Survey of Gas Expansion in Li-Ion NMC Pouch Cells

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This preliminary study investigates initial gas formation in Li[Ni0.4Mn0.4Co0.2]O2 (NMC442) pouch cells with three different electrolytes: 3:7 ethylene carbonate : ethyl methyl carbonate (EC:EMC) w/ 1 M LiPF6 as the control, control + 2% prop-1-ene-1,3-sultone (PES) and control + 2% vinylene carbonate (VC). In situ volume measurements reveal three main features of gas evolution, an initial gas step, gas absorption, and a second gas step at higher voltage. Gas chromatography-mass spectrometry is employed to identify the gaseous compounds. This work illustrates the strong dependence of volume change due to gas evolution on additives, charging rate and temperature.

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The electrolyte in lithium-ion cells reacts with both the positive and negative electrode during the very first charge of the cells called the formation cycle.1,4 In addition, further reactions occur as cells are continuously operated and the rates of these reactions generally increase with temperature.1,5,6 Products of these reactions are solids, liquids and/or gases.1,3 It is difficult to probe the solid and liquid reaction products in situ in commercial Li-ion cells but the volume of gas phases produced can be easily probed in situ in Li-ion pouch cells using the method proposed by Aiken et al.7 which relies on Archimedes’ principle. Detailed studies of the impact of electrolyte additives, temperature and cell chemistry on the amount and nature of gases produced during formation and cycling have yet to be published. This is surprising because minimizing gas evolution in pouch-type Li-ion cells is critical to their successful application. A recent recall of Samsung cells due to excessive swelling caused by gas evolution highlights the need for understanding how gas is produced and how gas evolution can be minimized. Knowledge of gas production is important not only for the safety and design of Li-ion cells, but can also help in understanding the nature of reactions occurring during use.

This work is the first, as far as the authors know, to report in situ gas measurements at high voltage and high temperature. A previously unreported but significant feature, gas consumption, is also revealed by the measurements. Cells are further studied with varying electrolyte additive composition for both VC and PES at different temperatures. Finally, cells with 2% VC are tested at different C-rates to show the importance of current and time on gas evolution. These studies focus on the formation cycle of so-called NMC/graphite Li-ion cells.

Different gas creation reactions have been suggested in the literature to occur on the graphite negative electrode:1,3

\[
2EC + 2e^- + 2Li^+ \rightarrow (CH_2OCO_2Li)_2 + C_2H_4 (g) \tag{1}
\]

\[
2ROCO_2Li + H_2O \rightarrow 2ROH + Li_2CO_3 + CO_2 (g) \tag{2}
\]

\[
EC + 2Li^+ + 2e^- \rightarrow Li_2CO_3 + C_2H_4 (g) \tag{3}
\]

\[
LiPF_6 \rightarrow LiF + PF_3 (g) \tag{4}
\]

\[
PFO_3 (g) + Li_2CO_3 \rightarrow 2LiF + POF_3 + CO_2 (g) \tag{5}
\]

Although no quantitative model has been adequately presented with regards to the above reactions for Li-ion cells, there have been theoretical studies of both EC and VC reduction pathways,9,10 where produced gases include ethene (C_2H_4) and ethyne (C_2H_2).

Gas creation at the positive electrode and gas consumption occur through other mechanisms. It has been argued, both experimentally and through computational work, that EC can be oxidized to produce mainly carbon dioxide (CO_2) and carbon monoxide (CO) in much smaller quantities.11-13 Gas consumption has, to the authors’ knowledge, however not been the subject of much scholarship, but, as will be shown, occurs and is important. There nonetheless have been suggestions that gases could polymerize on the surface of electrodes, e.g. ethyne could form polyethylene (polyacetylene) on the anode due to its high reactivity.14

In this work, pouch cells using an electrolyte containing EC:EMC 3:7 (99.99 % purity) with 1 M LiPF6 (control), with or without additives were studied. The volume change in the Li-ion cells was measured using Archimedes’ principle7 while the cells were charged and discharged. This work introduces three important features in terms of volume change: a first gas step at low voltage, gas consumption, and a second gas step at higher voltage. Gas chromatography-mass spectrometry (GC-MS) was used to identify gaseous species other than H_2 in cells using control, VC and PES electrolyte during the formation cycle.

