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A review of gas evolution in lithium ion batteries

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Abstract

This is a review on recent studies into the gas evolution occurring within lithium ion batteries and the mechanisms through which the processes proceed. New cathode materials such as lithium nickel manganese cobalt oxides are being heavily researched for the development of higher specific capacity electrodes. These materials often suffer from rapid degradation which coincides with gas evolution. Further sources of gas evolution include electrolyte reduction at the anode during the initial cycles culminating in formation of a solid electrolyte interphase and surface layer compounds formed on the cathode during production and storage. There have been several techniques established for detection and quantification of gas evolution in *ex situ* and *in situ* studies, primarily gas chromatography mass spectrometry and differential/on-line electrochemical mass spectrometry.

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1. Introduction

Lithium ion batteries are one of the most commonly used energy storage technologies with applications in portable electronics and electric vehicles. Characteristics such as high energy density, good cycling ability, high operating voltage and low self-discharge are pivotal in making lithium ion batteries the leading technology for these applications. As such, there is a desire to increase energy density further to improve the range of electric vehicles. In most batteries, it is the cathode (positive electrode) material that is the limiting factor to increased energy density due to having the lowest specific capacity of the two electrodes, however high specific capacity cathode material often suffer from degradation issues limiting their utilisation [1–3]. Added to this one of the main areas for improvement for lithium ion batteries is with regards to safety, especially with the increase in use for electric vehicles [2,4]. Thermal runaway and gassing of cells are two of the major areas of interest especially when operated under abuse conditions such as overcharge, operation outside temperature limits and cell deformation by crushing or puncturing [5,6]. Gas evolution arises from many sources in lithium ion batteries including, decomposition of

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electrolyte solvents at both electrodes and structural release from cathode materials are among these. Several of the products such as hydrogen and organic products such as ethylene are highly flammable and can onset thermal runaway in some cases. Additional to the safety issues attributed to gas evolution it can also heavily impact cell performance and is associated with electrode degradation, diminished shelf life, reduced cycle lifetime, electrolyte displacement and increased cell impedance. A mechanical property impacted by the gassing of pouch cells due to the lack of rigidity is variation of stack pressure arising from the correlating volume changes [7]. The change in pressure culminating in cell deformation can negatively impact electrode contact which can lead to a reduced Coulombic efficiency. This paper will aim to provide a review of gas evolution occurring within lithium ion batteries with various electrode configurations, whilst also discussing the techniques used to analyse gas evolution through ex situ and in situ studies.

2. Methods for the detection and quantification of gas evolution

The simplest method for monitoring gas evolution is through measurement of pouch cell thickness, the variation of cell thickness should provide insight into the extent of gas evolution or consumption of lithium ion batteries this however, inaccurately assumes that expansion is uniform across a cell [8]. Archimedes' principle has been used to engineer a method for monitoring the volume of pouch cells during operation and gives a more accurate representation of the quantity of gas evolution than measuring cell thickness [7–14]. Compared with other gas evolution measurement techniques this allows for cycling of commercial cells (pouch cells) and is a non-invasive technique as it does not involve the removal of gas from the cell which could impact on the constituents and hence performance of the cell. Additionally, it is easier to monitor cell volume in situ than through cell thickness measurements. However, it must be noted that some of the gaseous products are soluble in the electrolyte and may also undergo further parasitic reactions culminating in gas consumption, therefore simple measurements of the volume of the pouch cell can underestimate the volume of gas produced [14].

Whilst volume measurements will give indication of the extent of gassing, they give no information relating to the constituents of the gas evolved, this is why volume measurements are often combined with gas chromatography mass spectrometry. Gas can be extracted from cells post mortem through the use of a syringe, the resulting gas can then be injected into a gas chromatography mass spectrometer for analysis to ascertain the species present. Gas chromatography separates volatile species after injection into the capillary this is coupled with time-of flight mass spectrometry which is used to derive the species present in the sample by determining an m/z value for molecule mass fractions [15]. This is a mature technique with a high volume of published articles including in the field of lithium ion batteries [8,11–22]. To enable studies into a larger range of species produced during cycling Bachot et al. [17] combined gas chromatography mass spectrometry with electrospray ionisation-high-resolution mass spectrometry (ESI-HRMS). GC–MS was utilised to analyse products with a high volatility whereas ESI-HRMS identified moderately volatile species such as ethylene oxide oligomers.

