A Comparative Study of Pyridine Containing Lewis Acid-Base Adducts as Additives for Li[\(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\)]O\(_2\)/graphite Pouch Cells

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Three Lewis acid-base adducts including pyridine boron trifluoride (PBF), pyridine phosphorus pentafluoride (PPF) and pyridine sulfur trioxide (PSO) were used as electrolyte additives in Li[\(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\)]O\(_2\)/graphite pouch cells (NMC532/graphite). PBF, PPF and PSO have a common Lewis base (pyridine) but have different Lewis acids. Experiments included ultra-high precision coulometry (UHPC), electrochemical impedance spectroscopy (EIS), gas evolution, long-term continuous charge-discharge cycling and charge-hold-discharge cycling. The results showed that cells containing PBF and PPF had the smallest voltage drop during storage at 4.5 V and at 60 °C compared to cells with PSO and other adducts such as triaryl phosphates (TAP) and vinylene carbonate (VC). UHPC results showed that the coulombic efficiency (CE) of the cells could be improved by using PBF or PPF either singly or in combination with other additives. The charge-hold-discharge cycling protocol can be used to distinguish the difference between additives relatively quickly compared to continuous cycling. Cells with 2% PBF had the best capacity retention compared to cells with the other additives at 40 °C.

Incorporating electrolyte additives into the electrolyte of Li-ion batteries (LIBs) is one effective method for extending their lifetime.1–3 Pyridine boron trifluoride (PBF) and other amine: boron trifluoride complexes have been proposed and tested as electrolyte additives for NMC-based LIBs.4,5 This type of additive includes a Lewis acid and a Lewis base as the two major functional groups. It is important to carefully screen the same Lewis base with various Lewis acids, and vice-versa.

PBF has been demonstrated to improve the lifetime and cycle life of various NMC/graphite lithium ion cells.6–8 Speculation about the roles of the BF\(_3\) and pyridine functional groups is based on statements found in References 7–10. Amines as Lewis bases are widely used as corrosion inhibitors for metals including iron, steel and copper in acidic environments,9 so Lewis base amines might help to prevent transition metal dissolution from NMC positive electrodes by neutralizing acidic impurities in the electrolyte. BF\(_3\), as a boron-based anion receptor, might dissolve LiF from the solid electrolyte interphase (SEI) layers on both the positive and negative electrodes to help prevent impedance growth.9,10 Our previous work involved fixing BF\(_3\) as the Lewis acid and varying the Lewis base between molecules such as pyridine, lutidine, 2-fluoropyridine, pyrazine, triazine, etc.6,8 Those Lewis acid-base adducts were tested as additives in NMC/graphite cells using storage experiments, ultra high precision coulometry (UHPC), impedance spectroscopy and long-term cycling, etc.

In this work, instead of changing the Lewis base, various Lewis acids have been selected to bond with pyridine and the solid products were evaluated as additives in NMC532/graphite pouch-type Li-ion cells. PF\(_5\), similar to BF\(_3\), was selected and yielded a white crystalline product - pyridine phosphorous pentafluoride (PPF). Pyridine sulfur trioxide (PSO), using SO\(_3\) as a Lewis acid, has been patented by A123 Systems, which claimed that sulfur trioxide amine complex additives could improve the cycle life and delay thermal decomposition of the electrolyte in lithium ion batteries.11,12 Hence, a careful comparison of PBF, PPF and PSO was made to quantify the impacts of different Lewis acids in Lewis acid-base adducts used as electrolyte additives.

Pouch cells and electrolyte preparation.—1 M LiPF\(_6\), EC/EMC (3:7 wt ratio, BASF) was used as the control electrolyte in the studies reported here. To this electrolyte, pyridine boron trifluoride (PBF, 3 M Co., > 99%), pyridine phosphorus pentafluoride (PPF, 3 M Co., > 99%) or pyridine sulfur trioxide (PSO, Sigma-Aldrich, > 99%) electrolyte additives were added either singly or in combination with other additives. Figure 1 shows the chemical structures of these additives. Additive components were added at specified weight percentages in the electrolyte. Other standard electrolyte additives were also used for comparison, including vinylenecarbonate (VC, BASF, 99.97%), triaryl phosphate (TAP, TCI, > 94.0%) and ethylene sulfite [1,3,2-dioxathiolane-2,2-dioxide (DTD, Sigma-Aldrich)].

