Rapid Impedance Growth and Gas Production at the Li-Ion Cell Positive Electrode in the Absence of a Negative Electrode

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The effects of electrolyte additives on gas evolution, gas consumption and impedance growth at elevated temperature have been studied using Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O_2 (NMC442)/graphite pouch cells and pouch bags containing delithiated NMC442 or lithiated graphite electrodes plus electrolyte. It was found that there was much more gas, mostly CO_2, generated in pouch bags containing charged positive electrodes than pouch cells. It was found that the impedance of the charged positive electrodes stored in pouch bags increased dramatically, while those stored in pouch cells did not. The two observations show that there are interactions between positive and negative electrodes that limit gas evolution and reduce impedance growth in Li-ion cells. To verify this, CO_2 intentionally added to pouch bags containing lithiated graphite and electrolyte was consumed. The use of several electrolyte additives, known to affect gassing and high voltage cycling did not substantially alter these conclusions. XPS studies were used to eliminate some possible mechanisms responsible for these phenomena.

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Lithium-ion battery packs for electrified vehicles and grid energy storage need longer lived cells, operating over a wide range of temperatures. A pouch-type lithium-ion cell, cycled at elevated temperature, may experience volume expansion due to gas production, leading to rapid capacity fade.1–6 When Li-ion cells are charged above 4.2 V, reactions between the electrolyte and the positive electrode can cause charge-transfer impedance (Rct, electron transfer and diffusion of lithium ions through the SEI) growth at the positive electrode-electrolyte interface, depletion of liquid electrolyte, capacity loss and eventual cell failure.7–12 The use of electrolyte additives is an effective way to suppress gas evolution and impedance growth for cells cycled at high voltage and high temperature.13–19

Xia et al. and Li et al. found that prop-1-ene-1,3-sultone (PES) suppressed gas evolution when cells were cycled to an upper cutoff voltage of 4.2 V at elevated temperature.13,14 Nie et al. found that pyridine boron trifluoride (PBF) also suppressed gassing at high temperature, when cells were cycled to 4.4 V.16–18 Vinylen carbonate (VC) is a popular additive which is widely used in industry and has been extensively studied.20–24 This additive can cause severe gas evolution at high temperature and high voltage if residual VC remains in the electrolyte after the formation cycle.25

Some effective electrolyte additives for high voltage applications of Li[Ni_{0.4}Mn_{0.4}Co_{0.2}]O_2 (NMC442)/graphite Li-ion cells include PBF,16–18 triallyl phosphate (TAP),25 and a blend of additives containing PES, 1,3,2-dioxathiolane-2,2-dioxide (DTD) + tris-(trimethylsilyl) phosphate (TTSPi). The blend with 2 wt% of each of the three additives in the control electrolyte (1 M LiPF_6 ethylene carbonate (EC)/ethyl methyl carbonate (EMC) 3:7 w:w electrolyte) is called PES222 here.26–28 However, impedance growth for NMC442/graphite cells containing these additives or additive blends cannot yet be controlled as the cutoff voltage increases above 4.4 V.27 Figure 1 shows that the impedance of NMC442/graphite cells increases dramatically as the cycle number increases. Symmetric cells made from electrodes harvested from pouch cells tested above 4.4 V showed that the impedance growth originates from the positive electrode (Figure 1b) rather than from the negative electrode (Figure 1c). Detailed information on the preparation and testing of these cells was reported by Nelson et al.27

Pouch cells and pouch bags have been shown to be suitable tools to study the origin of gas evolution29,30 and the mechanisms of gas consumption.31 Kim et al. found that pouch bags containing delithiated LiCoO_2 (LCO) or delithiated Li[Ni_{0.8}Co_{0.16}Al_{0.04}]O_2 (NCA) and additive-free electrolyte produced a significant amount of gas; however, pouch bags containing lithiated graphite electrodes did not produce gas at all.32 They found that impurities, such as Li_2CO_3, on NCA were mainly responsible for gas evolution in NCA cells, and reactions between delithiated LCO and electrolyte were the major reason for gas evolution for LCO cells. Xiong et al. found that pouch bags containing delithiated Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2 (NMC111) produced a significant amount of gas, mostly CO_2 while pouch bags containing a lithiated graphite electrode did not generate gas.29 Xiong et al. proposed that CO_2 generated at the delithiated NMC111 can be consumed at the lithiated graphite electrode. The effect of electrolyte additives on CO_2 consumption at the lithiated graphite electrode has not yet been explored.

