Li-ion pouch cells were made to study the factors that influence gas evolution during formation (first charge). Electrode materials, electrolyte additives and temperature were varied. Measurements were made using the Archimedes In Situ Gas Analyzer at Dalhousie University. When cells are charged to high voltages (>4.2 V) there is gas evolution, presumed to be from reactions on the surface of the positive electrode. This is separate from the gas evolution known to happen at lower voltage (<3.5 V) caused by reactions on the negative electrode. Both evolutions were characterized by the magnitude of volume changes and their onset voltages. Gas volumes appear to increase and onset voltages decrease, respectively, with increasing temperature. Use of the additive prop-1-ene-1,3-sultone at 2% by weight in Li[Li0.42Ni0.25Co0.33]O2/graphite cells yields smaller volume and higher onset voltage of gas evolution at all temperatures, compared to other additives tested. Certain cathode materials, namely some coated LiCoO2 samples, can be charged to high voltages (>4.7 V) without producing gas at high voltage.

A Survey of In Situ Gas Evolution during High Voltage Formation in Li-Ion Pouch Cells

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Current Li-ion technology would be improved by increasing energy density while ensuring longer lifetimes. Charging to higher voltages can increase the energy density, but this can come at the cost of long lifetime. Increased voltages may cause failure mechanisms that are not present at lower voltages. Instead of operating to an upper cutoff voltage of 4.2 V, cells now often operate to 4.3 V, 4.4 V, and higher. Lifetime issues with “common” lower voltage cells are just as much a concern in higher voltage cells. They are compounded by possible additional failure mechanisms present in the higher voltage regime.

Electrolyte selection for high voltage Li-ion cells is important due to the fact that positive electrodes become ever more oxidizing at high state of charge and risk decomposing the electrolyte. Oxidation of electrolyte components has been known to occur since the early advent of Li-ion cells. Reaction products can accumulate into a surface film on the positive electrode, similar to the SEI formed in the negative electrode. This is separate from the gas evolution known to happen at lower voltage (<3.5 V) caused by reactions on the negative electrode. Both evolutions were characterized by the magnitude of volume changes and their onset voltages. Gas volumes appear to increase and onset voltages decrease, respectively, with increasing temperature. Use of the additive prop-1-ene-1,3-sultone at 2% by weight in Li[Li0.42Ni0.25Co0.33]O2/graphite cells yields smaller volume and higher onset voltage of gas evolution at all temperatures, compared to other additives tested. Certain cathode materials, namely some coated LiCoO2 samples, can be charged to high voltages (>4.7 V) without producing gas at high voltage.

Experimental

A variety of wound pouch cells were obtained, vacuum sealed, without electrolyte. Table I contains relevant information about the cells used in this study. The positive electrodes used included different NMC formulations, namely Li[Li0.42Mn0.25Co0.33]O2 (NMC 442) and Li[Ni0.5Mn0.3Co0.2]O2 (NMC 111), LiCoO2 (LCO), or physical mixtures of NMC and LCO. Graphite negative electrodes were used in all cells, however, differences in the graphite used occur between different cell types. All cells were manufactured either by Umicore, by Lifun Technology (Xinma Industry Zone, Gold Dragon Road, Tianyuan District, Zhuzhou City, Hunan, PRC, 412000), or by Shenzhen BAK Company (Shenzhen, China). Cells referred to by the prefix “AL” are cells containing Umicore positive electrode materials, received from Umicore. The cells described above are all balanced for high voltage, with the exception of the LCO/graphite cells produced by BAK and one type of NMC111/graphite cells produced by Lifun. Specific upper charge voltages can be found in Table I. The graphite particles in the Lifun cells were sized between 15–30 μm, while those in the BAK cells were 10–25 μm.

