Quantifying, Understanding and Evaluating the Effects of Gas Consumption in Lithium-Ion Cells

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Lithium-ion cells produce a considerable amount of gas in their first cycle. If the gases are not removed in a degassing step, most are consumed by the cell over time. This phenomenon has never been investigated explicitly in the literature. In this paper, the evolution and subsequent consumption of gas in typical lithium-ion cells are measured by Archimedes’ principle and gas chromatography. It is found that all evolved gases are subsequently consumed to some degree, except for saturated hydrocarbons. The consumption of gas occurs predominantly at the negative electrode, where the gases are reduced to form part of the solid-electrolyte interphase (SEI). Changes to the negative electrode SEI upon gas consumption are investigated using X-ray photoelectron spectroscopy. The effect of gas consumption on cell performance is studied with ultra-high precision charging and high voltage storage experiments. It is found that gas consumption does not result in measurable adverse effects to cell performance.

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Lithium-ion cells can produce a significant amount of gas during the first charge (in the formation cycle), as electrolyte and additives react at the surfaces of the charging electrodes to form passivating films. If lithium-ion cells are packaged in a flexible casing, these gases are normally removed by the manufacturer in a degassing step, to prevent deformation of the cell and to ensure uniform stack pressure on the electrodes. If the degassing step is omitted, a large portion of the gas evolved is consumed over time.1 The reactions that consume gas are presumably prevalent in hard-cased cylindrical cells, such as 18650 s, which are often hermetically sealed before the first charge, and therefore cannot be easily degassed. The reactions that consume gas are presumably less prevalent in pouch-type cells, which are degassed.

Several authors have speculated about the rates of gases in lithium-ion cells.2,4−6 There has been no work explicitly dedicated to understanding the phenomenon of gas consumption. There is no consensus as to whether the effects of gas consumption are beneficial or harmful to cell performance. For example, it has been argued by some that the consumption of CO2 is beneficial to cells, as it reacts to form a passivating film on the negative electrode.3,4,8 However, it has also been argued that the consumption of CO2 is detrimental to cells, as it may reduce at the negative electrode to form Li2C2O2, which causes continual self-discharge at high voltage.2

It is important for both scientists and manufacturers of lithium-ion cells to understand the causes and the effects of gas consumption. If gas consumption is quick, benign, or even beneficial to cell performance, then the time-consuming degassing step for lithium-ion pouch cells might be skipped.1 The gases evolved in lithium-ion pouch cells could be left for consumption within the cell, perhaps leaving the pouch cell flat and rigid after several hours if all the gases were consumed. If gas consumption in a cell produces undesirable effects, such as self-discharge, then gas consumption should be avoided. It would then be desirable to devise a method to degas hard-cased lithium-ion cells. In either case, understanding the chemical reactions that consume gas is interesting and important, as it may help to explain differences in performance between otherwise identical cells in different packaging, or between cells which consume different amounts of gas.

This work begins with the quantification and characterization of gases evolved and consumed in lithium-ion cells. Archimedes’ principle is used to measure gas evolution and gas consumption of cells in real time, as they are being cyclic. Gas chromatography (GC) is used to identify the gases evolved from lithium-ion cells, and identify the gases which disappear from inside the cell over time. X-ray photoelectron spectroscopy (XPS) is used to characterize the effect of gas consumption on the surface chemistry of the solid electrolyte interphases (SEI) of the electrodes. Ultra-high precision charging (UHPC) and high voltage storage tests are used to investigate the effects of gas consumption, by comparing the performance of cells which were degassed and not degassed. The chemical fates of the gases consumed in lithium-ion cells are discovered, by reacting individual gases with charged electrodes.

Experimental

Lithium-ion pouch cell construction.—Four types of machine-made lithium-ion pouch cells were obtained, without electrolyte, from LiFun Technologies (Xinma Industry Zone, Golden Dragon Road, Tianyuan District, Zhuzhou City, Hunan Province, PRC, 412000). The four cell types differed only in the composition of the positive electrode material: Li[Ni0.6Mn0.2Co0.2]O2 (NMC442), Li[Ni0.6Mn0.2Co0.2]O2 (NMC622), NMC622 with an Al2O3 coating, and NMC622 with an undisclosed coating, appropriate for high voltage cycling, henceforth referred to as “coating B.” The positive electrode particles were 5−15 μm in size and obtained from Umicore, Korea. The positive electrode coating was composed of 96% wt NMC, 2% carbon black conductive diluent and 2% wt polyvinylidene fluoride binder. The negative electrode of these cells was 96% wt artificial graphite particles (15−30 μm), 2% wt carbon black conductive diluent and 2% wt sodium carboxymethylcellulose/styrene butadiene rubber binder. The ratio of negative/positive electrode capacity allowed for cell voltages of 4.7 V to be reached without lithium plating on the negative electrode, delivering a capacity of ~250 mAh.

Prior to filling with electrolyte, the cells were opened and dried under vacuum for 14 hours at 80°C, to remove residual moisture. The cells were then transferred directly to an Ar-filled glove box, without exposure to air. To each cell, 0.8 mL of electrolyte was added. This amount was in slight excess of the volume required for adequate electrode wetting. For all cells, unless otherwise specified, electrolyte was simply 1 M LiPF6 dissolved in a 3:7 wt blend of ethylene carbonate (EC): ethyl methyl carbonate (EMC) (BSAF, USA, EC purity: 99.95%, EMC purity: 99.9%, water content < 20 ppm). Electrolyte without electrolyte additives was used in order to amplify the gas evolution and consumption processes. Commercially available lithium-ion cells are likely to contain proprietary additive blends in order to mitigate gas evolution. To observe the effect of gas evolution

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and gas consumption in cells with additives, several cells were made with common electrolyte additives, added to the base electrolyte: 2% wt vinylene carbonate (VC, BASF, 99.97%), or 2% wt prop-1-ene-1,3-sultone (PES, Lianchuan Medicinal Chemistry Co., Ltd., China, 98.20%). After filling with electrolyte, the aluminum-laminate cell casings were heat sealed at a temperature of 150 °C, under a gauge pressure of ~90 kPa, using a vacuum heat sealer (Model MSK-115 V from MTI Corp.).