A large quantity of gas evolution studies involve ex situ analysis and thus provide little information on the gases produced during cycling, making it difficult to assign a reaction mechanism to a generated species. Differential electrochemical mass spectrometry provides the ability to detect species evolved in real time, quantifying gas evolution whilst simultaneously measuring cell potential or cell current [23]. The value of DEMS is evident by its usage in the study of gas evolution of lithium ion batteries and their constituents during electrochemical cycling of the cell [23–43]. DEMS operates by flowing a carrier gas, often argon or helium, through an electrochemical cell where it collects the gaseous products evolved and transports them to the mass spectrometer for analysis. To ensure the cell does not dry out by the continual removal of volatile species, especially the electrolyte, the carrier gas is often flown through a bubbler prior to introduction into the cell [35]. Additionally, a cold solvent trap may be included in between the electrochemical cell and the mass spectrometer unit to attempt to minimise the solvent background signal detected.

Slight modifications to commonly used battery constituents have been carried out to facilitate improvements in the accuracy of DEMS measurements. One example of this switching a common battery electrolyte which comprises a mixture of carbonate solvents for an electrolyte containing a solitary electrolyte. Ethylene carbonate is the candidate used in literature [24], this solvent is chosen for its low vapour pressure in comparison with other carbonate solvents (DMC, EMC) reducing the impact of the electrolyte solvent on the OEMS signal whilst maintain stable SEI formation. The use of lithium ion conducting glass ceramic to allow for separation of the anolyte and catholyte in cells is another modification that has been demonstrated in literature [24,30]. Separation of the electrodes is

commonly used in cells containing lithium as the counter electrode as the glass ceramic prevents the catholyte coming into contact with highly reductive lithium. As the cell is sealed, species that would readily react with the lithium counter electrode can be tested for their impact on the positive electrode in the confidence that there will be no influence from the counter electrode. Metzger et al. [24] utilised this technique to investigate the impact of higher water content in the electrolyte on the performance and gas evolution of positive electrode constituents such as conductive carbon and polymer binder.

Solubility of the gaseous species can impact the detection rate through the use of DEMS. Carbon dioxide is one species impacted by this as it has a higher solubility than oxygen in organic solvents and so can suffer from a delay in signal in relation to oxygen resulting in the determination of onset potential possibly being misleading [29]. Another drawback to the use of mass spectrometry is the inability to accurately determine the source of some m/z values detected during the use of differential electrochemical mass spectrometry. The m/z value of 28 is particularly problematic as it can account for CO, C₂H₄ and fragments of CO₂ and C₂H₆ [34]. Berkes et al. [42] developed a technique to couple both differential electrochemical mass spectrometry and Fourier transform infra-red spectroscopy. Through the use of this technique they were able to ascertain the magnitude of the constituents that comprised the $m/z = 28$ signal detected through DEMS measurements. This method successfully demonstrated the ability to unambiguously assign the volume of gas responsible for signals detected during DEMS measurements of NMC 532/graphite cells for products such as carbon monoxide, carbon dioxide and ethylene [42].

Neutron imaging is an in situ technique that was used by Michalak et al. [44] to directly observe gas evolution during operation of lithium-ion batteries. Qualitative and quantitative information was obtained giving insight into volumes of gas evolution of different electrode configurations. The high neutron cross section of carbonate solvents used in lithium ion battery electrolytes allows for visualisation of electrolyte degradation during cell operation, especially mechanisms involving gaseous products [44].

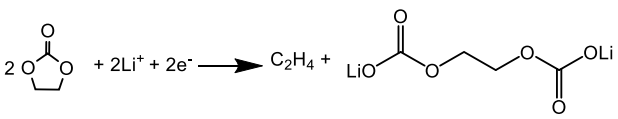
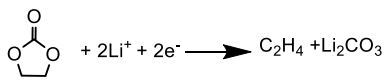
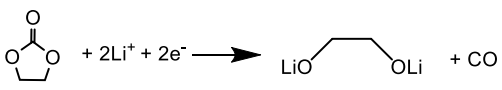

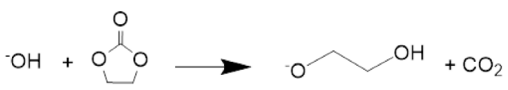
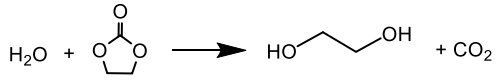
3. Gas evolution mechanisms in lithium ion batteries