Construction details for the Lifun pouch cells are known and are reported here. The Lifun pouch cells are 40 mm long × 20 mm wide × 3.5 mm thick. The electrode composition in the cells was as follows: Positive electrode - 96.2%:1.8%:2.0% Active Material:Carbon Black:PVDF Binder; Negative electrode - 95.4%:1.3%:1.1%:2.2% Active material:Carbon Black:CMC/SBR. The positive electrode coating had a thickness of 105 μm and was calendared to a density of 3.55 g/cm3. The negative electrode coating had a thickness of 110 μm and was calendared to a density of 1.55 g/cm3. The electrode coating in the cells was as follows: Positive electrode - 96.2%:1.8%:2.0% Active Material:Carbon Black:PVDF Binder; Negative electrode - 95.4%:1.3%:1.1%:2.2% Active material:Carbon Black:CMC/SBR. The positive electrode coating had a thickness of 105 μm and was calendared to a density of 3.55 g/cm3. The negative electrode coating had a thickness of 110 μm and was calendared to a density of 1.55 g/cm3. The positive electrode coating had a thickness of 105 μm and was calendared to a density of 3.55 g/cm3. The negative electrode coating had a thickness of 110 μm and was calendared to a density of 1.55 g/cm3.
Table I. Information about cells used in this study. Anode density is used as the metric to compare negative electrodes, since more is not known. HV stands for high voltage grade.

<table>
<thead>
<tr>
<th>ID</th>
<th>Cell maker</th>
<th>Capacity (mAh)</th>
<th>Cathode material</th>
<th>Anode Density (g/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NMC111</td>
<td>Lifun</td>
<td>225 @ 4.2 V</td>
<td>Li[Ni1/3Mn1/3Co1/3]O2</td>
<td>1.55</td>
</tr>
<tr>
<td>NMC442</td>
<td>Lifun</td>
<td>245 @ 4.7 V</td>
<td>Li[Ni0.2Mn0.2Co0.6]O2</td>
<td>1.55</td>
</tr>
<tr>
<td>NMC111</td>
<td>Lifun</td>
<td>240 @ 4.4 V</td>
<td>Li[Ni0.15Mn0.2Co0.65]O2</td>
<td>1.55</td>
</tr>
<tr>
<td>AL988</td>
<td>Unicore</td>
<td>180 @ 4.4 V</td>
<td>HV LiCoO2</td>
<td>1.4</td>
</tr>
<tr>
<td>AL1050</td>
<td>Unicore contractor</td>
<td>200 @ 4.4 V</td>
<td>HV LiCoO2 + Ni and/or Mn</td>
<td>1.27</td>
</tr>
<tr>
<td>AL1051</td>
<td>Unicore contractor</td>
<td>200 @ 4.4 V</td>
<td>HV LiCoO2 + Ni and/or Mn</td>
<td>1.27</td>
</tr>
<tr>
<td>AL1052</td>
<td>Unicore contractor</td>
<td>200 @ 4.4 V</td>
<td>HV LiCoO2 + Ni and/or Mn</td>
<td>1.27</td>
</tr>
<tr>
<td>AL1019</td>
<td>Unicore</td>
<td>160 @ 4.35 V</td>
<td>LiCoO2</td>
<td>1.4</td>
</tr>
<tr>
<td>AL1171</td>
<td>Unicore</td>
<td>168 @ 4.35 V</td>
<td>HV LiNi0.5Mn0.3Co0.2O2 + LiCoO2</td>
<td>1.4</td>
</tr>
<tr>
<td>BAK LCO</td>
<td>Shenzhen BAK Co.</td>
<td>320 @ 4.2 V</td>
<td>LiCoO2</td>
<td>Unknown</td>
</tr>
</tbody>
</table>

Results

High voltage behavior of gas evolution.— Figure 1 shows the cell voltage and the capacity-normalized volume change of NMC/graphite pouch cells as functions of time. The reported volume change is normalized by capacity to facilitate comparison between different types of pouch cells. Two cathode materials were used, as indicated in the legend. The cell containing NMC442 was balanced to an upper cutoff voltage of 4.7 V, while the cell containing NMC111 was balanced to 4.2 V. It has been shown from previous work that a volume change occurs at the beginning of the first charge, due to gas evolution.20 This behavior is present in the volume change of both cells in Figure 1. At the beginning of charge, the volume increased rapidly, in a step-like fashion, and, upon stopping, started to decrease. The decrease in volume occurred at a much slower rate relative to the initial production of gas. This volume change behavior at lower voltages can be thought of as having two parts: a region in which gas production is dominant, and a region in which gas consumption is dominant. Despite these similarities in volume change at low voltage, there are small but noticeable differences between both cells. Considering the voltage curves of the individual electrodes, and previous work, it is reasonable to suggest that the low voltage pulse of gas evolution may be caused by reduction of electrolyte solvent on the surface of the negative electrode.22,22,10

The cell manufacturer states that the negative electrode materials used in these cells are the same, yet the NMC 442 cell produces more gas during this first pulse. This is because the NMC442 cell has a larger amount of excess graphite capacity than the NMC111 cell so there is irreversible capacity loss and some fade with cycling. C/10 charges normally took longer than 10 hours. Charging was performed by a Neware BTS3000 battery charger. After completing a single charge, the voltages of the cells were monitored in open circuit conditions for some amount of time. All testing occurred at 40.0 ± 0.1 °C unless otherwise indicated.