Lithium-Ion pouch cell charging and degassing.—After filling with electrolyte, the cells were held at a terminal voltage of 1.5 V for 24 hours, at room temperature. This allowed time for the electrolyte to permeate the electrodes. The voltage of 1.5 V was applied to lower the potential of the graphite electrode to about 2.0 V vs Li/Li+, to prevent oxidation of the copper current collector, which occurs above 3.2 V vs Li/Li+. Cells were then transferred to a 40.0 ± 0.1 °C temperature-controlled box, and charged using a Maccor 4000 series test system. The charging procedure began with an 11 mA (C/20) charge to 3.5 V, followed by a constant voltage hold at 3.5 V for one hour. During this step, some EC and some other electrolyte components are reduced, forming the negative electrode SEI and causing gaseous by-products. This gas was removed from the cells which underwent the normal pouch cell formation procedure. To degas the cells, they were transferred to an Ar-filled glove box, where the cell casings were cut open to release the gas. The cells were then resealed under ~90 kPa gauge pressure. The degassed cells were returned to the temperature-controlled box, where the charging procedure continued to 4.4, 4.5 or 4.6 V. A separate set of cells were never degassed at all. They were charged to 4.5 V and left to rest at open-circuit voltage in the temperature-controlled box for gas consumption to occur.

Storage of electrodes in gas-inflated pouch bags.—After charging, some cells were transferred to an Ar-filled glove box, where the cells were opened carefully to avoid short circuiting and the electrodes were removed. Charged positive electrodes underwent a very rigorous rinsing procedure to remove as much electrolyte as possible from the electrodes. Each positive electrode was rinsed five times with fresh 10 mL aliquots of dimethyl carbonate, dried under Ar, then dried under vacuum. This was done because the reaction of electrolyte with charged positive electrodes in pouch bags (i.e., without the presence of the negative electrode) is known to cause significant gas evolution and impedance growth,8 which would have interfered with the observation of gas consumption. Charged electrodes were then placed inside “pouch bags”. Pouch bags were made from the same aluminum-laminate material (Contemporary Amperex Technologies Limited, Ninge, Fujian, 352100, China) as the casing of pouch cells. Rinsed and dried positive electrodes were placed in pouch bags alone, without electrolyte (which would have oxidized to cause gas evolution).8 Negatively charged electrodes were placed in pouch bags with the addition of 0.4 mL electrolyte (to more accurately simulate the environment of a pouch cell). Rubber septa (Thermo Scientific, C4000-30) were adhered firmly to the outside of the pouch bags, using a generous amount of silicone sealant (“Silicone 1’, General Electric). One quarter inch stainless-steel ball bearing was placed in each pouch bag, approximately underneath the rubber septum. The pouch bags containing charged electrodes were sealed under vacuum in the same manner as the pouch cells described above. The purpose of the ball bearings was to create space in the pouch bag for a syringe needle to pass through the rubber septum, puncturing only the single layer of aluminum-laminate directly under the attached rubber septum, without puncturing the other side of the bag, thus avoiding a leak in the bag. The pouch bags containing charged electrodes were inflated with 8 mL of CO2, H2, C2H4 or CO (>99.99%, Praxair Technology Inc.) using a syringe filled with gas. The casing of the pouch bags was then heat-sealed a second time, below the rubber septum, creating a gastight seal, equivalent to that of a pouch cell, once the rubber septum was cut away. It was proven that the CO2-inflated and the H2-inflated pouch bags were gastight. They were first stored at an external gauge pressure of ~10 kPa for 3 hours. Then the H2-inflated pouch bags were stored for an additional week at 60 °C. The volume of the inflated bags did not shrink during storage, indicating no leaking had occurred. All inflated pouch bags in this work were submerged under water before and after testing for visual inspection for leaks. Figure S1 in the supplementary section shows a picture of an inflated pouch bag and results of the leak tests. Inflated pouch bags containing charged electrodes were stored, either at 40.0 °C or 60.0 °C for one week, unless otherwise specified.

Quantification of gas volume using Archimedes’ method.—Changes in cell volume due to gas evolution and gas consumption were measured using Archimedes' method. In this method, cells are weighed while suspended from a fine wire and submerged under a fluid. According to Archimedes’ principle, since the mass of the cell remains constant, the change in cell volume is proportional to the difference in the submerged weight before and after testing. Certain samples with large gas volumes floated above the fluid, and required a 2 g weight to be attached to the pouch bag casing to enable submersion. Ex-situ measurements were done at room temperature, by weighing cells suspended from a fine wire attached to the underhook of an analytical balance (Shimadzu, AUW200D), while the cells were submerged under de-ionized water (18.2 MΩ/cm2, Thermo Scientific Barnstead NANOpure Water Purification System). In-situ measurements were done in temperature-controlled boxes at 40.0 ± 0.1 °C, by weighing cells using a strain gauge (Strain Measurement Devices, 55 Barnes Industrial Park N, Wallingford, CT 06492, USA), while the cells were submerged under silicone mechanical pump oil. Cells were simultaneously charged using a Neware BTS-5V1mA testing system (Neware Technology Limited, Shenzhen, China). Details of the Archimedes volume measurement instruments at Dalhousie University can be found in several publications.10