3.1. Anodes

In lithium ion batteries the most common electrode used for the anode (negative electrode) is graphite due to the ease of intercalation into the spacing between layers and high theoretical specific capacity of 372 mAh g⁻¹. There are several gassing mechanisms attributed to the graphite electrode in lithium ion batteries, of which the primary source is through electrolyte reduction during the first cycle coinciding with the formation of a solid electrolyte interphase (SEI) on the electrode surface. One of the most dominant reactions involves the production of ethylene from electrolyte reduction which is onset at a potential of 0.8 V vs. Li/Li⁺ and is continuously evolved until the charge cycle has ended and the cell starts discharging and can occur through many reaction pathways [39]. The peak in ethylene production rate occurs at 0.5 V vs. Li/Li⁺ for cells using 1M LiTFSi in EC/EMC 3/7 electrolyte [30]. Lithium ethylene dicarbonate (LEDC) is one of the products detected from electrolyte reduction and a constituent of the stable SEI layer formed on the graphite electrode [39]. From the detection of ethylene and LEDC within the first cycle it has been proposed that the reduction of ethylene carbonate proceeds through a 2-electron process such as that shown in Eq. (1) in Table 1. Alternative reduction pathways are also included in Table 1 in the form of Eqs. (2) and (3) both of which only require one EC molecule as opposed to two as is the case for Eq. (1). Li₂CO₃ has been observed to be a major constituent of the SEI formed on graphite electrodes suggesting that Eq. (2) could be a dominant pathway for electrolyte reduction [45]. In subsequent cycles the rate of ethylene generation is greatly reduced due to the production of a solid electrolyte interphase on the graphite electrolyte preventing continued electrolyte reduction. Therefore, for cells which have undergone formation cycling, and have been degassed, as is common practice for production of commercial lithium ion batteries, there is significantly reduced gas evolution [30].

Contaminants within the cell, mainly in the electrolyte, are another source responsible for gas evolution deriving from a reduction process at the anode surface. Water is one of the main contaminants within lithium ion batteries and can be present in the electrodes from insufficient drying or contained in the battery electrolyte. The reduction of water was proposed to take place through a single electron process as evidenced from findings obtained through the utilisation of DEMS by Bernhard et al. in agreement with the process shown in Eq. (4). In their studies the quantity of hydrogen detected correlated with the expected water content of the cell, which concurred with other studies which found that over 80% of the hydrogen produced was sourced from reduction of water [30,36]. On the other hand, Metzger et al. [39] present that water reduction is not the major source of hydrogen in lithium ion

Table 1. Reduction reactions occurring at the anode in lithium ion batteries [46,47].

Reactions occurring at the anode during lithium ion cell operation	Equation	Reference
 $2 \text{EC} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{C}_2\text{H}_4 + \text{LiO-C(=O)-O-CH}_2\text{-CH}_2\text{-O-C(=O)-OLi}$	1	[10]
 $\text{EC} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{C}_2\text{H}_4 + \text{Li}_2\text{CO}_3$	2	[17]
 $\text{EC} + 2\text{Li}^+ + 2\text{e}^- \rightarrow \text{LiO-CH}_2\text{-CH}_2\text{-OLi} + \text{CO}$	3	[46]
 $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{OH}^- + 1/2 \text{H}_2$	4	[23]
 $\text{OH}^- + \text{EC} \rightarrow \text{LiO-CH}_2\text{-CH}_2\text{-OLi} + \text{CO}_2$	5	[23]
 $\text{H}_2\text{O} + \text{EC} \rightarrow \text{HO-CH}_2\text{-CH}_2\text{-OH} + \text{CO}_2$	6	[24],[47]

batteries and suggested that the magnitude of hydrogen evolution equates to four times the magnitude expected from the water content within the cell. In addition to the reduction of water, the hydroxide ions produced can facilitate electrolyte decomposition through Eq. (5), water has also been observed to undergo a hydrolysis reaction with EC with the reaction shown in Eq. (6) [24] highlighting the multitude of gassing reactions that can occur from the presence of water in the cell.

Lithium titanium oxide ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, LTO) is an alternative material used as the negative electrode (anode) in a lithium ion cell in the place of a graphite electrode. LTO electrodes have a higher redox potential than graphite at 1.55 V vs. Li/Li^+ which is inside the stability window of commonly used lithium ion battery electrolytes [48]. Operating within the stability window of the electrolyte removes the mechanism of SEI formation on the negative electrode surface and as such should lower the initial gassing that is observed during formation cycling of cells containing a graphite negative electrode. However, in comparison to graphite they have been shown to exhibit substantial gassing during storage with hydrogen the main contributor to the gas evolution as the reduction of water can be onset at a potential of 2 V vs. Li/Li^+ indicating that controlling water content within the cell is of paramount importance to minimise gas evolution [30].