Table II. List of electrolyte additives used in this study, along with their abbreviation used in the text of this article, the chemical supplier and purity as obtained.

<table>
<thead>
<tr>
<th>Additive name</th>
<th>Abbrev.</th>
<th>Supplier</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinylene carbonate</td>
<td>VC</td>
<td>BASF</td>
<td>&gt;99.97</td>
</tr>
<tr>
<td>Prop-1-ene-1, 3-sultone</td>
<td>PES</td>
<td>Lianzhang pharmaceutical</td>
<td>&gt;98.2%</td>
</tr>
<tr>
<td>Vinyl ethylene carbonate</td>
<td>VEC</td>
<td>BASF</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>Fluoroethylene carbonate</td>
<td>FEC</td>
<td>BASF</td>
<td>&gt;99.94</td>
</tr>
<tr>
<td>Bis(trifluoromethane)sulfonamide lithium salt</td>
<td>LiTFSI</td>
<td>3M Co.</td>
<td>&gt;99.99</td>
</tr>
<tr>
<td>Lithium bis(oxalato)borate</td>
<td>LiBOB</td>
<td>Chemetall</td>
<td>&gt;99.9</td>
</tr>
<tr>
<td>1,3-Propane sulfone</td>
<td>PS</td>
<td>Aldrich</td>
<td>&gt;99.0</td>
</tr>
<tr>
<td>Succinonitrile</td>
<td>SN</td>
<td>Aldrich</td>
<td>&gt;99.0</td>
</tr>
<tr>
<td>Methylenediaminesulfonate</td>
<td>MMDS</td>
<td>Tinci Materials</td>
<td>&gt;98.7</td>
</tr>
<tr>
<td>Trimethylene sulfite</td>
<td>TMS</td>
<td>Aldrich</td>
<td>&gt;98</td>
</tr>
<tr>
<td>Triallyl phosphate</td>
<td>TAP</td>
<td>Tokyo Chemical Industry Co.</td>
<td>&gt;94.0</td>
</tr>
<tr>
<td>Tris(trimethylsilyl)phosphate</td>
<td>TTSP</td>
<td>Tokyo Chemical Industry Co.</td>
<td>&gt;98.0</td>
</tr>
<tr>
<td>Tris(trimethylsilyl)phosphate</td>
<td>TTSPi</td>
<td>Tokyo Chemical Industry Co.</td>
<td>&gt;95.0</td>
</tr>
</tbody>
</table>
more graphite surface per unit positive electrode on which SEI must form. The gas production is associated with the SEI formation.6,12–16

Figure 1. Voltage and capacity normalized volume change for NMC/graphite pouch cells that were charged at ∼C/10 at 40°C and left open circuit. The cells illustrate general differences between the gas evolution in regular cells and high voltage cells. Reference curves for NMC442 and graphite are included to show the approximate behavior of each electrode in the NMC442 cell during the charge. Data during the 24 hour hold at 1.5 V has been omitted to provide a closer view of data during the charge.

Figure 2 shows why a second step of gas evolution occurred in the NMC442 cells and not the NMC111 cells. The onset of this second step occurred around 4.3 V, which is a voltage never reached by the NMC111 cells, as they were balanced for and charged to 4.2 V. If one considers the electrode voltages versus Li/Li⁺, which are included in Figure 1, the voltage of the negative electrode is constant while the full cell voltage changes from 4.2 V to 4.3 V. It is therefore virtually certain that this second pulse of gas evolution occurred due to a process on the positive electrode, whose voltage does change between 4.2 V and 4.3 V. Given that the positive electrode at this state of charge is strongly oxidizing, it would make sense if this process is oxidation of the electrolyte resulting in gaseous products. As an alternative possibility, transition metal dissolution from the positive electrode would lead to an “excess” of oxygen atoms which, as radicals, could react with the electrolyte and produce gas. At the level of this paper, which is a survey, no attempt is made to rigorously identify the mechanism of gas production at the positive electrode. Figure 2 also shows that there was no volume change activity below ∼2.75 V for the NMC111 cells and below 2.9 V for the NMC442 cells, which was the onset of the first gas production. This means that during the constant voltage hold at 1.5 V, to facilitate wetting and prevent dissolution of the copper current collector, these cells are inactive and do not produce gas.