Quantification and identification of gases using GC-TCD.—Quantification and identification of the gases inside lithium-ion cells were done using a gas chromatograph (GC, Bruker 436-GC) and a thermal conductivity detector (TCD, Bruker). The instrumentation, detector calibration, sample preparation and analysis methods were the same used by Petibon et al.11 Lithium-ion cells were placed in an air-tight gas extraction device (GED). The GED containing the cell was evacuated to 60 mbar absolute pressure, after which the cell casing was punctured, without shorting the cell, using a gastight, pointed piston. The GED was then filled to a pressure of 1 atm, with argon gas (>99.99%, Praxair Technology Inc.). 200. μL of the gas mixture was injected into the GC-TCD. The procedure was repeated with a pair cell to ensure reproducibility. The TCD detector is sensitive to H2, CO, CO2 and light hydrocarbons.

X-Ray photoelectron spectroscopy (XPS).—Electrode samples were transferred to an Ar-filled glove box and rinsed several times with EMC to remove the LiPF6 and EC that remained from liquid electrolyte solutions. Removal of these species is essential for the SEI components to be observed by XPS. Removal of EC and LiPF6 is also important for maintaining low pressures in the XPS system and for preventing damage to the detector from PF5(g) (generated from the thermal decomposition of LiPF6 under unmonochromatized irradiation). Rinsing with EMC is not expected to significantly dissolve any SEI components, as EMC is the major component of the electrolyte in which the SEI was formed. Once the rinsed samples were dried, they were mounted onto a myoglobin sample holder, using double-sided, ultra-high vacuum-compatible copper tape. The sample holder was then transferred into the XPS system, without exposure to air, using a vacuum suitcase.15 Electrodes were left under ultra-high vacuum overnight to allow for off-gassing of any remaining volatile components. The samples were then transferred to the analysis chamber of the XPS, which had a base pressure <2 × 10−10 mbar, which was always at a pressure >2 × 10−7 mbar during analysis. Analysis was performed with a SPECTROMAT spectrometer equipped with a Phoibos 150 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 occurred during analysis. The binding energy of the adventitious carbon peak was observed to be 284.7 eV on all samples, indicating the absence of sample charging. No correction to the binding energy scale was applied. 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 heights.

**Symmetric cells.**—Symmetric cells are cells in which the working and counter electrodes are identical. EIS on symmetric cells allows the charge transfer resistance, $R_{ct}$, of a single electrode to be determined. This is extremely difficult to do unambiguously in a half cell or full cell configuration, where dissimilar electrodes both contribute to an averaged $R_{ct}$. The importance of using symmetric cells for determining $R_{ct}$ of electrodes can be found in the literature.\(^{13,14}\) After storage, the inflated pouch bags containing pouch cell electrodes were transferred to an Ar-filled glove box. The pouch cell electrodes were removed from the pouch bags. Disks 1.02 cm\(^2\) in diameter were punched from the electrodes and assembled into symmetric cells, using 2325-type coin cell hardware, blown-microfiber (3M Co) separators, and 1 M LiPF\(_6\) in 3:7 EC:EMC as electrolyte.

**Electrochemical impedance spectrometry (EIS).**—EIS measurements were conducted on symmetric cells, and on full cells that had undergone 500 hours of high-voltage storage, either degassed or not degassed. EIS measurements were performed at 10.0 ± 0.1°C, using a BioLogic VMP3 potentiostat to induce a 10 mV bias, at frequencies ranging from 100 kHz to 10 mHz. $R_{ct}$ was taken to be the diameter of the mid-frequency semicircle in the Nyquist plot.\(^{13,15,16}\)

**High voltage storage.**—The effect of gas consumption on self-discharge was tested in a high voltage storage experiment. In this experiment, only the voltage of the cells was monitored as a function of time. Therefore, this experiment probes the impact of electrolyte oxidation at the positive electrode side (because the negative electrode potential versus lithium composition curve does not vary significantly when a Li-ion cell is fully charged) which causes insertion of Li\(^+\) to maintain charge neutrality at the positive electrode. This type of self-discharge is often called “reversible” self-discharge in the literature because it can be reversed by charging the cell. In this paper, such self-discharge is called “self-discharge at the positive electrode”. The cells used for this experiment contained control electrolyte, and positive electrodes made from uncoated NMC622, Al\(_2\)O\(_3\)-coated NMC622 or NMC622 with coating B. Two of each set of cells had been degassed during and after the first charge to 4.5 V. The other two sets of cells in each set were never degassed during or after the first charge to 4.5 V. All cells were stored, unclamped, at room temperature, to promote dissolution and consumption of any gases in the cells. The cell voltages were measured every hour for 400 hours. After storage, the volume change of the cells were measured, using Archimedes’ principle, and the cells were cycled using UHPC.

**Ultra-high precision coulometry (UHPC) cycling.**—After high voltage storage, both groups of cells (degassed and not degassed) were clamped tightly inside polyethylene holders, using rubber blocks to sandwich the cells firmly between aluminum shims (cut to be the same size as the pouch cell), as described in another paper.\(^{17}\) Clamping the cells firmly in this manner created similar stack pressure between the degassed and non-degassed cells and forced any remaining gas in the non-degassed cell to the edge of the pouch away from the electrode stack. The cells were loaded into 20.0 ± 0.1°C temperature-controlled boxes. This relatively low cycling temperature was chosen to prevent further evolution of gas during cycling. The cells were then cycled using a UHPC system, designed and built at Dalhousie University, as described in several publications.\(^{18,19}\) All cells were cycled continuously at 10 mA (C/20), between 2.8 and 4.5 V. After 10 UHPC cycles the cells were equilibrated at 3.8 V, and gas volume changes were measured. The experimental error of a typical UHPC experiment is evaluated in the supplementary section, Figure S3.