The pouch bag method can also be used to probe the origins of impedance growth in Li-ion cells. After a storage period, the state of charge and the impedance spectra of the individually stored electrodes were compared to the electrodes from the parent cell. Xiong et al.27 showed by the pouch bag method that positive electrodes stored individually had Rct dramatically larger than that of identical positive electrodes that had been stored in cells, in the presence of the negative electrode. This finding suggests that the chemical dialogue between the positive and negative electrodes, likely involving the electrolyte oxidation products generated at high voltages, plays a role in the impedance growth of positive electrodes at high voltage. The impact of electrolyte additives on the impedance of positive and negative electrodes stored in pouch bags has not been studied before and that is a focus of the work here.

In this work, pouch bags containing delithiated NMC442 or lithiated graphite electrodes, taken from pouch cells with control, control +2% VC, control +2% PES, control +2% PBF, control +2% triallyl phosphate (TAP) or control + PES222 electrolytes, were used to investigate gas production, impedance growth and gas consumption at high temperature and high voltage. The results from the pouch bag experiments were compared to results from corresponding pouch cells which contained both electrodes. Pouch bags containing lithiated graphite electrodes to which CO_2 was added were used to study how additives affect CO_2 consumption at high temperature. XPS studies were made in order to eliminate some possible mechanisms for impedance growth of electrodes stored in pouch bags.

Experimental

Pouch cells and pouch bags.—Dry (no electrolyte) NMC442/graphite (240 mAh) pouch cells balanced for 4.7 V operation were obtained from Li-Fun Technology (Xiimna Industry Zone, Golden Dragon Road, Tianyuan District, Zhzhou City, Hunan
Province, PRC, 412000, China). Prior to shipping, these cells were vacuum sealed in a dry room in China without electrolyte. In Canada, before electrolyte filling, these cells were cut below the seal and vacuum dried at 80 °C for 14 h. The pouch cells were filled with 0.9 g of 1M LiPF₆ in EC:EMC (BASF, USA, EC purity: 99.95%, EMC purity: 99.9%, water content < 20 ppm; 3.7 by weight) in an argon-filled glove box and vacuum sealed in the same glove box. To some electrolytes, 2 wt% VC (BASF, USA, purity: 99.97%, water content < 50 ppm), 2 wt% PES (Lianchuang Medicinal Chemistry Co., China, purity: 98.2%), 2 wt% PBF (synthesized in-house, purity > 99%), or 2 wt% TAP (TCI America, purity: 94.0%) were added. PES, DTD (Aldrich, purity: 98%), and TTSPi (TCI America, purity: > 95%) were added to control electrolyte in amounts of 2% by wt each to form the ternary additive blend, called “PES222”. After electrolyte filling, cells were placed in a 40. ± 0.1 °C temperature controlled box, and held at 1.5 V for 24 h. They were then charged to 3.5 V at C/20 and transferred to a glove box for degassing (cut open below the seal and re-sealed under vacuum). After degassing, they were charged to either 4.2 or 4.4 V, discharged to 2.8 V and charged back to the same upper charge cutoff voltage and held at that voltage for 30 hours.

At each condition, either at 4.2 V or 4.4 V, six cells were used for head-to-head comparison in the gas evolution experiments and four cells at 4.4 V were used for the impedance studies. In each case two cells were moved to a 60 °C temperature box for storage. The other identical cells were transferred to an Ar-filled glove box and disassembled there. For the gas evolution studies and for the impedance studies, four delithiated NMC442 electrodes collected from the pouch cells were inserted into pouch bags with 0.3 g EMC, except in the case of pouch bags containing PES222. The addition of 0.3 g EMC to the pouch bags created a similar electrolyte environment as in the original pouch cells since EC and LiPF₆ remained in the electrode and some EMC evaporated during the time (less than 5 minutes) it took to assemble the pouch bags. 0.15 g of EMC was added to the pouch bags containing electrodes from cells that initially had PES222 electrolyte. This unfortunate difference is not expected to impact the results significantly. Readers can find more details about the steps and processes used to make and test these pouch cells and pouch bags in reference.²⁹ For other gas evolution experiments, two delithiated NMC442 electrodes harvested from the full cells were rinsed with DMC three times, to remove LiPF₆, dried, and then inserted into pouch bags with 0.4 g of EC/EMC (3.7 w/w). The liquid in the pouch bags with rinsed NMC442 electrodes contained very little LiPF₆. The volume of the pouch bags and pouch cells during the 500 h storage period were measured from time to time, using the ex-situ gas volume equipment described in Reference 31.