Figure 1 also shows that gas production stopped in the NMC442 cell, and gas is consumed while it is at open circuit potential after being charged to 4.7 V. Even though the cell voltage remained above 4.5 V and initial gas production began at about 4.3 V, no further gas was produced. Instead, gas was consumed. It has been shown by Self et al.35 and by others23–24 that the majority of the gas produced at the positive electrode is CO₂. This CO₂ gas could be consumed by reactions at the lithiated negative electrode, for example in the production of Li₂CO₃, as suggested by Sloop et al.36 Careful observation of Figure 1 yields details of the different behavior of the two cells after the first gas production and prior to the second. While the NMC111 cell showed gas consumption similar to what has been discussed above, the NMC442 cell did not exhibit notable consumption, and even had a small hump where consumption might be expected. Another gas which is known to be produced at the negative electrode is ethene. Ethene could be consumed as polyethylene, for example, during the slow gas consumption that takes place in the NMC111 cell after the initial gas production.

Additive and temperature survey in NMC442 cells.— Figure 3 shows the voltage and capacity-normalized volume change as a function of time for NMC442 cells that were formed with a variety of additives at a variety of temperatures. The additives and temperatures can be found in the legend and labels. Of all the general features found in the data for the NMC442 cell shown in Figures 1 and 2 were present in these cells. The volume of gas produced in each step generally increased with temperature. Furthermore, closer inspection shows that the production of gas occurred at a lower cell potential as the temperature increased. Both of these points will be presented and discussed in greater detail in the next paragraphs. The gas evolution behavior varied significantly with the additive used in each cell. In addition to gas volume and onset voltage, the different additives affected the rates of gas production and gas consumption. In fact, many of these additives did not exhibit any significant gas consumption, especially at lower temperature. At 25°C, the cells containing 2% PES and 2% MMDS did not exhibit obvious gas production at high voltage. The reason for this is given below. The sharp corner and subsequent plateau in the volume change curves of 2% TTSP and 2% TTSPi at 70°C are due to the fact that the cells floated in the liquid because they produced so much gas. Cells containing 2% PES, 2% VC and 2% FEC exhibited kinks in their volume change curves during the high voltage production of gas at 70°C. This was not present with other additives or at other temperatures. While the cause of this behavior is unknown, the discrete nature of this kink suggests two different reactions occurring that generate gas, with different durations. One of the reactions may run out of reactant or the SEI may achieve sufficient passivation to stop one reaction. Such explanations are purely speculative, and further research is certainly necessary to determine the true cause of this behavior.

Figure 4 shows capacity-normalized volume change as a function of voltage for the cells introduced in Figure 3. Figure 4 better illustrates the differences in the onset voltage of gas evolution reactions for cells containing the various additives. This can be observed in the change of the horizontal position at which volume increase begins. The onset points appear to be tightly grouped for the lower voltage onset, while the higher voltage onset points tend to be more varied. Because these cells are identical except for additive chemistry, the previous fact tends to support the notion that additive choice, at these loadings, has a much larger impact on the onset of electrolyte oxidation, than the onset of electrolyte reduction. Further discussion of this data will be presented below.

Figure 5 shows the volume change during the first and second steps of gas production, plotted as a function of temperature for the cells described by Figure 3. The volume change reported is the maximum...
Figure 3. Voltage and capacity normalized volume change for high voltage NMC442/graphite pouch cells, containing various electrolyte additives, that were charged at \( \sim \) C/10 at 25°C, 40°C and 70°C and left open circuit. The differences between the cells illustrate the effect of temperature and electrolyte additives on gas evolution. Dark orange vertical lines are drawn to guide the eye between different regions of the charge and the volume profile.

Figure 4. The capacity normalized volume change plotted versus voltage for the cells presented in Figure 3.

