Surface-Electrolyte Interphase Formation in Lithium-Ion Cells Containing Pyridine Adduct Additives

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The use of electrolyte additives to form a passive solid-electrolyte interphase (SEI) at one or both electrodes is a common method for improving lithium-ion cell lifetime and performance. This work follows the chemical and electrochemical processes involved in SEI formation on graphite electrodes for two Lewis acid-base adducts, pyridine boron trifluoride (PBF) and pyridine phosphorus pentafluoride (PPF). The combination of experimental methods (electrochemistry, in situ volumetric measurements, gas chromatography, isothermal microcalorimetry, and X-ray photoelectron spectroscopy) with quantum chemistry models (density functional theory) provides new insight into the interfacial chemistry. PBF and PPF are reduced at ~1.3 V vs. Li/Li+ and ~1.4 V, respectively. This is followed by radical coupling to form 4,4’-bipyridine adducts, hydrogen transfer to ethylene carbonate solvent molecules, and reduction of the solvent to produce lithium ethyl carbonate. The reduced bipyridine adducts, Li2(PBF)2 and Li2(PPF)2, are shown to compose part of the SEI at the negative electrode surface.

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Over the past decade, the predominant electrolyte solution used in lithium-ion cells has remained lithium hexafluoroarsenate (LiPF6) salt dissolved in some blend of organic carbonate solvents. This is not, however, an indication that advances in cell solution chemistry have stagnated, but it is rather a result of a major shift to focus on electrolyte additives. By adding just a few weight percent of the right compounds to the electrolyte solution before cells are filled, one can significantly improve charge-discharge cycling performance, extend calendar lifetime, decrease detrimental gas formation, and improve lithium-ion cell safety. This move to electrolyte additives has the rather practical aspect that the battery industry can tweak performance with minimal changes to their existing supply chains for LiPF6 and solvents. This article will focus on Li(Ni0.54Mn0.24Co0.22)/graphite (NMC622) cells, for which vinylene carbonate (VC),10-15 prop-1-ene-1,3-sulfone (PES),16-18 methylene methane disulfonate (MMDS), tris(trimethylsilyl) phosphite (TTSPi),16,17 and triallyl phosphate (TAP)18,19 are among the best reported additives. Recently, Nie et al. introduced a series of Lewis acid-base adducts that may be used individually or as part of an additive blend.20-22 In particular, pyridine boron trifluoride (PBF) and pyridine phosphorus pentafluoride (PPF) offer improved charge capacity retention after cycling at high temperature and high cell voltage.20 However, these latter two additives that will be closely examined in this article, chosen because they are still quite new and, so far, relatively unstudied.

If one is to optimize the solution chemistry in lithium-ion cells for various applications (high temperature, high power, etc.), it is clearly desirable to have thoroughly characterized the chemical and electrochemical reactions in a cell, including all of the various electrolyte additives. Unfortunately, such a detailed understanding of the many processes in an operating cell remains elusive, in part due to the complexity of modern cell design. It is widely accepted that many additives are film-forming; that is, they act by decomposing at one or both electrodes to form a stable barrier layer, termed the solid-electrolyte interphase (SEI).23 However, elucidating a more complete picture for the many additives in industrial and academic use remains an open challenge. Concerning the pyridine adducts, it has been suggested that they are reduced at the surface of the graphite electrode during the first charging step, also known as cell formation.20 However, the chemical compositions of the resultant SEIs remain unknown.

It is well-established that quantum chemistry (QC) calculations are an effective approach to study complex chemical systems. In lithium-ion cells, QC has been used to study the chemical and electrochemical stability of solvents,24-28 shuttle molecules,29-31 anions,32-34 and film-forming additives.35-42 In the present work, experimental data (electrochemistry, volumetric gas measurements, gas chromatography (GC), XPS, isothermal microcalorimetry) collected from PBF- and PPF-containing cells is used in tandem with computational modeling to develop new insights into solution and interfacial chemistry. It is, perhaps, only by the pairing of theory with experiment that a detailed understanding of the nature of the SEI in PBF- and PPF-containing cells can be obtained.