Experimental

The pouch cells employed in this study were all Li[Ni0.4Mn0.4Co0.2]O2 (NMC442)/graphite cells with a capacity of 245 mAh balanced for 4.7 V operation. The cells were produced by Li-Fun Technology (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000).

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 at 80 °C under vacuum for 12 h to remove any residual water. Then the cells were transferred immediately to an argon-filled glove box for filling and vacuum sealing. The NMC/graphite pouch cells were filled with 0.9 g of electrolyte. After filling, cells were vacuum-sealed with a compact vacuum sealer (MSK-115A, MTI Corp.). The electrolyte used had 1 M of LiPF_6 (99.97% pure, BASF) in EC:EMC 3:7 (by volume, BASF, water content < 20.0 ppm) for the “control” electrolyte. For the studies involving additives, VC (BASF, 99.99%), PES (Lianchuang Medicinal Chemistry Co., Ltd., China, 98.20%) or fluoroethylene carbonate (FEC, BASF) were used. Before charging, all cells were held at 1.5 V for 24 h to ensure excellent wetting of the electrolyte in the jelly roll of the pouch cell.

In order to measure the change in volume of pouch cells as a function of time, Archimedes’ principle was employed. A strain gauge load cell was used to measure changes in the buoyant force of cells submerged in mechanical pump oil kept at a steady temperature as the pouch cells were charged and discharged. A detailed account of this method can be found in Aiken et al. In this paper, measurements were taken at least every ten minutes. The random error in the strain gauge measurements, due to the resolution, has been measured to be...
0.01 mL. However, from duplicate measurements of pouch cell gas evolution, the systematic error is actually much larger, judged to be 0.1 mL.

For certain cells, GC-MS was used to analyze the different gases other than H₂ present at either 3.7 V or 4.7 V. Prior to GC-MS analysis, cells were charged on a Neware battery cycler in a 40.0 ± 0.1 °C temperature box at current density of C/10. After reaching the set potential cells were immediately removed from the temperature box and put in a brass chamber. The chamber was fitted with a swage lock quick connect on one end, and a septum on the other end. The cap of the chamber was fitted with a shaft, having a sharp point, allowing the pouch cell bag to be punctured. The shaft was fitted with two o-rings to prevent gas exchange between the exterior and the interior of the chamber.

The brass chamber with the cell fitted inside was pumped down to an absolute pressure of 100 mTorr. The shaft was lowered to puncture the bag of the pouch cell (not through the jelly roll). The low pressure in the chamber forces the gas out of the pouch cell inside the chamber, along with any high vapor pressure compounds potentially formed during battery use. The chamber was then back-filled with argon to equilibrate the pressure inside and outside the chamber. The gas from the chamber was then extracted from the chamber using a gastight syringe.

The extracted gas was then injected in the GC-MS. The GC-MS used was a Bruker 436-GC equipped with a split/split-less injector and a Q-PILOT (Bruker) 30 m column with an inner diameter of 0.25 mm and a coating thickness of 8 μm. Helium was used as carrier gas at a constant flow rate of 1.0 mL/min. The GC was coupled to a Bruker Scion single-quadrupole mass spectrometer equipped with an electron impact ionization module. The injector temperature was set to 250 °C and the oven temperature was programmed to get the best component separation in the shortest amount of time. A high injector temperature was used to ensure the complete removal of non-gaseous compounds and prevent carry-over from one injection to the next. The end of the oven temperature cycle was set to 250 °C for 5 min to ensure the elution of heavier highly retained compounds (mostly compounds coming from septum bleed). The transfer line was set to 250 °C, the ion source to 250 °C and the electron energy to 70 eV. The MS used did not allow for the detection of hydrogen since it had a lower mass detection limit of 10 amu. The column used and the minimum oven temperature available on this instrumental setup did not allow the separation of O₂, N₂, and CO, therefore the mass spectrometer was set to a single ion monitoring mode (SIM) for the measurement of these three gases during the first 3 min of the oven program and to a full scan mode for the rest of the oven program. Since CO and N₂ have similar principal ionic mass (m/z of 28), CO was monitored using the fragment with a m/z of 12 (0.5% of the intensity of the principal ion).