Figure 5. The capacity normalized volume change during the first and second steps of gas evolution, plotted as a function of temperature for the cells introduced in Figure 3.

value of volume change after the gas production from which the minimum value of volume change just before the gas production is subtracted. This means the points that are subtracted may be at slightly different voltages and times for different cells. For instance, re-examining Figure 1, the maximum value of volume change for the first gas production occurs at 2 hours for the NMC111 cell, while it occurs at 12 hours for the NMC442 cell. In other words, the small extra amounts of gas evolution that occur after than main step are included in the values that are reported in Figure 5. As mentioned previously, the amount of gas produced increased as temperature increased. This appears to occur in monotonic fashion. This generally makes sense, as increased temperature allows exponentially activated reactions to occur at higher rate. In addition, the solubility of most gases in the electrolyte probably decreases with temperature. However, Henry’s law constants versus temperature for the possible gases involved (CO\(_2\), ethylene, ethane, etc.) in 1 M LiPF\(_6\) EC:EMC are not available to our knowledge. Orthogonal to the main trends, the cells containing 2% VEC showed decreasing volumes of gas produced during the second gas production with increasing temperature. Because VEC produces a large quantity of gas at low voltage, which increases with temperature, so much VEC may be consumed at low voltage that it may become a limiting reactant for the higher voltage reaction(s). More work is...
needed to understand if this is truly the case. Two other additives worth noting are 2% PES and 2% MMDS as they did not produce gas during the second gas production at 25°C. This will be discussed in the conjunction with the next figure.

Figure 6 shows the onset voltage of gas evolution plotted as a function of temperature for the cells introduced in Figure 3. The onset voltage was determined by fitting two straight lines on either side of the ‘elbow’ in the volume change curves in Figure 4, where gas evolution began. The voltage at which these two lines intersect is defined as the onset voltage. The onset voltage of the first gas production appears to be monotonically decreasing with temperature, in general, and the data points appear to follow a similar trend with temperature, which is displayed by most additives. The major difference is simply an offset on the voltage (vertical) axis. This decrease in onset voltage possibly occurs because the potential of the positive electrode can decrease with increasing temperature,36 hence reducing cell voltage.36 The potential of the graphite is not as strongly influenced by temperature, so the measured onset voltage, measured across the full cell, is decreased due to the change of the positive electrode potential. Additional considerations would be enhanced kinetics and increased thermal contributions to meeting the required activation energy.

The data points in Figure 6 appear much more irregular for the second gas production. The rate at which the onset voltage changed with temperature was more variable among different additives. Outliers existed, such as 2% SN, which evolved gas at a higher voltage at 40°C compared to 25°C, and 2% VEC, which evolved gas at a higher voltage at 70°C than both 25°C and 40°C. Again, 2% PES and 2% MMDS are notable due to their lack of second gas production at 25°C. If the data is extrapolated and the trends for other additives remain true, it appears that cells containing 2% PES and 2% MMDS would undergo a second gas production, but at voltages higher than these cells are balanced for (~4.7 V). This demonstrates that such additives provide resistance to electrolyte oxidation, but the mechanism is unknown. The fact that various additives can alter onset voltages of gas production raises questions about their action. If additives are decomposed before solvents can be decomposed, why is gas not observed until higher voltage with certain additives? To preserve the solvent, the additive should react at a lower voltage. When compared to control electrolyte, PES-containing electrolyte shows oxidative gas production at a higher voltage. Once the second gassing onset voltage for control electrolyte is reached, even with PES-containing electrolyte, it is expected that the carbonate solvents oxidize. It may be the case that the surface film on the positive electrode is altered by the additive in such a way that the film is not strongly oxidizing to the majority of electrolyte components until a higher voltage.

A number of the additives studied demonstrate gassing behavior that can be explained by the findings of other researchers. MMDS has been shown here to have a positive effect on reducing the gas produced at high voltage. It has also been shown to be effective at reducing parasitic reactions on the positive electrode31 and electrolyte oxidation,39 which are believed to be the source of high voltage gassing. Similarly, PS has been shown to decrease solvent reduction.30 This correlates well with the decreased low voltage gas production for PS, compared to control electrolyte, shown here. Both of these examples support the idea that solvent reduction and oxidation, respectively, are responsible for low and high voltage gas evolution.