Experimental

Electrolyte solutions.—All solutions in this work used a 3:7 solvent blend, by mass, of ethylene carbonate (EC) and ethyl methyl carbonate (EMC), as received from BASF (water content < 20 ppm). The electrolyte salt, 1 mol L−1 LiPF6 (BASF, 99.94%, water content < 14 ppm), was added no more than 6 hours before cell filling. PBF or PPF was added to this control solution in the specified concentration. The synthesis of PBF and the evaluation of its purity by 1H NMR (Bruker Avance 300, Figure S1 and Figure S2) has been described previously.20 The synthesis of PPF was performed by the following procedure. Anhydrous pyridine (9.41g, 0.1191 mol) was charged into an oven-dried high pressure reactor under nitrogen. The reactor was sealed and cooled to 0 °C. Once cooled the reactor was depressurized. Phosphorus pentafluoride (20g, 0.1588 mol) was charged to the reaction vessel gradually to control heat release and the reaction was stirred at room temperature for 18 hours. Excess PF5 was vented through a bath before the desired pyridine:PF5 was isolated under a nitrogen atmosphere. Solid white product was confirmed by NMR (Figure S1 and Figure S2) and used without further purification.

Pouch cells.—Dry LiNi0.54Mn0.24Co0.22O2/graphite (NMC442) and LiNi0.54Mn0.24Co0.22/graphite (NMC622) cells (C ∼ 220 mAh) were received from LiFun Technology (Xinma Industry Zone, Tianyuan District, Zhuzhou, Hunan, China). All pouch cells were vacuum sealed without electrolyte in China and then shipped to our laboratory in Canada. Before electrolyte filling, the cells were cut just below the heat seal and dried under vacuum at 80 °C for 14 h. The cells were transferred directly into an argon-filled glove box, where they were filled. The cells were then vacuum-sealed at a gauge pressure of ∼90 kPa using a compact vacuum sealer (MSK-115A,
MTI Corp.). Every measurement reported in this work was performed on a minimum of two replicate pouch cells, to ensure experimental precision.

In situ volumetric measurements.—In situ measurements of the gas volume produced in pouch cells containing 0%, 1%, and 2% (w/w) PBF were performed using the “measuring Archimedes’ gas expansion” (MAGE) apparatus, also known as the Archimedes’ in situ gas analyzer (AISGA), as described previously.43,44 Following filling, cells were immediately loaded into a 40 ± 0.1 °C temperature-controlled box and held at 1.5 V for 24 h to ensure proper wettting. The same temperature was used during the wettting and charge steps with this instrument because it takes several hours for the temperature and mass measurements to fully stabilize. The cells were then charged at 10 mA (C/20). The volume change is reported relative to the start of the charging step.

Gas chromatography (GC).—Pouch cells were filled with 3:7 EC/EMC containing 1 mol L−1 LiPF6 and 0 or 2 % PBF. Cells were held at 1.5 V for 24 h at room temperature, charged to C/20 to 2.7 V at 40 °C, and then immediately moved to a brass chamber for gas extraction. The chamber was equipped with a Swagelok Quick-Connect, a septum, and a sharp-tipped shaft. The chamber was first pumped to an absolute pressure <0.1 Pa. Next, the shaft was driven through the pouch cell for gas extraction. Care was taken not to puncture the electrodes themselves. This was easier with the NMC622/graphite pouch cells because they had longer ‘gas bags’ than the NMC442/graphite cells. Therefore, only the NMC622/graphite cells were used for the GC experiments. The chamber was then back-filled with argon via the Quick-Connect. The gas was extracted from the chamber via the septum and injected into the GC using a syringe. A detailed description of the extraction procedure was reported by Petibon et al.45