**Results and Discussion**

**Evolution of gas in a cell.**—Figure 1 shows the evolution of gas in a lithium-ion pouch cell with NMC442 and a typical electrolyte (1M LiPF\(_6\) in 3:7 v/v EC:EMC). Figure 1a shows both voltage and volume change of the cell during its first charge (formation) cycle. Two gas producing events are observed: the first at a cell voltage <3.5 V, and the second at a cell voltage >4.2 V, in agreement with previous work.\(^1\) Figure 1b shows the gases evolved, determined by GC-TCD, in the first and second gas producing events. The first event produces over 1 mL of gas: a mixture of C\(_2\)H\(_4\), H\(_2\), CO and very small amounts

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**Figure 1.** a) voltage vs time and volume change vs time for a fresh lithium-ion cell during the first charge cycle. B) the composition of the gas, measured by GC-TCD, evolved from the cell in Figure 1a during the first charge.
of CH₄ and C₂H₆. C₂H₄ arises from the reduction of EC, during the formation of the negative electrode SEI (Equation 1).²⁰

\[
2\text{Li}^+ + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3
\]  

Disappearance of gas in a cell.—Figure 2 shows the disappearance of gas an NMC442 lithium-ion pouch cell, with control electrolyte, left to rest at open circuit voltage (OCV) for 80 hours at 40 °C. Figure 2a shows both voltage and volume change. Over 0.6 mL (40%) of the gas evolved during the first charge is consumed within the first 100 hours of storage. The disappearance of gas is not due to dissolution of gas in the electrolyte, nor to diffusion of gas through the aluminum laminate casing, which is proven in the supplementary section, Figures S1 and S2.

Figure 2b shows the composition of gases, determined by GC-TCD, in cells at different storage times. The total volumes of gas found by GC-TCD correlate very well to the gas volumes measured by Archimedes’ method. The gases consumed are CO₂, H₂, C₂H₄ and CO. The saturated hydrocarbons, CH₄ and C₂H₆, are not measurably consumed. Of all the gases, CO₂ is consumed the most readily. It is almost entirely consumed within the first 100 hours of storage. Because CO₂ is highly soluble in organic carbonate electrolytes, the actual amount of CO₂ consumed is much larger than 0.2 mL. Considering the consumption of the CO₂ dissolved in the electrolyte (2.3 mL/mL of electrolyte, at 40 °C), the total amount of gas consumed may be close to 3 mL.²³

Evolution and consumption of gas in cells with additives.—The electrolyte used in the cells shown in Figures 1 and 2 contain no additives to control gas evolution. Therefore, the amount of gas generated in the first cycle, 1.4 mL, is large relative to the volume of the cell, (2 mL). Commercially available lithium-ion cells are likely to contain proprietary additive blends to reduce gas evolution. This work studies cells without electrolyte additives to amplify and better understand the gas evolution and consumption processes. The use of electrolyte additives would alter the amounts and proportions of the gases evolved, although the use of electrolyte additives does not prevent the consumption of gases.¹

Figure 3 shows the voltage and volume change of the cells with common electrolyte additives: 2% PES and 2% VC. Cells were charged to 4.5 V and left to rest at open-circuit voltage. As with the cell in Figure 1, which had no additives, there are two gas-producing events: one <3.7 V and one >3.7 V. The amount of gas produced in cells with additives is less than half the amount produced in the cell without additives, shown in Figure 1. The composition of the gas produced in NMC442 cells with 2% PES and 2% VC has already been reported, however the GC-MS technique used did not permit the detection of H₂ or CO.¹ It was found that C₂H₄ comprises 80–90%, and C₂H₆ comprises 5% of the gas evolved <3.7 V in cells with 2% VC and 2% PES. CO₂ comprises 10% of the gas evolved <3.7 V in cells with 2% VC, and ~5% in cells with 2% PES. Propene, and small amounts of methylpropene are evolved in cells with 2% PES. After the second gas evolution, CO₂ comprises ~80% of the gas in cells with 2% VC or 2% PES. The difference in the rate of gas consumption in cells with 2% VC or 2% PES is roughly proportional to the differing amounts of CO₂ evolved.

Effect of gas consumption on charge-transfer resistance.—The consumption of gas in a cell must result in either liquid or solid reaction products for a decrease in cell volume to be observed. The
formation of solid reaction products on the surface of the electrodes could increase the charge-transfer resistance (R_{ct}) of the cell. For this reason, electrochemical impedance spectrometry (EIS) was done on a cell, after 500 hours of storage (the same cell used for the data in Figure 2), and an identical cell that was degassed prior to the 500 hours of storage. Figure 4 shows the resulting Nyquist plots of the EIS experiment. The R_{ct} is taken to be the diameter of the mid-frequency feature in the Nyquist plot.\(^\text{13}\) The R_{ct} of a cell is the sum of the charge transfer resistance of the negative and positive electrodes, which are affected by the SEI films on the electrodes. Figure 4 shows that the consumption of gas in NMC442 cells does not significantly change the cell R_{ct}. This indicates that while solid reaction products must have formed from the consumption of gas, these products have no adverse effect on the R_{ct}. EIS was done on symmetric cells made from all the electrodes that were stored in pouch bags with gas, described below. No increase in impedance was observed in any case where gas consumption occurred.