Results and Discussion

Figure 1 shows the volume change (ΔV) of pouch cells charged to 4.7 V and then left on open circuit. The change in volume at a given time is taken between the start of the charging process and the given time, or equivalently after the 24 h 1.5 V wetting procedure and the given time. All cells, in all three sets of panels, show two distinctive gas production steps: a low voltage step, which occurs around 3.7 V, and a high voltage step, which occurs around 4.3 V. The reader is reminded that these cells have sufficient graphite in the negative electrode so that Li plating does not occur, even at 4.7 V, so the high voltage gas step is not caused by lithium plating. Between these two steps is a gas consumption feature, more noticeable for VC and PES than for control cells. There is also gas consumption after the second gas step. Higher temperature, in all cases, causes more gas production in both steps. The results reveal that cells with 2% wt PES electrolyte produce less gas than the cells with control electrolyte or the cells with 2% VC when charged to 4.7 V. Certain cells are shown with duplicate experiments to illustrate the reproducibility of the data.

Figure 2, in the first column of panels, shows the chromatogram of the gas extracted from pouch cells after being charged to 3.7 V or 4.7 V. The gas peak identifications were made based on the mass spectra associated with each step. For the first panel, at 3.7 V, the number of counts for both the ethene and ethane (C₂H₆) peaks is considerably larger for the control electrolyte than for 2% VC or 2% PES, which could mean that these additives help prevent the creation of these gases. Due to its low signal, methyl formate possibly results from a side reaction from formation of the solid electrolyte interphase (SEI) on the anode. At atmospheric pressure, methyl formate is gaseous above 32 °C. The extraction procedure involving low pressure at room temperature is useful for identifying this compound which is noticeable for all electrolytes studied at 4.7 V (bottom left panel).

In the second column of Figure 2, the area of the GC-MS peaks for compounds gaseous at room temperature was integrated and normalized in order to obtain a quantitative estimate of the relative composition of the gas mixture for gases other than H₂ in each cell. The first gas step was studied for control, VC and PES using GC-MS data of cells charged at 3.7 V (top row panels in Figure 2). For the second step, cells were charged to 4.7 V before being analyzed by the GC-MS (bottom row panels). For the first gas step (3.7 V), ethene is the most abundant gas, as shown by the top right panel. This gas was likely formed by reactions involving the solvent and the anode, such as reactions 1 or 3. Previous scholarship has argued that EC can produce ethene through reduction on the anode and does not produce any noticeable amounts of ethane. Thus, it is possible that the ethene results from reactions involving EMC and the anode. VC prevents ethene production since the fractional amount of ethene is less for VC-containing cells and the volume change is dramatically reduced compared to control electrolyte for the first step. Namely, with 2% VC, at 3.7 V, there is a volume increase of 0.30 mL, while for control, it is 1.17 mL. This is consistent with suggestions that VC is preferentially reduced over EC on the negative electrode to form a SEI, which can prevent gas otherwise formed by reactions between EC and the negative electrode. PES also reduces the amount of ethene produced. This may indicate that PES participates in the formation of the SEI at the negative electrode. Here, the total volume change at 3.7 V is about 0.18 mL. Also, the compound propene is identified only for the PES-containing cells, but due to its low signal is perhaps simply produced during a side reaction involving the formation of the SEI. CO₂ in this first step could have been formed from water impurities as suggested by reaction 2. Due to a low signal to noise ratio, certain compounds could be present in very small quantities (less
than 0.01% of peak area) but are not shown in the second column of Figure 2, e.g. propene in cells with VC.