All gas chromatography (GC) separations were performed using a Bruker 436-GC. For GC-mass spectrometry (MS), a split injector (250°C) and a Q-PILOT column (Bruker, 30 m, 0.25 mm ID, 8 μm coating) was coupled with a Bruker Scion single-quadrupole mass spectrometer equipped with an electron impact ionization module (electron energy = 70 eV). Helium carrier gas was used at a constant flow rate of 1.3 mL min−1. For GC-thermal conductivity detector (TCD) measurements, a splitless injector (270 °C) and a custom-made column was coupled with a Bruker thermal conductivity detector (TCD). The reference cell flow rate of the TCD was set to 30 mL min−1 and the make-up flow rate of the analytical cell was set to 5 mL min−1. The TCD temperature was set to 230°C and the filament temperature was set to 370°C. The column used for GC-TCD measurements consisted of 5A molecular sieve column (Bruker, 10 m, 0.32 mm ID, 30 μm coating), in parallel with a Q-PILOT column (Bruker, 50 m, 0.53 mm ID, 20 μm coating). This custom column allows obtaining good separation of permanent gases (H2, O2, N2, CO) as well as light hydrocarbons (CH4, C2H6, C2H4, etc.) and CO2 in a single injection. Argon was used at a flow rate of 9 mL min−1 for the GC-TCD measurements.

Isothermal microcalorimetry.—Heat flow measurements using isothermal microcalorimetry were performed using a TAM III calorimeter (TA Instruments) at a temperature of 40.0 °C. The specifics of the instrument calibration and operation, background information, and methods are discussed in detail by Krause et al.46 The heat flow measurement uncertainty was ±1.0 μW, the noise level of the instrument is about 10 nW and the baseline drift from 0.0 μW was less than 500 nW over the time frame of the experiments conducted here.

X-ray photoelectron spectroscopy (XPS).—Electrodes destined for XPS analysis were dissected from cells inside an Ar-filled glove box. The electrodes were rinsed with EMC, to remove dried electrolyte. The electrode samples were then transferred into ultra-high vacuum for at least one night, to allow for off-gassing, prior to their introduction into the analysis chamber, which was maintained at a pressure below 2 × 10−10 mbar at all times during analysis. Analysis was performed with a SPECS spectrometer, equipped with a Phoibos hemispherical analyzer, using unmonochromatized Mg Kα radiation and a pass energy of 20 eV. Preliminary and final survey scans were compared to ensure that no photochemical degradation was induced during analysis.

Computational methods.—All calculations were performed using the Gaussian software package (G09,d01).48 Density functional theory (DFT) geometry optimization and free energy calculations were performed using the B3LYP and M06-2X functionals. The B3LYP hybrid functional provides an excellent balance of speed and accuracy, whereas the M06-2X double hybrid functional may offer superior accuracy for molecules with charge separation.58,59,62 The 6-311++G(2df,2pd) basis set was used for all calculations.55,56 Diffuse Kohn-Sham functions were included on all atoms (denoted by the double plus, ‘+’ and injected into the analysis chamber, which was maintained at a

Results and Discussion

In general, most articles on electrolyte additive research focus on the measured improvements to various performance metrics, such as the coulombic efficiency and cell impedance growth during charge-discharge cycling, or the charge retention during storage at elevated temperatures. The present article is, therefore, somewhat unusual because no such data will be shown or discussed at any length. Interested readers may find such data for several Lewis adduct additives, including PBF, elsewhere.30–22 Rather, this work is focused almost entirely on the first few hours of the first time that a cell is charged, when the initial formation of a passive SEI at the negative electrode surface occurs.4 This first charging step, commonly termed cell formation, is a pivotal moment that can affect the ultimate lifetime and performance of a cell, even several years later. For this reason, the primary goal of this work was to develop a deep understanding of the electrochemical and chemical processes during formation in PBF- and PPF-containing cells.