**Effect of gas consumption on the surface chemistry of electrodes.**—To determine the chemical species which are deposited on the electrodes as a result of gas consumption, XPS analysis was conducted on electrodes taken from cells in which the formation gas had been consumed and twin cells which had been degassed prior to storage. The top panel of Figure 5 compares the XPS spectra of a negative electrode from a cell in which gas was consumed and a negative electrode from a cell which was degassed before storage, demonstrating the effect of gas consumption on the negative electrode SEI. The SEI of the negative electrode from the cell in which gas was consumed has twice as much carbon in the outer SEI as the negative electrode from the cell that was degassed prior to storage. The SEI of the negative electrode from the cell in which gas was consumed also has fewer inorganic species, LiF and phosphates. These observations suggest that gases evolved during formation react at the negative electrode and coat the negative electrode in a carbon-rich SEI.

The bottom of Figure 5 compares the XPS spectra of the positive electrodes from cells, with control electrolyte, in which either gas was...
consumed or where the cell was degassed before storage, demonstrating the effect of gas consumption on the positive electrode SEI. The SEI of the former has slightly more carbon and less inorganic species than the SEI of the positive electrode from the cell that was degassed prior to storage. This follows the same trend as the negative electrode SEI, however the difference between the two positive electrodes is much less than the difference between the two negative electrodes. The relative thickness of the SEI of the positive electrode can be inferred from the relative intensities of the Ni, Co and Mn 3p peaks (between 40 and 80 eV), and the NMC lattice oxygen O1s peak (at 529 eV). These peaks are smaller in the XPS spectra of the positive electrode from the cell in which gas was consumed. This indicates that gases react at the positive electrode to cause thickening of the positive electrode SEI.

Understanding the fate of gases in lithium-ion cells.— Figure 6 shows voltage and volume change of cells, with control electrolyte, that were charged to 4.5 V at 40 °C, and then quickly discharged to lower voltages for OCV storage. The rate of gas consumption is higher when cells are at higher voltages and states of charge. It is unclear from this data whether the increase in gas consumption is due to higher voltages at the positive electrode, resulting in oxidation of the gases, or whether the increase in gas consumption is due to higher degrees of lithiation at the negative electrode, where the gases could be reduced by lithium. To separate the reactions occurring at the positive and negative electrodes, individual electrodes were hermetically sealed in pouch bags and inflated with one of the gases evolved during formation: CO2, H2, C2H4 or CO.

Reactions of CO2.— Figure 7a shows volume change vs time for pouch bags inflated with CO2, containing charged positive or negative electrodes. Pouch bags inflated with CO2 and containing charged positive electrodes show no appreciable change in volume, after the first three hours in which they expand to thermally equilibrate at 40 °C from room temperature. Pouch bags inflated with CO2, containing lithiated graphite negative electrodes decrease in volume steadily over time. After 100 hours of storage at 40 °C, 0.5 mL of CO2 had been consumed by the lithiated graphite negative electrode. Over time, the rate of CO2 consumption slows, as the negative electrode becomes better passivated.3,4 It is strongly suspected that an amount of CO2 larger than 0.5 mL was consumed in the storage experiment shown in Figure 7a because the consumption of CO2 was fast upon injection, even at room temperature. Measurement of volume change began approximately 1 hour after CO2 was first injected, as this time was needed to hermetically seal the pouch bags and stabilize the strain gauges. The rapid decrease in volume after addition of CO2 is not due to dissolution of CO2 in the electrolyte, which must be a very fast process, as is shown in Figure S2 in the supplementary information.

The reaction of CO2 at the negative electrode has been observed several times in the literature.2–4 However, the reaction mechanism causing CO2 consumption and the subsequent effects on cell health have been a subject of debate. In the early days of lithium-ion research, CO2 was used as an electrolyte additive, as it was observed

![Figure 6.](image-url) a) voltage vs time and b) volume change vs time for fresh lithium-ion cells that were charged for the first time to 4.5 V, then rapidly discharged to several lower voltages and left to rest, open circuit for 100 hours at 40 °C.

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![Figure 7.](image-url) a) volume change vs time for pouch bags inflated with CO2, containing charged positive or charged negative electrodes, stored at 40 °C. B) the C1s regions and C) the P2p regions of the XPS spectra of negative electrodes stored in pouch bags, either under vacuum or inflated with CO2.
to create a lithium-rich SEI. Those early studies were conducted in beaker-type half-cells, in the absence of a positive electrode and with a large excess of electrolyte and active lithium. Those experimental conditions masked the potential adverse consequences of CO2 reduction, such as consumption of active lithium and creation of species than can cause self-discharge, which could lead to the failure of a commercial lithium-ion cell, where the volume of electrolyte and amount of active lithium are limited. The adverse effects of CO2 consumption in lithium-ion cells were first suggested by Sloop et al. It was shown that the presence of CO2 could cause reversible self-discharge through a “chemical dialogue” or “shuttle reaction” between negative and positive electrodes at high voltage. In this shuttle reaction CO2 is reduced at the lithiated negative electrode to form lithium oxalate (Equation 5), which diffuses to the positive electrode and is oxidized to reform CO2 (Equation 6).

$$2\text{CO}_2 + 2\text{Li} \rightarrow \text{Li}_2\text{C}_2\text{O}_4$$ \[5\]

$$\text{Li}_2\text{C}_2\text{O}_4 \rightarrow 2\text{CO}_2 + 2\text{Li}^+ + 2\text{e}^-$$ \[6\]

It is unlikely that this chemical dialogue occurs in commercial lithium-ion batteries, since the solubility of lithium oxalate in electrolyte is very low, and the oxidation potential for oxalate, shown by Sloop, is higher than the potentials which positive electrodes experience in normal operating conditions.