Dry (no electrolyte) Li[\(\text{Ni}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\)]O\(_2\) (NMC532)/graphite pouch cells (220 mAh) balanced for 4.7 V operation were obtained from Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuhai City, Hunan Province, PRC, 412000, China). All pouch cells were vacuum sealed without electrolyte in China and then shipped to our laboratory in Canada. Figure S1 in the supplementary information shows an SEM image of the top surface of the NMC532 positive electrode used in this work. The NMC532 used here has larger and smoother primary particles than typical NMC grades. Before electrolyte filling, the cells were cut just below the heat seal and dried at 80 °C under vacuum for 14 h in a heated glove box antechamber to remove any residual water. The cells were then transferred directly to the same argon-filled glove box for electrolyte 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 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 NMC532/graphite cells destined for 4.5 V operation were degassed a second time at 4.5 V. The amount of gas created during formation to 3.5 V and between 3.5 V and 4.5 V was measured and recorded.

Experimental

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 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.

**UHPC and storage experiments.**—The cells were cycled using the Ultra High Precision Charger (UHPC) at Dalhousie University12 between 2.8 and 4.5 V at 40.0 ± 0.1°C using currents corresponding to C/20 for 15 cycles where comparisons were made. The cycling/storage procedure used in these tests is described as follows. Cells were first charged to 4.5 V and discharged to 2.8 V two times. Then the cells were charged to 4.5 V using a current of C/20 (11 mA) and then held at 4.5 V for 24 hours. 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.13 Storage experiments were done at 60. ± 0.1°C.

**Long term and charge-hold-discharge cycling.**—Long term cycling was conducted with an upper cutoff potential of 4.6 V. The cells were cycled with two different protocols: (1) cells were continuously charged and discharged at 60 mA (C/3) between 2.8 and 4.6 V at 40. ± 0.1°C and (2) cells were charged to 4.6 V using currents of 60 mA, held at 4.6 V for 2 hours and then discharged at 60 mA to 2.8 V using either a Neware (Shenzhen, China) charger system or a Maccor series 4000 cycler.

**Determination of volume of gas evolved in pouch cells.**—Ex-situ (static) gas measurements were used to measure gas evolution during formation and during cycling.14 The measurements were made using Archimedes’ principle with cells suspended from a balance while submerged in de-ionized “nanopure” water (18.2 MΩ·cm). In-situ measurements were made using the apparatus and procedure described in by Aiken et al.15 The apparatus can measure the gas evolution in up to six pouch cells simultaneously during operation. During the in-situ measurements, the cells were suspended in silicone vacuum pump oil and their mass was measured using sensitive strain gauges (or load cells) while they were charged and discharged. All in-situ gas volume measurements were made in a temperature box at 40. ± 0.1°C.

**Results and Discussion**

Figures 2a, 2b and 2c show the voltage, V, of the NMC532/graphite cells containing different additives as a function of capacity, Q, during the first charge to the first degassing point (3.5 V), the differential capacity, dQ/dV, vs. V of the same cells and the volume of gas produced vs. voltage, respectively. Figure 2a shows plateaus that appeared at ~2.1 V and ~2.3 V (about 1.4 and 1.2 V, respectively vs. Li/Li+) for both PBF and PPF-containing cells. The capacities of these plateaus increased with PBF or PPF content. However, no plateau was observed for PSO-containing cells. Figure 2b shows the peaks from PBF/PPF-containing cells at around 2.1–2.3 V, which correspond to the plateaus in Figure 2a and that the intensity of the peaks increase with the concentrations of PPF/PBF. Besides the reduction peaks from the PBF/PPF additives, the second set of peaks at ~2.9 V are caused by the reduction of EC, which is consistent with the control cell. However the reduction peak from EC is significantly suppressed in PSO-containing cells compared to PBF or PPF-containing cells. Figure 2c shows the in-situ gas evolution during formation to 3.5 V measured using an apparatus designed at Dalhousie University.15 The gas onset points of all the cells are at 2.9 V and there is no gas generated during with the reduction peaks of PBF or PPF at ~2.1 V or 2.3 V. Therefore the reduction reactions of PBF or PPF do not generate