To begin, the differential capacity (dQ/dV) of NMC442/graphite cells, prepared with 0–2% PBF, was measured (Figure 1). At the very start of this charging step, the potential of the NMC442 electrode is ~3.1 V (cell voltage), there is a peak that onsets at ~2.20 V (Figure 1). This peak has an additional feature is observed in cells that contain PBF, which onsets at ~2.15 V and that is centered at ~2.20 V. This peak has been suggested to correspond to the reduction of ethylene carbonate (EC) at the graphite surface, to form various lithium carbonate salts and ethylene gas.7,40 An additional feature is observed in cells that contain PBF, which onsets at ~2.15 V and that is centered at ~2.20 V (Figure 1). This peak has been suggested to correspond to the reduction of ethylene carbonate (EC) at the graphite surface.23,24 Furthermore, the coulombic charge associated with this feature (i.e., the peak area) is related to the amount of PBF added to the electrolyte solution. Beyond this, little is known about this reaction, such as the nature of the product or products. Furthermore, the second peak, which onsets at ~2.10 V and is centered at ~2.15 V, was previously unassigned.
One key assumption in this work is that at low cell voltages (i.e., $E_{\text{cell}} < 3.0 \text{ V}$), any electrochemical processes that occur take place at the negative electrode. This is based on the half-cell voltages of NMC and graphite coin cells, such as those shown in Figure 4 in Ref. 2. The assumption was tested by repeating the experiment in Figure 1 using NMC622/graphite cells (Figure 2, solid blue line). As previously, there are two peaks that are separated by $<0.05 \text{ V}$. However, the peak positions are slightly shifted to higher cell voltages. The first peak is centred at $2.15 \text{ V}$ and $2.22 \text{ V}$ in NMC442/graphite and NMC622/graphite cells, respectively, and the second peak is centred at $2.20 \text{ V}$ and $2.26 \text{ V}$, respectively. This small shift is attributed to small differences in the positive electrode potential. The relative areas are not an exact match between the two cell types. However, it was observed that these areas vary sample to sample, even in the same cell type prepared multiple times (for example, compare Figure 1 in this work with Figure 2 in Ref. 20).

A comparison of the formation data from PBF- and PPF-containing cells (Figure 2) offers new insight into the unassigned second peak. When LiPF$_6$ is used as the electrolyte salt, PBF yields two broad features, whereas the introduction of PPF to the cell results in a single, sharp peak at $\sim 2.15 \text{ V}$. It is here postulated that PBF interconverts in a cell to form PPF via a simple acid-base reaction with PFO$_4$ anions:

$$\text{PBF} + \text{PF}_4^- \rightleftharpoons \text{PPF} + \text{BF}_4^- \quad [1]$$

To test this hypothesis, cells were prepared with LiBF$_4$ as the electrolyte salt (Figure 2). For both additives, a single, sharp peak is observed during formation at $\sim 2.28 \text{ V}$. From these results, one can make the following conclusions: 1) The $dQ/dV$ peak at $E_{\text{cell}} \approx 2.25 - 2.30 \text{ V}$ corresponds to the reduction of PBF; 2) the $dQ/dV$ peak at $E_{\text{cell}} \approx 2.1 - 2.15 \text{ V}$ corresponds to the reduction of PPF; and 3) the equilibrium constant of reaction 1 favors the left side (i.e., $K_{eq} < 1$). This final point is consistent with the presence of two peaks for cells prepared with PBF and LiPF$_6$ but just one peak in cells prepared with PPF and LiBF$_4$, bearing in mind that the concentration of the additive is much lower than the concentration of the electrolyte salt.

It was noted above that the coulombic charge of PBF reduction is qualitatively related to the additive concentration in the electrolyte solution. The number of electrons involved in PBF reduction were measured previously.$^{20,61}$ However, the authors suggest that there may have been some error in their measurements if some of the electrolyte solution was excluded from the electrode ‘jelly roll,’ the wound electrode and separator stack, by segregation in the pouch bag (the components of a pouch cell are shown in Figure 1.10 in Downie’s Ph.D. thesis).$^{62}$ Therefore this experiment was repeated for the present work, where cells were prepared with 1% or 2% PBF or PPF, but the cells were under-filled to avoid the exclusion of any solution from the jelly roll. Only 0.6 g of electrolyte solution was used in pouch cells that are routinely filled with 0.9 g. The coulombic charge was then integrated for $E_{\text{cell}} < 2.4 \text{ V}$ and compared with the amount of additive introduced. The results in Figure 3 show that both PBF and PPF reduction are two-electron processes.