**Analysis of the gas composition in NMC442/graphite pouch cells and NMC442-containing pouch bags.**—GC-MS was used to analyze the gases evolved in the pouch cells and pouch bags. The GC-MS procedure enabled detection of all gases other than H₂ and CO. The gas extraction procedure followed that described by Petibon et al.³² In this procedure, gas from the cell or pouch bag is mixed with a fixed amount of argon before injecting into the GC-MS. In order to keep signals in the linear range of the GC-MS, it was necessary to adjust the amount of gas injected when the amount of gas in the pouch cells or pouch bags was large. For most of pouch cells and pouch bags, 100 μL of the gas was injected from pouch bags containing delithiated NMC442 electrodes rinsed with DMC. The GC-MS used was a Bruker 436-GC coupled to a Bruker Scion single-quadrupole mass spectrometer. The operating parameters are described in reference.³³

To quantitatively analyze gas compositions in these pouch cells and pouch bags, a calibration gas mixture was purchased from Praxair for retention time determination and signal calibration. The gas mixture contained ten different gases which were butane, carbon dioxide, carbon monoxide, ethane, ethylene, hydrogen, methane, propane, propylene and argon. Each gas made up 10.0% mole percent of the mixture.
Investigation of CO2 consumption in pouch bags containing lithiated graphite electrodes and intentionally added CO2.—It is first important to describe how gas was intentionally added to the pouch bags. First, one side of a rubber septum was roughened with a hand file. The roughened septum was glued to a pouch bag using Gorilla glue (a polyurethane-based waterproof glue, available at many hardware stores—see www.gorillalatough.com). A heat gun, coupled with light pressure, was used to dry the glue rapidly. Rubber septa, attached to pouch bags by this method, provided a gastight seal, as evidenced by immersion of inflated pouch bags under water for several minutes. Figure 2 shows a pouch bag with a septum attached.

Lithiated graphite electrodes, taken from pouch cells with control, control + 2% VC, control + 2% PES and control + 2% PBF, were inserted into the pouch bags with 0.3 g EMC in glove box. A 6 mm diameter hardened steel ball was placed in the pouch bag, near the septum, to assist in injecting CO2. The purpose of the ball was to make space so the gas syringe needle could be inserted into the pouch bag, through the septum, without puncturing the back side of the pouch bag. The bulge due to the steel ball can be seen in Figure 2. After the pouch bags were vacuum sealed (the first seal shown in Figure 2), CO2 (more than 5 mL) was injected using a syringe through the septum. The pouch bags were then heat sealed at a position below the septum and ball (the second seal shown in Figure 2), without the application of vacuum. Then the portion of the pouch bag containing the septum and the hardened steel ball was cut away, above the second seal. Then the pouch bags containing electrode and electrolyte were stored at elevated temperature. Pouch bags with 1 mL of EC/EMC (3:7) + intentionally added CO2 (no electrodes) were also made for comparison.

The volumes of the pouch bags with injected CO2 were measured, from time to time, using the ex-situ gas volume measurement described above. Normally, the pouch bags floated on water so the same “bulldog” paper clamp was clamped to the edge of the pouch bag (at the heat seal) to cause submersion. The weight of the bulldog clamp (measured under water) was subtracted from all the weights measured where the bulldog clamp was employed. The absolute amounts of CO2 in the initial and final inflated pouch bags cannot be determined unless all details of the pouch bags and electrodes are known, but the amount of gas consumed can be accurately measured, and this is what was desired to be measured.

Symmetric cell and half cell construction.—Some NMC442/graphite pouch cells and NMC442-containing pouch bags were assembled in an Ar-filled glove box after the 500 h storage period. Li/graphite and Li/NMC442 half cells and NMC442/NMC442 symmetric cells were constructed from electrodes harvested from both pouch cells and pouch bags. The importance of using symmetric cells to determine Rct of electrodes was detailed by Petibon et al.34 Coin cells were made using one polypropylene (Celgard 2320) separator for half cells and one additional polypropylene blown microfiber separator (available from 3M Co., 0.275 mm thickness, 3.2 mg/cm2) for symmetric cells. A voltmeter was used to measure the open-circuit voltage of the half cells, once their voltage stabilized after a few minutes. EIS measurements were conducted using a Biologic VMP-3 potentiostat, with ten points per decade from 100 kHz to 10 mHz and a 10 mV input signal amplitude. All EIS spectra were collected at 10°C. This temperature was chosen to magnify the difference between the impedances of the cells.