In order to characterize the chemical species formed by the reaction of CO2 at the negative electrode, XPS analysis was done on lithiated graphite negative electrodes stored in electrolyte, either in pouch bags that were vacuum-sealed or in pouch bags injected with CO2. Figure 7b shows the C1s region of these negative electrodes, and illustrates one of two reactions which consume CO2. The most prominent of these two reactions is the reduction of CO2 by Li to form insoluble organic SEI compounds. The C1s region shows that the electrode stored in CO2 has more intensity in the region surrounding 289 eV, indicating the presence of an oxalate-type compound or semi-carbonate. This suggests that the consumption of CO2 occurs through the reduction by Li to form lithium oxalate, as shown in Equation 5. The reduction of CO2 to oxalate has been shown to occur at potentials below 2.8 V vs Li/Li+. The potential of lithiated graphite is below 2.8 V vs Li/Li+, therefore the reduction of CO2 would occur continually in a cell, except when the graphite is completely free of lithium.

Figure 7c shows the P2p region of the XPS spectra of lithiated graphite negative electrodes stored in electrolyte, either in pouch bags that were vacuum-sealed or in pouch bags injected with CO2. The P2p region of the electrode that was stored in CO2, which has more intensity at 134 eV, indicates the presence of phosphates or fluorophosphates. This suggests a second reaction is involved in the consumption of CO2. This reaction would involve the formation of a carbonate intermediate, which subsequently reacts with LiPF6. The formation of carbonates from CO2 through the reduction of CO2 by lithium, is shown in Equation 7. The formation of bicarbonate from the reaction of CO2 with OH−, is shown in Equation 8. The reaction of inorganic carbonates with LiPF6 is described by Equation 9.

$$\text{CO}_2 + \text{OH}^- \rightarrow \text{HCO}_3^-$$ \[8\]

$$2\text{Li}_2\text{CO}_3 + \text{LiPF}_6 \rightarrow 2\text{CO}_2 + 4\text{LiF} + \text{Li}_2\text{PO}_4$$ \[9\]

The formation of lithium oxalate, via Equation 5, is likely preferred over the formation of carbonates, via Equations 7 and 8. This is evidenced by the net decrease in volume of pouch bags with charged negative electrodes, inflated with CO2. The continual consumption and evolution of CO2 from Reactions 6–8 would not result in a net volume change at steady state. The cyclical reactions in Equations 6–8 would also have notable adverse effects on cell performance: continual loss of active Li from the negative electrode as well as continual loss of LiPF6 from the electrolyte. Significant differences in performance are not observed in the UHPC cycling of cells in which CO2 has been consumed, which will be shown later in this work. It is possible however that the reactions in Equations 7–9 could contribute to the failure of cells cycled to very high voltages, when very large amounts of CO2 are evolved from electrolyte oxidation. Cells cycled aggressively at high voltage appear to show loss of electrolyte salt at end of life, which could be explained by the consumption of LiPF6 through Equation 9, (Li2PO4F2 is soluble to only about 0.1 M at room temperature in the organic carbonates used in this work). At moderate cycling voltages, when CO2 is not continually evolved upon every cycle, the consumption of CO2 does not produce negative consequences, as was shown in the UHPC study discussed below.

Reactions of H2.—Figure 8a shows volume change of pouch bags inflated with H2, containing charged positive or negative electrodes, after one week of storage at 40.0 or 60.0 °C. The volume of pouch bags containing both negative and positive electrodes decreased during the storage period. Of all the gases studied in this work, H2 was the only gas that caused shrinkage of pouch bags containing positive electrodes. Although H2 is a very small molecule, it is unlikely that shrinking of the pouch bags containing H2 was due to leaking of H2 through the hydrogen-laminated pouch bag material, since pouch bags containing positive and negative electrodes, inflated with the same amount of H2 and stored at the same temperature, shrank by different amounts. Further proof that H2 did not leak from the pouch bags is shown in Figure S1 of the Supplementary Information.
Figure 8a shows that negative electrodes charged to cell voltages of 4.4 or 4.6 V and stored at 40.0 °C consume 0.5 mL of H2 over one week. In the same amount of time, negative electrodes charged in cells to 4.6 V and stored at 60.0 °C consume a much larger quantity, 3 mL of H2. The reaction of H2 with lithiated graphite has not been reported before. It is possible that consumption of H2 at the negative electrode is due to the reduction of hydrogen by lithium, to form lithium hydride, as shown in Equation 10.

\[ 2\text{Li} + \text{H}_2 \rightarrow 2\text{LiH} \]  
\[ \Delta G^\circ = -151.24 \text{kJ/mol H}_2 \]  

The \( \Delta G^\circ \) for Equation 10 was calculated using \( \Delta G^\circ \) of LiH and a value of 7.14 kJ/mol to account for the intercalation of Li in graphite, as LiC6.32-33 The strong temperature dependence on the extent of the reaction indicates that it may not be kinetically favorable at lower temperatures. The lithium hydride produced by this reaction is a strong base and a reducing agent. LiH produced by this reaction would likely react further inside a cell, by reducing electrolyte solvent molecules or reacting to form OH⁻, which could promote dissolution of transition metals from the positive electrode.