Thus far, electrochemical data has provided important information about the electrochemistry of these additives. However, electrochemistry alone cannot determine the nature of the products from either PBF or PPF reduction. Therefore, these processes were modeled using quantum chemistry (QC) calculations, as was recently demonstrated for prop-1-ene-1,3-sultone (PES).$^{35}$ First, the simple reduction of PBF and PPF (Figures 4a-4b) was modeled via the addition of an electron and Li$^+$ cation to produce LiPBF and LiPPF (Figures 4c-4d), and the standard potentials were calculated (Table 1). For comparison, the standard potentials were estimated from the differential capacity plots in Figure 1, assuming the potential of the NMC442 electrode is initially $\sim 3.5 \text{ V}$ vs. Li/Li$^+$.$^2$ The results are an excellent match, supporting the current assignment of the differential capacity peaks in Figure 1, as well as the proposed reaction 1.

The simple reduction reactions 2 and 3 only represent one-electron processes, whereas it is known that two-electron reduction occurs for both PBF and PPF. The simplest pathway is the subsequent reduction of LiPBF and LiPPF bearing in mind that the additive concentration is much lower than the concentration of the electrolyte salt.

Table 1. The standard potentials were calculated for the simple electrochemical reduction of PBF (2) and PPF (3) using the B3LYP and M06-2X functionals. The experimental values, estimated from Figure 1, are provided for comparison.

| Reaction | B3LYP | M06-2X | Exp. |
|----------|-------|--------|------|
| (2) PBF + Li$^+$ + e$^-$ ⇌ LiPBF | 1.30 | 1.27 | 1.3 |
| (3) PPF + Li$^+$ + e$^-$ ⇌ LiPPF | 1.41 | 1.40 | 1.4 |
Figure 4. Optimized molecular geometries of a) PBF, b) PPF, c) LiPBF, d) LiPPF, e) Li2PBF, and f) Li2PPF. Top and side viewing angles are shown for each.

electron and Li$^+$ cation to produce Li$_2$PBF and Li$_2$PPF (Figures 4e-4f), and the standard potentials were calculated (Table II). However, the calculated potentials are more negative ($E^0_2 < E^0_1$), which would result in two one-electron reduction peaks, approx. 0.5 – 0.6 V apart. Since this does not match the experimental data, this simple pathway must be incorrect.

Alternative pathways following the first reduction step were then considered. Both LiPBF and LiPPF are radical molecules and are, therefore, expected to be quite reactive. Two scenarios were examined: 1) reaction with themselves and 2) reaction with the solvent. For the first, the simplest reaction is a radical coupling, to produce a pyridine dimer (Reaction 6):

$$2 \text{Li}_2\text{PBF} \rightarrow \text{Li}_2\text{(PBF)$_2$}$$

This reaction is not spontaneous, presumably because of the loss of aromaticity on the pyridine rings. However, the free energy change is quite small ($\Delta G_{\text{B3LYP}} = 0.66$ kJ mol$^{-1}$) and the rate of radical coupling is expected to be fast, so an equilibrium is predicted to establish ($K_{\text{eq}} = 0.77$). It may be considered that the loss of an H atom from each pyridine reactant would produce a stable dimer. The simplest reaction for this is the evolution of molecular H$_2$ (Reaction 7):

$$2 \text{Li}_2\text{PBF} \rightarrow \text{Li}_2\text{(PBF)$_2$} + \text{H}_2$$

Only 4,4'-Li$_2$(PBF)$_2$, the PBF-derived dimer, is shown for simplicity. Moreover, the calculated geometry of the three constitutional isomers are shown in Figure 5, where the 4,4'-isomer was found to be the most stable. Reaction 7 is indeed spontaneous ($\Delta G_{\text{B3LYP}} = -52$ kJ mol$^{-1}$) but this pathway has the major failing that the overall number of electrons is one per PBF molecule, rather than the experimentally observed two.