3.2. Cathodes

For the development of lithium ion batteries the limiting factor is often the specific capacity of the cathode (positive electrode). One class of materials of interest for an increase of specific capacity are lithium nickel manganese cobalt oxides (NMC). Maximising nickel content within NMC materials has been shown to increase the achievable specific capacity of the cathode [4]. However, NMC materials with high nickel content have been known to suffer from poor cyclability which coincides with gas evolution. Gas evolution relating to interactions with the cathode can occur by electrolyte oxidation and surface contaminants. The initial gassing of NMC cathode materials at an onset potential of approximately 3.8 V is commonly attributed to the electrochemical decomposition of lithium carbonate (Li_2CO_3) which can form on the surface of NMC electrodes during manufacture and storage. Hatsukade et al. [38] investigated the source of carbon dioxide by removal of Li_2CO_3 which was replaced by carbon-13 labelled Li_2CO_3 . From this study it was observed that $^{13}\text{CO}_2$ evolution peaked during the first cycle and evolution rapidly decreased with subsequent cycles. However, this was not the only source of CO_2 with $^{12}\text{CO}_2$ detected at a comparable magnitude as $^{13}\text{CO}_2$ during the first cycle whilst exhibiting continued gassing in subsequent cycles. This shows that the $^{13}\text{CO}_2$ evolution source was of a finite amount in this case carbon-13 labelled lithium carbonate and that reactions involving the carbonate solvent are likely responsible for the rest of carbon dioxide evolution.

Further methods for studying the gas evolution deriving from lithium carbonate have included isotopically enriching transition metal oxide electrodes with ^{18}O [23] and cycling of lithium carbonate electrodes [49]. From all tests it was established that lithium carbonate was responsible for CO_2 generation in the low potential range of gas evolution <4.2 V. The decomposition of lithium carbonate is expected to produce gaseous products such as CO_2 and singlet oxygen [49] through reaction 7 in Table 2.

Table 2. Oxidation reactions occurring at the cathode in lithium ion batteries.

Reactions occurring at the cathode during lithium ion cell operation	Equation	Reference
$2\text{Li}_2\text{CO}_3$	$\longrightarrow 4\text{Li}^+ + \text{e}^- + 2\text{CO}_2 + {}^1\text{O}_2$	7 [42]
$2 {}^1\text{O}_2 + \text{C}_4\text{H}_6\text{O}_2$	$\longrightarrow 2\text{CO}_2 + \text{CO} + \text{H}_2\text{O}$	8 [24][39]

Mahne et al. [49] investigated the hypothesis that singlet oxygen is generated from the oxidation of lithium carbonate by cycling lithium carbonate electrodes with a singlet oxygen probe present in the form of 9,10-dimethylantracene (DMA). Following cycling the electrolyte was tested through high performance liquid chromatography and was found to contain endoperoxide, a product of the reaction of DMA and singlet oxygen. Given the role of the lithium carbonate in the initial gas generation of nickel containing electrode materials washing the electrodes prior to cycling is one method of lowering the extent of gas production at the cathode in the initial cycles [19]. The importance of removal of lithium carbonate from the surface of NMC is highlighted by the investigation into alternative cathode materials. Lithium cobalt oxide has significantly less free lithium available to form lithium surface compounds and thus produces very little CO_2 during the initial charging of the cell in the first cycle [19,26].

There are two regions of gas evolution attributed to the cathode in lithium ion batteries additional to the degradation of surface contaminants, at higher voltages electrolyte oxidation can be the main contributor to gas evolution. Two pathways for the oxidation of electrolyte solvents during the operation of a lithium ion battery are possible, electrochemical oxidation and chemical oxidation. Electrochemical oxidation is dependent on the surface area of the electrode surface as well as the electrochemical potential of the cell. As a result, the conductive carbon content within the electrode becomes significant as its surface area far exceeds that of the active material despite being a minority of the total electrode weight [25]. The second pathway, chemical oxidation, is reliant on the release or production of a highly reactive species during the operation of a cell, for example NMC electrodes can suffer from release of singlet oxygen from their layered structure, which initiates the oxidation reaction of the carbonate solvent in the electrolyte. To investigate the dominant pathway for electrolyte oxidation Jung et al. [25] tested conductive carbon electrodes at high voltages versus a lithium foil counter electrode. Through the use of on-line electrochemical mass spectrometry (OEMS) they observed that there was minimal gas evolution in the potential window from 3 V to 5 V for electrodes comprised of 50% conductive carbon, 50% PVDF, indicating that electrochemical oxidation is not expected within the potential range of lithium ion batteries. Further evidence for electrochemical oxidation occurring outside the operational potential window of lithium-ion batteries is exhibited with the cycling of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$ electrodes with Wang et al. [26] observing no gas evolution from cells containing an $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_2$ electrode below 5 V.