![Chemical structures of PBF, PPF and PSO.](image)
gaseous products during the initial formation charge between 2.0 and 2.4 V. The total amount of gas evolved during the entire formation is shown in Figure S2 in the supplementary information. Cells with PPF produced less gas than cells with PBF during the first formation step to 3.5 V and cells with either additive produced less than 0.1 mL of gas during the second formation step to 4.5 V. However, PSO showed a large amount of gas evolution during both formation steps.

Figure 3 shows the capacity of the plateaus near 2.3 V due to the reduction of PBF or PPF as a function of the amount of PBF or PPF in the electrolyte. The cells used to generate the data in Figure 3 were filled with only 0.6 g of electrolyte which is about the minimum that can be used to completely wet the electrodes and separators in these cells. This minimized the amount of electrolyte outside of jelly roll so that one can assume that all the PBF or PPF in the cell was involved in the reduction reactions. Figure 3 shows a linear relationship between the amount of additive in the cells and the capacities of the plateaus. The slope of the lines in Figure 3 indicates that both PBF and PPF underwent a two electron reduction reaction during formation.

Figure 4 shows the open circuit voltage (OCV) versus time during storage of the NMC532/graphite cells at 4.5 V and 60°C. The cells with 2% PBF, 2% PPF and 2% VC exhibited almost identical performance during 500 h of storage at 60°C and showed much smaller voltage drop than cells with PSO, TAP or no additive. Furthermore, the higher concentration (2%) of PBF or PPF improved the voltage retention of the cells compared to 1% PBF or PPF, which suggests that in this situation (high-voltage, high-temperature), increasing the amount of PBF or PPF effectively slows down the electrolyte oxidation as well as other reactions at the positive electrode surface.

Figure 5 summarizes the storage results of NMC532/graphite cells that underwent the same testing as the cells described by Figure 4. In addition to the cells containing single additives (PPF, PBF, PSO, TAP or VC), combinations of additives were evaluated. Figure 5a shows the summary of the voltage drop during 500 hrs of storage at 4.5 V and 60°C. Cells containing 2% PBF, 2% PPF and 2% VC showed the best results. When VC was combined with PBF or PPF, the cells did not show a significant improvement in voltage retention compared to PBF or PPF by itself. Combining VC with PSO dramatically decreased the voltage drop of PSO cells suggesting that VC can be used together with PSO to improve storage. In our previous study, NMC442/graphite cells containing 2% TAP showed competitive performance during high-voltage storage tests at 60°C.16 However, in the experiments here on NMC532/graphite cells, cells with 2% TAP had a voltage drop as large as control cells indicating that 2% TAP has little effect on the NMC532 cathode used here. Combining 1% PBF or 1% PPF with 2% TAP reduces the voltage drop of cells compared to that of
cells with 2% TAP alone, however, those still cannot outperform the 2% PBF or 2% PPF containing cells.

Figure 5b shows $R_0$ of the cells before and after storage. $R_0$ is the diameter of the overlapping semicircles in the EIS spectrum. Cells with single additives and control electrolyte have $R_0$ less than 200 $\Omega \cdot \text{cm}^2$. Cells containing 1% PBF, 1% PPF or 2% PPF have the smallest impedance after 60°C storage. Cells containing combinations of additives showed larger impedance compared to cells containing single additives, especially when PBF or PPF were combined with 2% TAP. Figure 5c summarizes the gas evolution during 60°C storage at 4.5 V for 500 h. Most of the cells had a volume expansion over 5% of the total volume (2.2 mL). For the cells containing single additives, cells with 2% PBF showed the smallest amount of gas (~0.15 mL). Cells containing PSO or TAP generated over 0.7 mL gas, which was the largest volume change in all cells studied. For the cells with additive combinations, adding TAP significantly increased the impedance of the cells, however, adding TAP reduced gas evolution when used with PBF, PPF or PSO compared to cells with single additives only. Adding VC to cells with PBF or PPF did not lead to improvements in gas evolution. VC only reduced gas evolution when used together with PSO. The mechanisms by which the various additives and their combinations change the impedance and gas evolution are unknown at this time and will require years of effort to elucidate.