Thus, a dilemma is reached. The radical coupling of the LiPBF or LiPPF molecules seems reasonable enough, as does the loss of the H atoms to restore aromaticity. Indeed, the electrochemical reduction of N-alkyl pyridines is known to proceed by this very pathway to produce

Table II. The standard potentials were calculated for the simple electrochemical reduction of LiPBF (4) and LiPPF (5) using the B3LYP and M06-2X functionals. The experimental potentials, from Figure 1, are shown for comparison.

| Reaction | B3LYP | M06-2X | Exp. |
|----------|-------|--------|------|
| (4) LiPBF + Li$^+$ + e$^-$ $\rightarrow$ Li$_2$PBF | 0.57  | 0.76   | ≥ 1.3 |
| (5) LiPPF + Li$^+$ + e$^-$ $\rightarrow$ Li$_2$PPF | 0.68  | 0.83   | ≥ 1.4 |

Figure 5. Constitutional isomers of Li$_2$(PBF)$_2$. The 4,4' isomer is 0.53 eV (51 kJ mol$^{-1}$) more stable than the 2,4' isomer and 3.0 eV (290 kJ mol$^{-1}$) more stable than the 2,2' isomer.
The solvent components, EC and EMC, seem the most likely candidates for the unknown species, R, and the standard potential was calculated (Table III). The calculated reduction potentials are all greater than the electrode potential of the initial reduction steps (2) and (3). Therefore, all of these reactions are predicted to occur at a large overpotential, which would rapidly drive the reactions to completion and release excess energy as heat. It is noted that whether hydrogen transfer occurs before or after the radical coupling does not affect the overall potential for these reactions.

Six of the eight reactions in Table III involve the evolution of a gas, which is a testable prediction. Cells were filled with 1–4% PBF and the total cell volume was measured, in situ, during the formation charge. As shown in Figure 6, no volume change was observed until the onset of EC reduction, when ethylene gas starts to evolve. Therefore, the bottom three rows in Table III are not part of the major PBF or PPF reduction pathways. PPF is included because the cell contained PPF in a cell produces only solids and/or solution species, which normally produced in cells by EC reduction. Hence, its presence here may indicate that PBF facilitates the onset of EC reduction at lower cell voltages. This is consistent with the apparent shift in the dQ/dV plot in Figure 1a. However, this is a very small effect, where the C2H4 peak area is 1/250 that measured from cells charged to 3.2 V. The origin of the acetone is unknown, but may have been residual from acetone used in the laboratory for cleaning. Finally, diethyl ether is probably an impurity from the boron trifluoride diethyl etherate used to synthesize the PBF. Therefore, it is concluded that the reduction of PBF and PPF in a cell produces only solids and/or solution species, which does not react with the reduced PBF or PPF to form a stable SEI.

The present reaction scheme for PBF reduction predicts an initial faradaic step that occurs near its standard potential (Table I), followed by a second reduction step that occurs at a large overpotential, η (Table III). Therefore, this second step is expected to release a corresponding amount of heat. This heat flow, dq/dt, may be estimated from the overpotential and the applied current, I (Reaction 1a):

\[
\frac{dq}{dt} = I \cdot \eta \tag{10a}
\]

\[
\eta = \frac{(E - E_{1}^{0}) + (E - E_{2}^{0})}{2} \tag{10b}
\]

\[
\left(\frac{dq}{dt}\right)_{PBF} = (2 \text{ mA}) \cdot \frac{(1.27 \text{ V} - 1.27 \text{ V}) + (3.92 \text{ V} - 1.27 \text{ V})}{2} = 2.65 \text{ mW} \tag{10c}
\]

\[
\left(\frac{dq}{dt}\right)_{PPF} = (2 \text{ mA}) \cdot \frac{(1.40 \text{ V} - 1.40 \text{ V}) + (3.95 \text{ V} - 1.40 \text{ V})}{2} = 2.55 \text{ mW} \tag{10d}
\]
Figure 6. NMC442/graphite pouch cells were filled with electrolyte that contained 1, 2, or 4 % PBF, as indicated on the figure. a) In situ volume change during formation. b) Differential capacity plot of cell formation at 10 mA (C/20).

These values were estimated using the standard potentials that were calculated with the M06-2X functional, since it is expected to give more accurate values than the B3LYP functional. It is noted that these heat flows are calculated assuming that a) the entropy change is negligible and b) the products are solution species. If the products are solids or adsorbed on the graphite surface, the heat flow will be larger than the estimate by the lattice energy or the adsorption energy, respectively. In order to test this prediction, the heat flow was measured during cell formation at 2 mA (∼C/100). The PPF and PBF reduction peaks, visible in the differential capacity plots shown in Figure 8a, are aligned with heat flow of ∼3 mW (Figure 8b). This is only slightly greater than the predicted heat flows, which is good support for the model presented in this article. Moreover, this result may support that the products are adsorbed or precipitated on the graphite surface.