**Electrode material survey.**— To this point, all discussion has focused on NMC cells, specifically of the NMC442 and NMC111 varieties. Results from LCO-containing cells have not been shown. This is true even of previous work, outside of this study, on gas evolution from Dalhousie University.21,25 Cells containing LCO positive electrode materials as well as blended LCO + NMC positive electrode materials will now be presented and compared. Figure 7 shows the voltage and capacity-normalized volume change as a function of time during formation for a variety of cells, containing electrolytes with no additives, or either 2% VC or 2% PES, as indicated in the legend and labels. This figure compares NMC442, NMC111, LCO and LCO + NMC532. It is unfortunate that these cells were sourced from different suppliers, and therefore contained slight differences in capacity, as well as positive and negative electrode materials (density, porosity, % binder, % carbon black, etc.). Nevertheless, this and subsequent figures are very useful for motivating cell design. Figure 7 also serves another purpose. Among the discussions that motivated these experiments and this paper, it was hypothesized that lithium plating may play a role in gas production. It was known that these NMC111 cells were not balanced for the manufacturer’s rating of 4.4 V, as obtained charging to 4.4 V and opening the cells in a glove box would show small but observable amounts of plated lithium on the graphite electrode. All cells were overcharged to 4.7 V to further induce Li plating (with the exception of the NMC442 cells, which were balanced to 4.7 V).

The cells containing LCO did not show a distinct second gas production like the cells containing just NMC. This could be explained by unique surface chemistry, only present in the NMC system, which allowed these gas producing reactions to proceed, or the use of LCO caused an increase in onset voltage to greater than 4.7 V. Both the NMC111 cell and the AL1171 cell with control electrolyte showed a rapid consumption of gas around 4.3 to 4.4 V where Li plating should occur. Li plating in these cells could cause consumption of gas. Alternatively, high cell potential may result in gas consumption that is not caused by Li plating, nor is it mitigated by the presence of plated Li. The issue of correlation and causation are currently unclear. Should fresh Li plate on the negative electrode, it would be highly reactive and react until passivation occurs. An abundance of ethene could polymerize to help form a passivating film, and hence reduce the gas present in the cell. CO2 could also be consumed as
lithium oxalate as suggested by Sloop et al.\textsuperscript{36} At high voltage, the NMC442 cell consumed gas at a significant rate. The onset voltage of such consumption may just happen to overlap with Li-plating, with no direct causality. The majority of the gas in the cell after the first gas production step was found to be ethene by Self et al.\textsuperscript{35} so this indicates ethene may be consumed by freshly plated Li. It is very interesting that in the case of VC and PES-containing cells, no impact of Li plating on gas evolution or consumption can be observed. The NMC111 cell continued to produce more gas when it was charged above 4.5 V, while the AL1171 cell did not. When 2\% VC or 2\% PES were used, the general shapes of the volume change curves were the same for NMC111 and NMC442.

When 2\% VC or 2\% PES containing electrolytes were used in BAK LCO cells, after the initial pulse of gas evolution, the cells exhibited a swelling that was approximately linear with time, until the volume eventually stopped changing and plateaued. When 2\% VC was used, the initial pulse was quite large, while the linear increase was small. The cells with positive electrodes of AL1171 and 2\% VC or 2\% PES showed very little gassing compared to all other cells. In terms of minimizing gas evolution, throughout this and previous work\textsuperscript{30} on NMC cells, 2\% PES typically outperformed 2\% VC, but with the cells containing LCO, this was not the case. Furthermore, the cells containing LCO appeared to consume gas at an appreciable rate only when control electrolyte was used. This suggests that things are very complicated and every system must be optimized separately.

Figure 8 shows the capacity-normalized volume change as a function of voltage for the cells from Figure 7. Comparing the second gas production of the NMC containing cells: NMC111 produced smaller amounts of gas, at a higher onset voltage, than NMC442, for all electrolytes used. Rephrasing a point from the previous paragraph: the consumption of gas appears to be dominant in LCO-containing cells.

![Figure 8](image-url)
at voltages larger than 3.75 V when control electrolyte is used. This is not the case when the 2% VC or 2% PES are used. Throughout most of this paper, use of 2% PES has produced some of the best results at minimizing gas volumes. In the BAK LCO cell that contained 2% PES, the cell produced gas at a mostly constant rate throughout the entire voltage range. This is undesirable because there is no clear point at which degassing should occur and gas production appears to extend beyond the first charge.