Figure 6 shows the continuous cycling data collected using the UHPC for NMC532/graphite pouch cells cycled between 2.8 and 4.5 V with control electrolyte and various concentrations of PBF, PPF and PSO at 40.± 0.1°C. Figure 6a shows the coulombic efficiency, Figure 6b shows $\Delta V$ (the difference between the average charge and discharge potentials). Figure 6c shows the discharge capacity of the cells and Figure 6d shows the charge end point capacity all plotted versus cycle number. In Figure 6a, the cells with 2% PPF have the highest CE, followed by cells with 2% PBF and then the cells with low concentrations of PBF or PPF. The cells with 1 or 2% PSO showed low CE, similar to the control cells. Figure 6b shows all cells exhibit increased polarization during cycling. The smaller slope of $\Delta V$ vs. cycle number for cells with 2% PPF and 2% PBF suggests a slower increase in overall resistance compared to cells with 1% PBF, 1% PPF, PSO or control cells. Figure 6c shows that the discharge capacity of all cells displayed gradual capacity fade, however, it is hard to distinguish between the cells in these early cycles. Figure 6d shows that the cells with PBF or PPF have much smaller charge end point slippage than the cells containing PSO or control electrolytes. By increasing the concentration of PBF or PPF to 2%, the slope of the charge slippage versus cycle number graph became even smaller than for cells with 1% PBF or 1% PPF. Figure 6 suggests that cells with 2% PBF or 2% PPF will have the longest lifetime under the testing conditions used (2.8–4.5 V at 40°C).

Figure 7 summarizes the UHPC results for the same cells (NMC532/graphite) containing 2% VC or 2% TAP as comparative additives and for the cells with combinations of PBF, PPF or PSO with VC, DTD or TAP. Previous work demonstrated that combinations of PBF with methylene methane disulfonate (MMDS) or DTD showed promising electrochemical performance in NMC442/graphite cells at high voltage (>4.4 V). NMC532/graphite cells containing 2% PBF + 1% DTD or 2% PPF + 1% DTD were tested here. Figure 7a shows the coulombic efficiency vs. cycle number. Cells containing
2% PPF + 1% DTD showed the best CE of all cells, followed by cells with 2% PBF + 1% DTD, 1% PBF or 1% PPF + 2% VC, 2% VC alone and 1% PBF or PPF + 2% TAP. Cells with 2% TAP alone showed much lower CE compared to other cells. Figure 7b shows ΔV versus cycle number for the cells. ΔV versus cycle number exhibits a similar increasing trend as the data shown in Figure 6b suggesting that these additive combinations do not prevent polarization increase during cycling to 4.5 V. Furthermore, cells with additive combinations showed a larger increase in ΔV vs cycle number than 2% VC alone. Cells containing 1% PBF or PPF + 2% TAP showed the largest increase in ΔV vs. cycle number, indicating a large overall impedance growth in those cells. Figure 7c shows the discharge capacity in the early cycles of the same cells. Cells containing 1% PBF or PPF + 2% TAP displayed much larger capacity fade which is consistent with the largest ΔV of those cells shown in Figure 7b. Figure 7d shows the charge end point capacity of the cells as a function of cycle number. Cells showed a gradual increase in charge end point capacity, except for cells containing 1% PBF or PPF + 2% TAP cells which did not due to their large impedance increase. Cells containing 2% PBF + 1% DTD showed the smallest reliable slope corresponding to the smallest slippage rate for all cells. [Charge end point capacity slippage indicates the occurrence of electrolyte oxidation at the positive electrode. The constant charge end point capacity of the cells with PBF + TAP or PPF + TAP combinations are caused by the continually increasing impedance as shown in Figure 7b, not due to an elimination of electrolyte oxidation. Due to this impedance growth, the charge end point is reached sooner than the other cells.]