Having predicted that PBF and PPF are SEI-forming additives, X-ray photoelectron spectroscopy (XPS) surface analysis was employed to examine the graphite electrode following formation. To begin, the binding energies (BEs) were adjusted for electrostatic charge buildup using the C1s peak from adventitious C-C/C-H. Whereas this adjustment is routine for clean metals and metal oxides,64 the fitting of the C1s region will be discussed in detail because the present work examines graphite-based materials that contain organic binders (sodium carboxymethyl cellulose and styrene butadiene rubber) and that are predicted to have an organic SEI surface layer.

There is a single broad peak in each Figures 9b and 9d that, based on the lineshape and width, likely consists of at least two overlapping peaks. In contrast, two overlapping peaks are clearly visible in each Figures 9f and 9h. It was first considered whether these spectra each contain two peaks from C-C/C-H and C-O species. However, the peak spacing and widths were not a good match with the typical values obtained with this instrument.47

It was then considered whether the two peaks may correspond to the reduced bipyridine adduct species, where the low BE peak corresponds to the aromatic carbon (C=C) and the higher BE peak corresponds to the carbon atoms directly bonded to nitrogen (C-N). The C-N peak is approximately expected to be at the same position as C-O. Therefore, the C/C/C-H peak was fixed at 1.9 eV below the C-N peak to assess the charge, which is convoluted with the more intense C=C peak correction (indicated by the dashed line in Figure 9). This is certainly an approximation, where the calibration error could be up to a few hundred meV. However, a more precise calibration was deemed impossible with the spectral resolution of the instrument used in this work. Finally, a higher BE peak from C≡O species, fixed at 3.6 eV greater than the C/C/C-H peak (determined from the fresh electrode material), was included but found not to significantly affect the peak.

Figure 8. The (a) differential capacity, (b) heat flow, and (c) cell voltage were measured during the first charging step (C/20) of NMC622/graphite pouch cells prepared with 0, 2, or 4 % PBF and 1 mol L$^{-1}$ LiPF$_6$.
positions and areas of the other peaks. The resulting peak assignments are supported by area ratio of C=C to C-N, which is \( \sim 3:2 \), consistent with the proposed bipyridine-derived compound.

It is notable that the C 1s region does not contain any clear signs of organic carbonate species, notably the peak expected at \( \sim 290-292 \) eV,\(^7\) given that lithium ethyl carbonate (LEC) is also suggested to form during the reduction of PBF and PPF. LEC is a semicarbonate that is frequently produced in lithium-ion cells including, notably, via the reduction of diethyl carbonate.\(^{65}\) However, it has been reported that LEC is not an effective SEI component because its solubility is too great.\(^{66,67}\) Therefore, the absence of LEC in the XPS may simply indicate that it is not a part of the SEI or that it was removed from the surface when the graphite was rinsed.

The N 1s binding energy (BE) region (Figures 9a, 9c, 9e, 9g) contains two overlapping peaks. PBF or PPF were the only N-containing species in these cells and, thus, this result strongly supports that these are both SEI-forming additives. The exact peak positions vary between samples (Table IV), but in all cases the two peaks are separated by \( \sim 2 \) eV. This separation is typical of reported N 1s BEs for nitrogen bases, such as pyridine, and their adducts with an acid, such as BF\(_3\) (e.g., PBF) or H\(^+\) (e.g., pyridinium).\(^{68-70}\) Alternatively, the two peaks may correspond to one species that is adsorbed onto different surface sites.\(^71\) Regardless, the XPS results strongly support the reduction pathway, via dimerization and reaction with EC, presented in this work.