XPS analysis.—Cells and pouch bags containing positive electrodes were dissected inside an Ar-filled glove box. The electrodes were rinsed with EMC, to remove dried electrolyte. The samples were transferred to ultra-high vacuum, without exposure to air, using a specially designed air-tight apparatus.35 The samples were left under ultra-high vacuum for one night prior to their introduction to the analysis chamber, which was maintained at a pressure below 2 \times 10^{-9} mbar at all times. 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 photodegradation was induced during analysis. Calibration of the binding energy scale was deemed unnecessary, as all peak positions remained constant while the X-ray flux was varied, indicating the absence of charging effects. XPS spectra were fit with a non-linear Shirley-type background. This background was subtracted from the signal, to allow for qualitative comparison of atomic concentrations between samples, using relative peak height.

Results and Discussion

Figure 3 shows the potential versus time for NMC442/graphite pouch cells during storage at 40°C and at 60°C. These cells had control + 2% VC electrolyte. Also shown are data points collected for Li half cells constructed from electrodes recovered from the pouch bags and pouch cells at 50, 175 and 500 h. The potential of the graphite electrode is about 0.087 ± 0.05 averaged over the six measurements shown. Therefore, a black, two-headed arrow, of length equal to 0.087 V has been placed on the pouch cell potential-time curve at 50, 175 and 500 h. The potential of the half cells containing the NMC442 is expected to be the pouch cell potential plus the graphite potential. Figure 3 shows this is approximately true which suggests that no strange unexplained processes are occurring in the pouch bags, even though the potential of the positive electrode cannot be directly measured in the pouch bag during storage. It is interesting that the potential (vs Li/Li+) of the electrodes in the pouch bags appears to be slightly higher than in the pouch cells. The pouch cells were opened extremely carefully to avoid short circuit so this difference in the positive electrode potential could indicate less self-discharge for the electrodes stored in pouch bags where a negative electrode is not present. Figures S1, S2 and S3 show similar results for the electrolytes, control + 2% PBF, control + 2% TAP and control + 2% PES, respectively. The potential of the positive electrode taken from the pouch bag (vs Li/Li+) is always greater than that of the electrode taken from the pouch cell. The difference is very striking for cells with control + 2% TAP. This is not understood at present, but is surely due to a negative electrode/positive electrode interaction which occurs in the pouch cell during storage.

Figure 4 shows the gas evolution in pouch bags containing lithiated graphite electrodes which were taken from pouch cells with control electrolyte, control + 2% PES, control + 2% VC or control + 2% PBF. No volume changes were detected for these pouch bags during approximately 500 h of storage at 60°C. This suggests that parasitic reactions between the lithiated graphite and electrolyte do not contribute to gas generation when a cell is stored at 60°C or lower temperature. This is consistent with the results found by Kim et al.36 and Xiong et al.37

Figure 5 shows the volume change versus time for pouch cells with control electrolyte, control + 2% VC, control + 2% PES or control + 2% PBF during the 500 h storage period at 60°C. Figure 5 also shows the volume change for pouch bags containing delithiated NMC442 positive electrodes taken from the brother pouch cells during the same storage period. Figure 5 shows that the gas volume of all the pouch

![Figure 2](image-url)
Figure 3. Open circuit voltage versus time for NMC442/graphite pouch cells with 2% VC during storage at 40 °C and 60 °C, as well as Li/NMC442 (a, c) and Li/graphite (b, d) half cells where the electrodes were taken out of the pouch cells and pouch bags at the times indicated. The black arrows are 0.085 V long.