For the second step (4.7 V, bottom panels in Figure 2), CO$_2$ becomes the most abundant gas in the cell. The bottom left panel shows that CO$_2$ at 4.7 V is comparable in relative amounts for all cells (control, VC and PES). However, after the second peak at 4.7 V, the total volume change for control, VC and PES are respectively about 1.49 mL, 0.90 mL and 0.30 mL. It is possible that the CO$_2$ is mainly caused by the oxidation of EC. The bottom panels show that carbonyl sulfide is produced in the cells containing PES charged to 4.7 V. This is consistent with oxidation of PES at the positive electrode, creating the fragment carbonyl sulfide, which is similar to CO$_2$ from the oxidation of EC. The bottom left panel also shows that methyl formate might be produced during this second gas step. For both the 3.7 V and 4.7 V gas step panels, the water is likely to arise from air as blank injections always show this water peak. Also, it is worth noting that for the second step, the gases other than CO$_2$, ethene and ethane are in very small quantities as the right column of panels in Figure 2 uses a logarithmic scale (e.g. less than 20 μL per gas compound in a total gas volume of 1.5 mL). The gas dimethyl ether probably arises from reactions involving the solvent component EMC.

The first gas step in Figure 1 around 3.7 V is likely largely due to the negative electrode, not only because of identification of gases tied to the anode such as ethene, but also, when the same experiment was carried for a different cathode (NMC442 coated with LaPO$_4$), the first step remained the same while the second step changed in its shape, as can be seen by comparing Figures 1 and 3. The second step is likely due mainly to reactions involving the cathode and solvent. This is further supported by the identification of CO$_2$ as the main produced gas in this second step.

Figure 4 shows the voltage versus capacity data for half cells, where the NMC442 cathode and graphite anode are studied against a pure Li electrode counterpart as well as the full Li-ion cell voltage capacity relation. This allows inspection of the voltage for a given
electrode with regards to the full cell voltage. When the full cell is at 4.7 V, the graphite half-cell voltage curve is flat, which implies that the reactions due to the change in voltage are occurring on the cathode. In other words, Figure 4 further supports the claim that the second gas step is due to the cathode.

Figure 5 shows the volume change of pouch cells containing electrolyte with different concentrations of VC charged to 4.7 V and then left on open circuit, where the first gas step, consumption and second step are clearly noticeable.

Figure 6 plots the volume increase due to the first gas step as a function of VC content based on the results in Figure 5. Figure 6 shows that the first gas step, if considered at 3.7 V, decreases with VC concentration. The negative change in volume for the cell with 6% VC at 70 °C is due to a significant consumption of gas that was produced during the 1.5 V wetting procedure preceding the charge (not shown here). This gas production during wetting is not significant at lower temperatures (e.g. 40 °C and below). Figure 6 also shows that the second gas evolution step, taken as the difference between the relative maximum around 4.7 V and the minimum in volume preceding the second step in Figure 5, increases in amplitude with higher concentrations of VC. The increase for 6% VC is dramatic for the 70 °C temperature, and the gas produced was in fact higher than

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**Figure 4.** Half-cell voltage-capacity curves for NMC442 positive electrode and graphite negative electrodes used in these pouch cells. The full cell voltage-capacity curve is also shown.

**Figure 5.** In situ gas evolution of NMC/graphite cells with different concentrations of VC at 25 °C, 40 °C and 70 °C. Voltage profiles are shown in the top row and volume change in the bottom row. This data was collected for the first charge, or formation cycle, of the cells. Data for a cell containing 2% FEC is also shown.

**Figure 6.** Volume change during gas steps for different NMC/graphite cells with different concentrations of VC. The top panel shows the volume change for cells at 3.7 V, i.e. the first gas step in Figure 5. The bottom panel shows the difference between the relative maximum around 4.7 V and the relative minimum volume preceding this second step. Blue, black and red symbols are, respectively, for 25 °C, 40 °C and 70 °C.
Figure 7. In situ gas evolution of NMC/graphite cells with different concentrations of PES at 25°C, 40°C and 70°C. Voltage profiles are shown in the top row and volume change in the bottom row. This data was collected for the first charge or formation cycle of the cells. Data for a cell containing 2% FEC is also shown.

Figure 8. Volume change during gas steps for different NMC/graphite cells with different concentrations of PES. The top panel shows the volume change for cells at 3.7 V, i.e. the first gas step in Figure 7. The bottom panel shows the difference between the relative maximum around 4.7 V and the relative minimum volume preceding this second step. Blue, black and red symbols are, respectively, for 25°C, 40°C and 70°C.