Having established proposed pathways for PBF and PPF reduction and SEI formation at the negative electrode, it is now considered how this relates to cell performance. For other film-forming additives, such as VC and PES, it is thought that the passivation of one or both electrodes leads to increased cell lifetimes.\(^1,15\) For the PBF-containing

### Table IV. Binding energies and full-width at half maxima (FWHM) used to fit the spectra in Figure 9.

| Peak | Add. | Salt | \( \text{BE}_1^a \) (eV) | FWHM\(^b\) (eV) | \( \text{Area}_1 \) (%) | \( \text{BE}_2^a \) (eV) | \( \text{Area}_2 \) (%) | \( \text{BE}_3 \) (eV) | \( \text{Area}_3 \) (%) | \( \text{BE}_4 \) (eV) | \( \text{Area}_4 \) (%) |
|------|------|------|------------------------|---------------|-------------------|------------------------|-------------------|-----------------|-------------------|-----------------|-------------------|
| C1s  | PBF  | LiBF\(_4\) | 285.00                | 1.73          | 16.2              | 286.90                | 34.7              | 288.60          | 2.8               | 285.49          | 46.3              |
|      |      | LiPF\(_6\) | 285.00                | 2.33          | 11.6              | 286.90                | 33.2              | 288.60          | 0.8               | 285.84          | 54.4              |
|      | PPF  | LiBF\(_4\) | 285.00                | 1.82          | 18.2              | 286.90                | 32.9              | 288.60          | 1.5               | 285.38          | 47.4              |
|      |      | LiPF\(_6\) | 285.00                | 2.10          | 13.5              | 286.90                | 37.5              | 288.60          | 1.5               | 285.71          | 47.5              |
| N1s  | PBF  | LiBF\(_4\) | 399.80                | 2.44          | 15.8              | 401.82                | 84.2              |                  |                  |                  |                  |
|      |      | LiPF\(_6\) | 400.10                | 2.45          | 26.5              | 401.99                | 73.5              |                  |                  |                  |                  |
|      | PPF  | LiBF\(_4\) | 399.96                | 2.41          | 24.5              | 401.90                | 75.5              |                  |                  |                  |                  |
|      |      | LiPF\(_6\) | 400.41                | 2.02          | 71.8              | 402.56                | 28.2              |                  |                  |                  |                  |

\(^a\)Fitted peak position was adjusted to 285.00 eV.

\(^b\)Full-width at half maxima were constrained to be equal for all four peaks.

\(^c\)Three C1s peak positions were fixed: \( \text{BE}_2 = \text{BE}_1 + 1.9 \) eV, \( \text{BE}_3 = \text{BE}_1 + 3.6 \) eV.
cells in Figure 1, however, a peak corresponding to EC reduction is clearly present. EC reduction features were similarly observed, but not shown, for all the formulations in Figure 2. Based on dQ/dV analysis alone, one might be tempted to suggest that the PBF and PPF do not form effective passivation layers. Nevertheless, the benefits of these additives are proven.\(^{20-22}\) Therefore, these additives may lead to new understanding of how additives affect SEI formation and stability. For example, Petitbon et al. recently suggested that some additives should be categorized as ‘SEI modifiers’ rather than SEI ‘formers’\(^{23}\). One might wonder if PBF and PPF are somehow both. Future work is therefore merited to understand how exactly these additives and their respective SEIs act to improve cell performance during cycling or storage at high voltage.

**Conclusions**

The chemical and electrochemical reactions of two pyridine adducts, PBF and PPF, during cell formation were studied in detail. Electrochemical data shows that these additives reduce at \(~1.3\) V vs. Li/Li\(^+\) and \(~1.4\) V, respectively, in a two-electron process. QC modeling shows that the first reduction step is a simple electrochemical process. The reduced species, LiPBF and LiPPF, react further via a radical coupling reaction, H transfer to the solvent molecule EC, and a second faradaic reduction. This reaction, which occurs at a large overpotential, produces lithium ethyl carbonate (LEC) and dimeric and a second faradaic reduction. This reaction, which occurs at a large overpotential, produces lithium ethyl carbonate (LEC) and dimeric and a second faradaic reduction. This reaction, which occurs at a large overpotential, produces lithium ethyl carbonate (LEC) and dimeric and a second faradaic reduction. 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