Figure 9 shows the voltage-time and volume change-time profiles of pouch cells containing a series of different LCO cathode materials. Cell details can be found in Table I. There was wide variability among the different cathode materials and electrolytes. The ordering of cells from smallest volume change to largest volume change was different for each electrolyte used, similar to the results presented in Figures 7 and 8. None of the cells containing just LCO showed a clear second gas production. This is different behavior to the NMC cells described in Figures 1 to 8. All the cells with control electrolyte showed enormous consumption of gas when the cell potential rose above 4.4 or 4.5 V. This corresponds to the point where Li plating in these cells should begin. Again, there is no strong consumption of gas at this point in the VC-containing and PES-containing cells and may indicate that the majority of gas produced for cells with control electrolyte is different (i.e. can be consumed by polymerization (e.g. ethene)) to the gas produced when VC or PES are used (e.g. it cannot be easily polymerized (e.g. ethane)). In general, the smallest gas volumes were typically found in AL1171 cells. It would perhaps be more useful to remark that AL1171 can be engineered to have very small gas production. Each system appears to require specific treatment as they each respond differently to each electrolyte. All of these cells (except AL1051 with 2% VC) were intentionally overcharged to 4.7 V, like the cells in Figure 8. This should induce Li plating near 4.4 or 4.5 V, which appears to coincide with the rapid consumption of gas in the cells with control electrolyte. This consumption is already ongoing by the time the cell starts to plate Li, and is not interrupted by this event.

Conclusions

The influences of electrolyte, electrode material and temperature on gas evolution have been surveyed in Li-ion pouch cells. The results have been presented to motivate cell designs and further work by researchers and cell makers. Gas evolution during formation occurs in NMC-containing cells in two steps; one at low voltage and one at high voltage, if a high enough voltage is reached. The volume of gas produced in these steps and the voltage at which they occur will increase and decrease respectively, with increasing temperature. Electrolyte additives can be used to alter these parameters for better or worse. While some additives tend to consistently perform well, namely 2% VC and 2% PES, it has been shown that a particular additive may only perform well in a particular system. Based on the additives tested, there is no single, universal best additive for every application in terms of gas production during formation. Many of the LCO-containing cells that were tested showed complete suppression of the high-voltage gas evolution. However, LCO may not be a general solution to reducing gas volumes, as BAK LCO cells were shown to increase in volume across the entire operating voltage range when 2% PES and 2% VC electrolytes were used.

An assumption that has existed while doing this work was that the low voltage gas production is due to electrolyte reduction on the negative electrode, which coincides with the formation of the negative electrode SEI, and this was independent of the positive electrode. Many of the cells tested had identical or near identical negative electrodes, yet had low voltage gas evolution that behaved differently from each other. In these cases, the difference between these cells was the positive electrode, which indicates that it may have a significant role in a place where it was assumed to have none. Lastly, the investigation...
of the relationship between Li plating and gas production shows that there is no rampant gas production that accompanies undesired Li plating in these pouch cells. Instead, it appears that Li plating causes a consumption of gas in cells with control electrolyte.

One very interesting observation is that three of the additives in Figure 6 that have the highest onset potential for the second gassing, PES, MMDS and TTSSPi, have been shown to yield NMC/graphite cells with excellent high voltage performance.60 Ma et al.60 showed that the combination of 2% PES + 1% MMDS + 1% TTSSPi led to cells that maintained low impedance and excellent charge-discharge cycling during testing to 4.4 V and above. It may be that the high onset potentials for gas evolution when these additives are used (Figure 6) are indicators of the value of additives for high potential applications.

It is clear from these experiments that the production and consumption of gas in Li-ion cells during the formation cycle is very complicated. The next step in our research is to quantify and identify all the gaseous species being produced so that reactions mechanisms can be proposed.

Acknowledgments

The authors thank NSERC for funding of this work under the auspices of the NSERC Automotive Partnership Canada program. The authors thank Dr. Jing Li of BASF, Dr. Bill Lamanna of 3M and Dr. Thorsten Buhrmester of Chemetall for supplying various additives and/or solvents free of charge. R. Petibon thanks NSERC and the Walter C. Sumner Foundation for Scholarship support.

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