Figure 8a shows that ~0.5 mL of H2 was consumed by positive electrodes charged in cells to 4.6 V and stored at 60.0 °C for one week. About 0.2 mL of H2 was consumed by identical positive electrodes stored at 40 °C for the same amount of time. The reaction of H2 with the positive electrode has been observed before. It is thought that H2 oxidizes at the positive electrode to form protons, as shown in Equation 11.

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \]  

Protons are known to be undesirable in lithium-ion batteries, as they promote the dissolution of transition metals from the positive electrode. Additionally, protons could diffuse to the negative electrode and be reduced, as shown in Equation 2, leading to the re-evolution of H2.

The continual consumption of H2 at the positive electrode and re-evolution of H2 at the negative electrode has been cited as a cause of reversible self-discharge from both electrodes.5 The results from this study show that this is unlikely to occur, and if it did, the amount of self-discharge at the positive electrode would be insignificant. This is because Figure 8a shows that a much greater amount of H2 is consumed at the negative electrode than at the positive electrode, at the same temperature and state of charge. This suggests that in a full cell, the reduction of H2 at the negative electrode would be faster than the oxidation of H2 at the positive electrode. The volume of H2 reacted at the positive electrode at 60 °C, 0.5 mL, would require 1 mAh of charge to be removed from the positive electrode, according to Equation 11. This amount of self-discharge corresponds to less than 1% of the electrode capacity and is twenty times less than the amount of charge lost irreversibly in high voltage storage of the same cell.34

Reactions of CO.—Figure 9 shows volume change of pouch bags inflated with CO, containing charged negative electrodes, after one week of storage at 40 or 60 °C. At both temperatures, only 0.1 mL of CO was consumed by the negative electrodes. This indicates that only a very small and finite amount of CO can be consumed by the negative electrode. This is supported by Figure 2, which shows that the same quantity, 0.1 mL, of CO is consumed in the full cell, during 100 hours of storage at 4.5 V. Storage for longer than 100 hours does not increase the amount of CO consumed, leaving excess unconsumed CO. Consumption of CO by charged positive electrodes was not observed.

Gas consumption in cells with electrode coatings.—Electrode coatings modify the surface of electrode particles, and can change the amounts and proportions of gases evolved, in a manner similar to electrolyte additives. Figure 10a shows the amount of gas evolved by cells with NMC622 positive electrodes, after charging to 4.5 V, the amount of gas remaining after these cells were left to rest at open-circuit voltage for 400 hours at room temperature, and the amount of gas remaining after ~800 hours of cycling at 20 °C. The cells all had identical graphite negative electrodes and NMC622 positive electrodes that were either uncoated, coated with Al2O3 (coating A), or coated with a proprietary high-voltage coating (coating B). Figure 10a shows that gas consumption occurred in cells with uncoated NMC622 and NMC622 with coating B, with and without electrolyte additives. The gas volume of cells with NMC622, coated with positive electrode SEL or the formation of a rock salt layer (RSL). Both a thicker SEI and a RSL would impede the transfer of lithium to the surface of the positive electrode. Irreversible creation of a RSL on certain crystal facets of NMC at high voltage has been described several times in recent literature.38,39 It is believed that the RSL is a cause of impedance growth, power and energy loss in lithium-ion cells that are charged to high voltages. It has been suggested that the RSL is created in a ‘pseudo-combustion’ reaction whereby oxygen is removed from the NMC lattice by electrolyte species that are oxidized at high voltage.40 It is possible that C2H4 pseudo-combusts in this manner, as C2H4 is a strong reducing agent and very reactive toward oxygen. This reaction likely does not play a significant role in full cells however, as Figure 4 shows that the R\text{p} of cells in which gas was consumed is not different from cells which were degassed before high voltage storage. It is possible that consumption of C2H4 at the negative electrode competes with its reaction at the positive electrode.
Figure 10. Results of high voltage storage and UHPC cycling of cells with positive electrode coatings: a) volume change during formation, storage and cycling, b) voltage drop during high voltage storage c) CIE d) charge end point slippage e) $\Delta V$, and d) discharge capacity loss after 10 UHPC cycles.
Effect of gas consumption on self-discharge.—To see whether the reaction of gases within lithium-ion cells caused capacity loss or self-discharge, degassed and undegassed lithium-ion pouch cells, with control electrolyte, were stored, open circuit, at 4.5 V for 400 hours. This experiment was conducted at room temperature, to promote dissolution of the gasses in electrolyte, and permeation of dissolved gasses to the electrodes for consumption. This experiment was conducted to investigate hypotheses from the literature, which posit that the reactions of gases inside lithium-ion cells cause reversible self-discharge at the positive electrode at high voltage. Sloop et al. suggested that CO2 is reduced at the negative electrode to form Li2C2O4, which diffuses through the electrolyte to the positive electrode, where it is oxidized to reform CO2. Similarly, Metzger et al. suggested that H2 is oxidized at the positive electrode to form protic impurities, such as alcohols, which diffuse through the electrolyte to the negative electrode, where they are reduced to reform H2. Both the reaction mechanisms of Sloop and Metzger are called upon to explain continuous and reversible self-discharge from both electrodes at high voltage. Figure 10b shows the voltage drop of cells with NMC622 positive electrodes, during high voltage storage. The cells underwent their first charge, to 4.5 V, before being stored, open-circuit, at room temperature. Two cells of each type were degassed. The remaining two cells were left, to observe the effect of gas consumption on self-discharge at the positive electrode. Figure 10b shows that there is no significant difference in self-discharge at the positive electrode between cells which were degassed and those which contained the gasses evolved from the first cycle to 4.5 V. This suggests that the reactions that consume gas in lithium-ion cells do not involve oxidation at the positive electrode. The experimental error of ΔV measurements is shown in the supplementary section, Figure S3c. For cells without electrolyte additives and without electrode coatings ΔV was slightly higher for cells in which gas was consumed. The difference in ΔV between these cells is larger than the experimental error. This may be due to the formation of a RSL on the surface of the uncoated positive electrode, if C2H4 reacts at the positive electrode, as was shown by Figure 9. Increased ΔV may also be due to loss of electrolyte conductivity, as LiPF6 was suggested by XPS measurements in this paper to react with the products of gas consumption. It is unlikely that the increase in ΔV is due to the thickened SEI of the negative electrode, as was shown by EIS analysis of symmetric cells of negative electrodes in this paper. Figure 10f shows the cumulative discharge capacity loss after 10 UHPC cycles. The difference in capacity loss between degassed cells and cells which had not been degassed is not consistent across cell types. Cells without electrode coatings and cells with Al2O3 coatings showed higher rates of capacity loss when degassing was omitted. This difference is much larger than the experimental error, shown in Figure S3d. However the cells with Al2O3 coated positive electrodes did not consume gas during storage or UHPC cycling, so it is unclear whether the increase in capacity loss in cells with uncoated electrodes can be attributed to gas consumption. Cells with electrode coating B showed the opposite trend; capacity loss was lower when the cell was not degassed and gas consumption occurred. This difference is larger than the experimental error for capacity fade measurements, shown in Figure S3d. While the active consumption of gas is expected to reduce capacity, as discussed before, it is likely that the consumption of gas results in a passivating SEI on the negative electrode, which prevents other parasitic reactions. Therefore, once in a gas in a cell has reacted to completion, the cell is expected to have lower CIE and lower rates of capacity loss.