Figure 4. Gas volume versus time for pouch bags containing lithiated graphite electrodes taken from pouch cells with control electrolyte (black crosses), control + 2% VC (blue crosses), control + 2% PES (red crosses) and control + 2% PBF (purple crosses). The storage was done at 60 °C.

cells and bags increased with time during storage, except for pouch cells with 2% PES or 2% PBF having an initial voltage of 4.2 V. Much more gas was generated in pouch bags with charged NMC442 than in charged pouch cells. Pouch bags containing the washed delithiated NMC442 electrode (DMC washing) + EC:EMC 3:7 produced a larger amount of gas than those containing the delithiated NMC442 electrode without washing. This implies that the presence of LiPF₆ can slow gas generating reactions at the positive electrode. This may be due to the increased oxidative stability of the electrolyte when LiPF₆ is present.36 There was concern about the size of the error bars in Figure 5 for the pouch bags with control + 2% PES electrolyte. These error bars originate from measurements on at least three different pouch bags. EMC can be lost during pouch bag loading and sealing, due to its high vapor pressure. In order to understand the origin of the large error bars, different amounts of EMC were added to delithiated NMC442-containing pouch bags, to examine how the amount of added EMC affected gas evolution. Figure 6 shows the gas volume (mL) versus time for pouch bags with delithiated NMC442, taken from pouch cells with control electrolyte, having an initial voltage of 4.4 V. Prior to the pouch bag sealing, 0.0, 0.15 or 0.3 g EMC was added to the pouch bags. Figure 6 demonstrates that the rate of gas production has a strong inverse correlation to the added amount of EMC. When more EMC was added, less gas was produced. It appears that electrolytes with higher EC concentration generate more gas. In any event, the dependence of gassing on EMC content suggests a source for the error bars in Figure 5. For example, the large error bars for pouch bags containing 2% PES may be due to small differences in the actual amount of EMC added to the pouch bags.
Figure 5. Gas volume versus time for pouch cells having an initial voltage of 4.2 V (black crosses) and 4.4 V (black diamonds), pouch bags containing the delithiated NMC442 electrode taken from pouch cells having an initial voltage of 4.2 V (red crosses) and 4.4 V (red diamonds) and pouch bags containing the delithiated NMC442 plus solvent (after DMC washing) taken from pouch cells having an initial voltage of 4.2 V (blue crosses) and 4.4 V (blue diamonds) with control electrolyte (a, e), control + 2% VC (b, f), control + 2% PES (c, g) and control + 2% PBF (d, h). The storage was done at 60°C.

The volume of gas produced in pouch bags containing electrodes without DMC washing was more than twice that of the corresponding pouch cells, despite the fact that the pouch bags and pouch cells initially contained identical positive electrodes and a similar electrolyte environment. As Figure 4 showed, reactions between lithiated graphite electrodes and electrolyte do not contribute to gas evolution. All of these observations strongly suggest that some gaseous products, generated at the positive electrode, can be consumed at the negative electrode in a full cell. Pouch bags containing delithiated NMC442, taken from pouch cells with control and control + different additives, produced a comparable amount of gas. This suggests that the addition of these additives to a cell does not significantly alter gassing at the positive electrode.

Figures S4, S5, S6, and S7 show chromatograms of the major gaseous products from pouch cells and pouch bags with charged NMC442 with different electrolytes studied here. Figure 7 shows a summary of the amount of the total gas measured by Archimedes principle and the amount of CO2 measured by the GC-MS method for...
these pouch cells and pouch bags. These pouch cells and pouch bags were stored at 60 °C for 500 h and then at room temperature for two months. During the two-month storage at room temperature, all the pouch cells shrunk while the pouch bags did not shrink. This further shows that gaseous products generated at the positive electrode can be removed by the negative electrode. Figure 7 shows that the volume of CO₂ measured by the GC-MS method in these pouch bags exceeded the total gas volume measured by Archimedes principle. The volume of CO₂ measured by the GC-MS method is larger than that measured by Archimedes principle since some CO₂ was dissolved in the electrolyte. This indicates that the majority of gas in these pouch bags is CO₂. However, almost no or a small amount of CO₂ was found in pouch cells. These indicate that CO₂ has been almost consumed by the lithiated graphite in full cells, explaining why the pouch cells produced much less gas than the corresponding pouch bags.