In Figure 10, C/100 charging clearly shows the first and second gas production steps are distinguishable from each other at 40°C and second step are once again clearly noticeable. Figure 8 shows that the first gas step, at 3.7 V, tends to decrease in amplitude with increasing concentration of PES. However, the second gas step, taken as the difference between the relative maximum and minimum around 4.7 V, decreases from 0.5% PES until 2% but, increases from 4% to 6%. Figures 5 and 7 show clearly that the cells with 2% FEC continue to produce gas at 70°C even in the open circuit period after the charge to 4.7 V. This suggests FEC may not be useful in NMC/graphite cells targeted for high temperature operation.

Figure 9 shows the volume change of pouch cells with 2% VC-containing electrolyte charged to 4.2 V and then held at that voltage, using different C-rates for charging (C/3, C/20 and C/100). The three panels in Figure 9 each show the data for a given temperature, while Figure 10 shows panels with the data organized for a given C-rate. In Figure 9, at C/100 and 40°C, the gas consumption is very significant, and the fractional volume reduction is on the order of \( \frac{1}{2} \). From the GC-MS results (Figure 2), during the first step the gas is mainly composed of ethene (>70%). Thus, if about half of the gas is being consumed, at least some ethene is also being consumed, presumably to form polyethylene. This argument holds provided different C-rates do not change the nature of the gases formed and the amount of H₂ produced during the first step is negligible. Sloop et al. have also argued that CO₂ can be reduced at the anode to form lithium carbonate, CO and hydrocarbons.¹⁵

At 40°C, if the gas consumption feature is mainly of ethene, this would explain why in Figure 5, second column, the cells with larger initial steps show more noticeable gas consumption. For example the cell with 0.5% VC shows a first step at about 0.5 mL, and then after the second step, there is gas consumption over time of about 0.5 mL as well. The cell with 6% VC, however, shows a much smaller first step, and after the second step the gas consumption feature is much less pronounced. Further work could be undertaken to confirm by GC-MS that the gas consumption feature is mainly caused by depletion of ethene, and that the gas consumed after the first gas step and the gas consumed after the second gas step is of the same nature. The cells with a coating on the positive electrode shown in Figure 3 show a less pronounced gas absorption feature after the second step than their non-coated counterparts, which indicates that the positive electrode influences the absorption.

In Figure 10, C/100 charging clearly shows the first and second gas production steps are distinguishable from each other at 40°C and...
70°C, with significant gas consumption occurring between both onset voltages. At the faster C/20 rate, the gas consumption has less time to occur between both gas steps, and at C/3 both gas steps are hardly distinguishable from each other. At 25°C, however, the second gas step is not observed for all C-rates, likely because the onset voltage for this step is higher than 4.2 V for this temperature. During the gas consumption phase, the local minima for volume change occur at the same time for all C-rates when comparing the 40 and 70°C data (e.g. ~80 h for C/100).

The results in this paper beg the following questions:

1) What are the dominant reactions that cause gas production during formation?

2) How exactly, i.e. quantitatively, are these reactions affected by voltage and temperature?

3) What are the principal gas consumption mechanisms?

4) How do these gas reactions and the consumption affect the SEI?

Answering these questions will be the subject of our future work.

Conclusions

Archimedes’ Principle was employed to study the gas features of cells with different electrolyte blends. For the control, VC and PES electrolytes, three gas features were commonly found: two gas steps and gas consumption. The amplitude of each step was shown to be strongly dependent on additive composition and temperature.

Using GC-MS, we identify the first gas step (3.7 V) to be likely mainly due to reactions happening at the negative electrode, with ethene as the main gas product. We can further infer that the second gas step (4.3 V) is likely mainly due to reactions happening at the positive electrode, with CO₂ as the main gas product. These results are supported by comparing in situ volume measurements for non-coated and coated NMC cells. Finally, we can infer that the gas consumption, happening between both gas steps, can be caused by the depletion of ethene, which may be forming polyethylene. Many researchers have found evidence for polyolefins within the negative electrode SEI.16,17

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