Figures 8a–8d show a summary of the UHPC data from the cells described in Figures 6 and 7. Figure 8a summarizes the coulombic inefficiency (CIE = 1 – CE). Figure 8b shows a comparison of the charge end point capacity slippage rate calculated from the slopes of the best fit lines to the last five cycles of charge end point capacity versus cycle number graphs (Figures 6d and 7d). Figure 8c shows the diameter of the “semicircle” in the EIS spectrum (Rct) of the cells before and after UHPC cycling. Figure 8d shows the gas evolution during UHPC cycling. Cells containing 2% PBF + 1% DTD or 2% PPF + 1% DTD had the smallest CIE in all the tested cells. Cells containing 2% PBF and 2% PPF showed similar CIE to other additive blends. Cells containing PSO, TAP and control electrolyte showed large CIE suggesting that more severe parasitic reactions occurred
during charge-discharge cycling to 4.5 V. The charge end point capacity slippage rate of cells shown in Figure 8b has a similar trend to the CIE data. Cells with PSO, TAP and control electrolyte showed much larger charge end point capacity slippage than cells with PBF or PPF and additive combinations. The charge end point capacity slippage data is consistent with the storage results shown in Figure 3 since cells with a large voltage drop during storage usually exhibit large charge end point capacity slippage. Figure 8c shows that most of the cells show an increased $R_c\Delta$ after UHPC cycling. $R_c\Delta$ of cells containing 1% PBF + 2% TAP or 1% PPF + 2% TAP dramatically increased after cycling, which is consistent with the increase in $\Delta V$ shown in Figure 7b. Figure 8d shows that all cells have a volume expansion less than 0.06 mL (less than 3% of the total volume) during cycling. The gas data suggests that PBF or PPF-type additives show good gas control on NMC532/graphite cells tested to 4.5 V at 40 °C.

Figure 9 shows the capacity and $\Delta V$ versus cycle number for NMC532/graphite pouch cells with 2% PBF, 2% PPF, 2% PSO and control electrolyte. The upper cutoff potential was increased to 4.6 V which was much smaller than the voltage drop of PSO cells. For single electrolyte additives, UHPC data indicated that 2% PBF and 2% PPF cells have the best combinations of CE, charge slippage rate and $\Delta V$ when cycled to 4.5 V. The results from blends containing PBF, PPF, PSO with selected additives showed that 2% TAP does not perform well in combination with PBF and PPF due to large impedance. Cells containing 2% VC along with PSO improved storage and UHPC results compared to 2% PSO. Combining 2% VC with 2% PBF or 2% PPF did not yield significant benefits. However, the combination of 1% DTD with either 2% PBF or 2% PPF led to cells with superior properties – high coulombic efficiency, low charge end point capacity slippage, low and stable impedance and no gassing during UHPC testing to 4.5 V at 40 °C.

Conclusions

Three different Lewis acid-base adducts including PBF, PPF and PSO were compared as additives in NMC532/graphite pouch cells. The experimental results indicated that cells with PBF and PPF have a similar voltage drop during storage at 4.5 V and 60 °C which was much smaller than the voltage drop of PSO cells. For single electrolyte additives, UHPC data indicated that 2% PBF and 2% PPF cells have the best combinations of CE, charge slippage rate and $\Delta V$ when cycled to 4.5 V. The results from blends containing PBF, PPF, PSO with selected additives showed that 2% TAP does not perform well in combination with PBF and PPF due to large impedance. Cells containing 2% VC along with PSO improved storage and UHPC results compared to 2% PSO. Combining 2% VC with 2% PBF or 2% PPF did not yield significant benefits. However, the combination of 1% DTD with either 2% PBF or 2% PPF led to cells with superior properties – high coulombic efficiency, low charge end point capacity slippage, low and stable impedance and no gassing during UHPC testing to 4.5 V at 40 °C.
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