Based on the results from the "pouch bag" experiments, the consumption of gas in a cell must result in a decrease in cell capacity. The "pouch bag" experiments showed that CO2, H2, and C2H4 are reduced at the negative electrode, which would result in loss of active lithium from the negative electrode. In theory, the one-electron reduction of 1 mL gas causes ~1 mAh of capacity loss, at standard temperature and pressure (1 mL = 0.041 mmol, by the ideal gas law; 0.041 mmol of electrons = 1.1 mAh). The total amount of gas consumed in the cells presented here, without electrolyte additives nor electrode coatings, is ~4 mL, including the additional consumption of dissolved CO2 in the electrolyte (2.9 mL CO2/mL electrolyte, at room temperature). The consumption of ~4 mL of gas would in theory lead to a decrease of cell capacity of ~4 mAh, corresponding to 2% capacity loss in our cells, assuming one electron reduction of all gases. This theoretical capacity loss could not be measured in a convenient manner using the UHPC method, since the variation in capacity between identical machine-made cells is of the same order of magnitude as the theoretical capacity loss, as shown by Figure S3e of the Supplementary Section.

Conclusions

This work began with the quantification and characterization of the gases evolved and consumed in lithium-ion cells. It was found that in cells with 3:7 EC:EMC electrolyte, large amounts of CH2=CH2, H2, and CO are evolved during the first charge, up to 3.5 V. CO2 and H2 gases are evolved at higher voltages during the first charge. Small amounts of saturated hydrocarbons, C6H6 and CH4 are also evolved during the first charge. After 300 hours of open-circuit storage, ~60% of the gases evolved during the first cycle had been consumed in the cell. CO2 was almost entirely consumed by the cell, while H2, C2H4, and CO were consumed in part.

The rates of the gases consumed in the cell were investigated by storing individual charged electrodes in pouch bags with gas. It was found that the gases that are consumed in a lithium ion cell—CO2, H2, C2H4, and CO—can be reduced at the charged negative electrode. The reduction of CO2 results in two reaction products. The major product of CO2 reduction is thought to be lithium oxalate. The mi-
nor products of CO2 reduction are carbonates, which are thought to be subsequently consumed by LiPF6 to form fluorophosphates and to reform CO2. H2 was the only gas observed to be consumed in measurable quantities at the positive electrode. The amount of H2 consumed at the positive electrode was much less than the amount consumed at the negative electrode at the same temperature and state of charge. This suggests that the H+/H2 shuttle reaction does not play a significant role in the reversible self-discharge of both electrodes at high voltage. C2H4 is apparently also consumed at the positive electrode, evidenced by a large increase in Rct at that electrode after storage in ethylene, although the total volume of these samples did not decrease upon storage. The consumption of H2 and C2H4 at both the positive and negative electrodes was accelerated by higher temperatures.

The effect of gas consumption on self-discharge and capacity fade was studied using high voltage storage and UHPC cycling. Gas consumption was not observed to affect self-discharge at the positive electrode, up to 4.5 V. UHPC cycling showed no difference in the capacity fade between cells that were degassed and cells in which gas was consumed. The inherent spread in capacity between pairs cells made it impossible to determine the capacity loss from the reduction of gases at the negative electrode. In theory, the loss of 1 mL of gas would correspond to the loss of ~1 mAh of capacity, assuming a one-electron reduction of all gases. The cells without electrolyte additives in this study are therefore expected to have lost up to 2% of their capacity due to gas consumption.

The results of this work show that omitting the degassing step does not increase the Rct, does not cause self-discharge at high voltage, nor increase the rate of capacity fade. It is likely that the consumption of gas leads to small amounts of capacity loss, which might be mitigated using electrolyte additives to suppress the evaporation of gases and therefore to decrease their subsequent consumption.

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