Figures S4, S5, S6, and S7 show that there is much more ethane left in pouch cells with control electrolyte than the other pouch cells with different additives. Ethane is one of the main gases left in the pouch cells and one of the byproducts of the reduction of EMC at the negative electrode as well. This means that the addition of VC, PES and PBF can hinder the reduction of EMC during the storage period at high temperature. This may be one reason why the addition of additives can suppress gassing at high temperature. The fluorinated alkane, CH₃CH₂F, was identified in all the pouch cells and pouch bags suggesting that LiPF₆ is involved in the reactions occurring. In order to investigate how additives affect CO₂ consumption in a pouch cell, pouch bags containing lithiated graphite electrodes taken from pouch cells with different additives + intentionally added CO₂ were made. The amount of CO₂ initially added to the pouch bags was targeted to be greater than 5 mL. According to the Henry’s law constant for CO₂ in 1M LiPF₆ in EC/DMC (1:1 w/w) at 25 °C and 1 atm measured by Dougassa et al., approximately 1 mL of CO₂ can be dissolved in the electrolyte in the pouch bags. This gas dissolves rapidly once the pouch bags are filled. After that, changes in the volume of the pouch bag correspond to CO₂ that has been consumed by the lithiated graphite. Figure 8 shows the consumption of CO₂ vs. time for pouch bags containing a lithiated graphite electrode and added CO₂. A control sample containing EC/EMC solvent plus added CO₂ was also measured and is included in the figure for comparison. Figure 8 shows that the volume of CO₂ in the pouch bag without a lithiated graphite electrode does not change significantly. This suggests that if the volume of the pouch bags with lithiated graphite and added CO₂ changes, this change is due to CO₂ consumption rather than CO₂ dissolution in electrolyte. For each curve in Figure 8, the average of two or three measurements on separate pouch bags were made and averaged. Figure 8 shows that the addition of additives affects the rate at which CO₂ is consumed. PES-containing pouch bags shrank by approximately 2 mL. This was about twice the volume change for the other pouch bags. Therefore PES may be effective in suppressing gassing in pouch cells at high temperature because it accelerates the consumption of CO₂ at the negative electrode. The data presented in this paper suggest that PES may not suppress gassing at high temperature at the positive electrode, but instead, suppresses the generation.
of ethane and accelerates CO$_2$ consumption at the negative electrode. Figure 8 shows that VC-containing pouch bags consumed CO$_2$ at the lowest rate compared to the other pouch bags. Figure 7 shows that the CO$_2$ peak area for pouch cells with 2% VC is larger compared to the other pouch cells. These results suggest that even though VC can suppress the generation of ethane, VC slows down the CO$_2$ consumption at the negative electrode, resulting in increased amounts of gas in pouch cells at high temperature as shown in Figure 5. However, the reader is cautioned that many more repeated experiments under a variety of conditions would be required to have full confidence in these statements.

Figures 9, S8, S9 and S10 show the area-specific Nyquist plots of positive electrode symmetric cells reconstructed from NMC442/graphite pouch cells and NMC442-containing pouch bags with control + 2% VC, control + 2% PBF, 2% TAP and PES222 stored at 40°C and 60°C. The first semicircle (high frequency) is due to the contact resistance between the double sided electrodes and the coin cell case.

The diameter of the second semicircle (low frequency) corresponds to twice the charge transfer impedance, $R_{ct}$, which is an important factor that affects cell performance. Its value is equal to 2$R_{ct}$ since there are two identical positive electrodes in the symmetrical cells. Figure 10 shows a summary of the average values of $R_{ct}$ measured for the electrodes taken from pouch bags and pouch cells. Figure 10 shows that positive electrodes taken from pouch bags have larger impedance than electrodes taken from pouch cells especially at 60°C. Nelson et al. found that $R_{ct}$ changes quasi-reversibly at high voltage in NMC442/graphite pouch cells containing EC-based electrolytes which shows that $R_{ct}$ of the positive electrode varies with different potential (vs Li/Li$^+$) for EC-based electrolytes. Therefore, it is important to compare the impedance of the positive electrode at the same potential vs Li/Li$^+$. After 500 h of storage at 40°C, the potential of pouch cells with control + 2% VC, 2% PBF, 2% TAP and PES222 dropped from 4.4 V to 4.25, 4.265, 4.28 and 4.27 V, respectively, as shown in Figures 3, S1, S2 and S3. In order to gain more insight about how $R_{ct}$ of the positive electrode changes before storage and after storage, Nyquist plots of positive electrodes taken from pouch cells before storage at both 4.4 V and 4.25 V (in the case of cells with 2% VC, and corresponding potentials for cells with the other electrolytes) are also included in these figures for comparison. Figures 9, S9, S10, S11 and 10 show that $R_{ct}$ of positive electrodes taken from pouch cells after 500 h storage remain almost the same as before storage.

