high temperature during operation (i.e. cells for power applications like PHEV and HEV). Based on these experimental results, this series of novel additives clearly needs to be combined with other additives and explored further as additive combinations have been shown to lead to enhanced properties. Such experiments are underway in our lab. Furthermore, we invite other researchers to assist in understanding the mechanisms involved in the function of PBF-based additives.

Acknowledgements

The authors acknowledge the financial support from NSERC and 3M under the auspices of the Industrial Research Chairs and Automotive Partnerships program. Useful discussions with Ang Xiao, Bill Lamanna and Kiah Smith of 3M Company are also gratefully acknowledged.

References

1. M. Armand and J.-M. Tarascon, Nature, 451, 652 (2008).
2. J. B. Goodenough and K.-S. Park, J. Am. Chem. Soc., 135, 1167 (2013).
3. M. S. Whittingham, Chem. Rev., 104, 4271 (2004).
4. A. Kratsisberg and Y. Elin, Adv. Energy Mater., 2, 922 (2012).
5. G. Q. Liu, L. Wen, and Y. M. Liu, J. Solid State Electrochem., 14, 2191 (2010).
6. N. P. W. Pieczonka, L. Yang, M. P. Balogh, B. R. Powell, K. Chemelewski, A. Manthiram, S. A. Kraczkovskiy, G. R. Wardow, M. Liu, and J.-H. Kim, J. Phys. Chem. C, 117, 26203 (2013).
7. J.-H. Kim, N. P. W. Pieczonka, Z. Li, Y. Wu, S. Harris, and B. R. Powell, Electrochimica Acta, 90, 556 (2013).
8. M. Park, X. Zhang, M. Chung, G. B. Less, and A. M. Sastry, Chem Mater., 26, 3128 (2014).
9. L. A. Shkrob, A. J. Krof, T. W. Marin, Y. Li, O. G. Poboeckov, J. Niklas, and D. P. Abraham, J. Phys. Chem. C, 118, 24335 (2014).
10. H. Liu and H. Zhou, Chem. Commun., 48, 1201 (2012).
11. J. Lu, C. Zhan, T. Wu, J. Wen, Y. Lei, A. J. Krof, H. Wu, D. J. Miller, J. W. Elam, Y. Sun, X. Qiu, and K. Amine, Nat. Commun., 5 (2014)
12. S. Komaba, B. Kaplan, T. Ohtsuka, Y. Kataoka, N. Kumagai, and H. Groult, *J. Power Sources*, **119**, 378 (2003).
13. S. S. Zhang, *J. Power Sources*, **162**, 1379 (2006).
14. S. Komaba, T. Itabashi, T. Ohtsuka, H Groult, N Kumagai, B. Kaplan, and H. Yashiro, *J. Electrochem. Soc.*, **152**, A937 (2005).
15. K. Wang, L. Jiang, Y. Zhang, J. Chen, and J. Fu, (2013) CN103280598A.
16. X. Zuo, C. Fan, J. Liu, X. Xiao, J. Wu, and J. Nan, *J. Electrochem. Soc.*, **160**, A1199 (2013).
17. Y. Wang, M. Zhang, U. V. Sacken, and B. M. Way, (2000) US6045948.
18. M. Matsui, (2014) US8765294.
19. C. Laurence and J.-F. Gal, *Lewis Basicity and Affinity Scales*, John Wiley & Sons, Ltd (2009)
20. T. M. Bond, J. C. Burns, D. A. Stevens, H. M. Dahn, and J. R. Dahn, *J. Electrochem. Soc.*, **160**, A521 (2013).
21. N. N. Sinha, T. H. Marks, H. M. Dahn, A. J. Smith, J. C. Burns, D. J. Coyle, J. J. Dahn, and J. R. Dahn, *J. Electrochem. Soc.*, **159**, A1672 (2012).
22. C. P. Aiken, J. Xia, D. Y. Wang, D. A. Stevens, S. Trussler, and J. R. Dahn, *J. Electrochem. Soc.*, **161**, A1548 (2014).
23. Y. Yan, E. L. Zeitler, J. Gu, Y. Hu, and A. B. Bocarsly, *J. Am. Chem. Soc.*, **135**, 14020 (2013).
24. D. Y. Wang, J. Xia, L. Ma, K. J. Nelson, J. E. Harlow, D. Xiong, L. E. Downie, R. Petibon, J. C. Burns, A. Xiao, W. M. Lamanna, and J. R. Dahn, *J. Electrochem. Soc.*, **161**, A1818 (2014).
25. N. N. Sinha, A. J. Smith, J. C. Burns, G. Jain, K. W. Eberman, E. Scott, J. P. Gardner, and J. R. Dahn, *J. Electrochem. Soc.*, **158**, A1194 (2011).
26. R. Petibon, L. Ma, and J. Dahn, *Abstract*, MA2014-02, 292, The Electrochemical Society Meeting Abstracts, Cancun, Mexico, Oct. 5-10 , 2014.
27. A. J. Smith, N. N. Sinha, and J. R. Dahn, *J. Electrochem. Soc.*, **160**, A235 (2013).
28. L. Ma, D. Y. Wang, L. E. Downie, J. Xia, K. J. Nelson, N. N. Sinha, and J. R. Dahn, *J. Electrochem. Soc.*, **161**, A1261 (2014).
29. B. Gyenes, D. A. Stevens, V. L. Chevrier, and J. R. Dahn, *J. Electrochem. Soc.*, **162**, A278 (2015).
30. L. Ma, J. Xia, and J. R. Dahn, *J. Electrochem. Soc.*, **161**, A2250 (2014).
31. Q. Shi and G. Sheng, (2014) CN103594729A.
32. J. C. Burns, A. Kassam, N. N. Sinha, L. E. Downie, L. Solnickova, B. M. Way, and J. R. Dahn, *J. Electrochem. Soc.*, **160**, A1451 (2013).
Erratum: Development of Pyridine-Boron Trifluoride Electrolyte Additives for Lithium-Ion Batteries [J. Electrochem. Soc., 162, A1186 (2015)]

Mengyun Nie, Jian Xia, and J. R. Dahn

Department of Physics and Atmospheric Science, Dalhousie University, Halifax, Nova Scotia B3H4R2, Canada

© 2015 The Electrochemical Society. [DOI: 10.1149/2.0241508jes] All rights reserved. Published May 6, 2015.

On page A1188, left column, the second paragraph under the Results and Discussion heading should be

Figure 3 plots the capacity of the plateau at 2.3 V from Figure 2a versus the concentration of PBF in the electrolyte. Figure 3 shows a linear relationship. If all the PBF added to the cell is reduced during the first charge, then the slope of the line in Figure 3 yields a 1.52 electron reaction. More likely is that the reaction is a two-electron reaction and that the PBF in portions of the electrolyte outside the jelly roll is not reduced. The linearity in Figure 3 suggests that PBF does not passivate the graphite electrode and, instead, passivation occurs in the following EC reduction. Further research is required to determine the mechanism of the apparent two-electron reduction of PBF.

On page A1188, right column, Figure 3 should be

![Figure 3](image_url)

**Figure 3.** Capacity of the plateau at 2.3 V vs. the concentration of PBF added to the electrolyte.