Figure 10 clearly summarizes that fact that the impedance of the positive electrode grows more rapidly during high voltage storage in a pouch bag (no negative electrode present) than in a pouch cell where there is a negative electrode present. EC and EMC-based electrolyte can be oxidized as the voltage vs Li/Li$^+$ increases above 4.2 V$^{38,39}$.

The oxidized species generated at the positive electrode in pouch bags probably remain in the electrolyte while these species could be consumed by the lithiated graphite in the pouch cells. This suggests that the consumption of oxidized species by the lithiated graphite electrode is essential for maintaining reasonable impedance in full cells to be stored at high potential (4.4 or 4.5 V), or otherwise the oxidized species apparently react with the surface of the positive electrode material leading to a high impedance film.

In order to gain insight about how $R_{ct}$ changes over time, positive electrode symmetrical cells were reconstructed from pouch cells and pouch bags with control + 2% PBF that had been stored for 80, 300 or 500 hours at 40 or 60°C. Figure S11 shows a summary of $R_{ct}$ versus time for the positive electrodes taken from these pouch cells and pouch bags. Figure S11 shows that $R_{ct}$ for positive electrodes taken from pouch cells remained constant over the 500 h storage period at both 40 and 60°C. However, $R_{ct}$ of positive electrodes taken from pouch bags stored at 40°C increased greatly at the beginning, then remained unchanged after 300 hours of storage. $R_{ct}$ of the positive electrode taken from pouch bags stored at 60°C increased significantly with time.

XPS was used to analyze the surfaces of the positive electrodes from pouch cells and pouch bags with control, control + 2% VC and control + PES222. Figure 11 shows the background-subtracted O1s spectra of positive electrodes aged in a) control electrolyte, b) control + 2% VC and c) control + PES 222. In all the cases, the trends are the same. The peak arising from the NMC lattice, at 529.5 eV, is larger for positive electrodes stored in bags than those stored in cells, suggesting, surprisingly, that the positive electrode SEI is much thinner in the case of electrodes stored in bags. The peaks arising from SEI components containing ether and carbonyl-type environments, at 531.5 eV and 533.3 eV, are smaller for the positive electrodes stored in bags than those stored in cells. These observations indicate that the organic portion of the SEI covering the positive electrodes stored in bags is thinner than that in the SEI formed on positive electrodes stored in cells. This is surprising, as $R_{ct}$ of positive electrodes stored in bags is much larger than those stored in cells. The thinned SEI of positive electrodes stored in bags gives evidence that a thin, non-organic, insulating phase is the dominant contributor to $R_{ct}$ growth. This insulating phase may be the reduced layer of rocksalt structure.

$\text{Summary of Observations and Concluding Remarks}$

It is very useful to summarize the findings of this paper here:

1. NMC442 positive electrodes stored at 4.4 V at 60°C in pouch bags with electrolyte create more gas than the same electrodes stored with the same electrolyte in pouch cells. This suggests the negative electrode can consume some of the generated gas.

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**Figure 8.** The volume change of CO$_2$ vs time for pouch bags containing EC/EMC solvent + intentionally added CO$_2$ and pouch bags containing intentionally added CO$_2$ + lithiated graphite electrodes taken from pouch cells with control, control + 2% VC, control + 2% PES and control + 2% PBF. The storage for lithiated graphite-containing pouch bags was done at 60°C.
2. Most of the gas generated in the pouch bags during storage is CO₂ and, surprisingly, the presence of electrolyte additives known to improve high voltage storage and cycling do not affect the gas generation rate strongly.
3. CO₂ intentionally injected into pouch bags containing lithiated graphite is consumed over time.

4. NMC442 electrodes removed from pouch bags after storage at 4.4 V and elevated temperature have dramatically larger values of Rₚ (at least double) than those removed from pouch cells.

5. Surprisingly, the positive electrode SEI is thinner (for all additives studied) on electrodes stored in pouch bags, even though their Rₚ is much larger than electrodes extracted from pouch cells. This suggests the SEI is not thicker even though Rₚ is larger and, instead, the surface of the NMC442 electrode may have been changed, perhaps to a rock-salt surface layer.

These observations underscore the complexity of the chemical and electrochemical reactions occurring in Li-ion cells charged to high potentials. There can be no doubt that the presence of the negative electrode “cleans” the electrolyte of harmful degradation products that otherwise adversely affect the positive electrode. We are working hard to understand what these degradation products, and the reaction mechanisms that involve them, might be.

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