Chemical oxidation of electrolyte requires the formation of a reactive species prior to its occurrence. Oxygen release can coincide with phase transitions that result from the cycling of cathodes in lithium ion batteries and culminates in the formation of oxygen depleted regions near the surface of the electrode. The lack of oxygen in close proximity to the surface of the electrode and the slow diffusion rate of oxygen through the material limit the rate of further oxygen evolution [48]. It has been found that oxygen evolution is not dependent on cell potential but is reliant on the state of charge (SOC) and is onset at a SOC of 80% for NMC materials [40,43]. The onset of oxygen, carbon dioxide and carbon monoxide evolution has been seen to decrease with increasing nickel content for NMC materials, from NMC111 to NMC811, all however still exhibit initial gas evolution from electrolyte decomposition at the cathode when the SOC reaches 80% [40].

As oxygen evolution is not dependent on electrochemical potential it provides a possible answer to the correlation found between O_2 , CO_2 and CO . The release of lattice oxygen from the cathode initiates chemical oxidation of electrolyte within the cell linking the three gases evolved in the process. This was highlighted by Wandt et al. [43], by monitoring singlet oxygen evolution from NMC electrodes through detection of photon emission at 633 nm for which the formation of a singlet oxygen dimer followed by transition to the ground state is responsible. NMC811 was the only NMC material observed to evolve CO_2 at a potential of 4.55 V with lower nickel fraction materials evolving gas at higher potentials. Additionally, NMC811 was the only electrode tested that suffered from singlet oxygen release from the electrode structure at the same potential and as such, it is highly likely that the two processes are linked. A mechanism for the reaction of single oxygen with EC was proposed by Jung et al. [25] and is shown in Fig. 1 with the overall equation shown in Table 2 as Eq. (8). This mechanism agrees with their findings with regards to CO and CO_2 evolution coinciding with oxygen evolution.

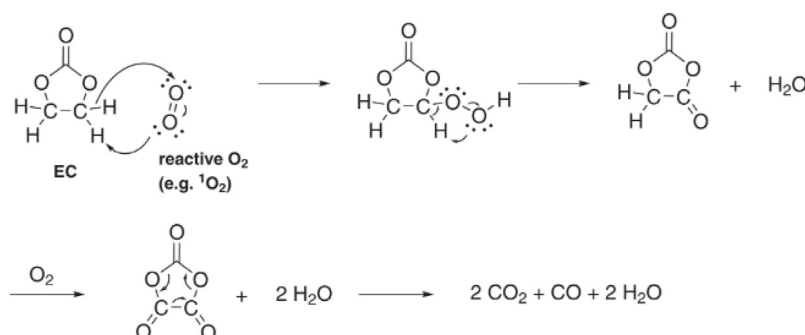


Fig. 1. Reaction mechanism for ethylene carbonate oxidation by singlet oxygen released from lithium nickel manganese cobalt oxide electrodes as proposed by Jung et al. [40].

Guéguen et al. [28] suggest an alternative mechanism for the gas evolution observed above 4.2 V vs. Li/Li^+ for cathode materials because of the detection of POF_3 indicating electrolyte salt degradation. Electrolyte salt degradation is attributed to the hydrolysis of $LiPF_6$ with reactive ROH species formed as a result of electrolyte oxidation at potentials above 4.2 V vs. Li/Li^+ .

3.3. Full cell electrode cross-talk

For the understanding of gas evolution in lithium ion batteries it is of paramount importance to consider a complete system with both electrodes. Gas produced from one electrode can be absorbed or consumed at the other, whilst parasitic reactions can be instigated by reaction products diffusing between the electrodes. Carbon dioxide consumption has been seen to be one of the most significant consumption reactions within lithium ion batteries. Carbon dioxide has been observed to react with lithium counter electrodes to form carbon deposits in the electrode surface [27]. Additionally, when in a full cell configuration, graphite can act as sink for carbon dioxide generated through oxidation reactions at the cathode [11]. This has been demonstrated by Xiong et al. [11] by the storage of lithiated NMC electrodes in the presence and absence of a graphite electrode. For the case with a graphite electrode present gas evolution was greatly diminished. To test gas consumption reactions Ellis et al. [12] injected various gases into pouch cells. From the gases tested CO_2 was found to be the most readily consumed, and was almost completely depleted after 100 h of storage, this was especially prominent in the presence of delithiated graphite electrodes where CO_2 is reduced forming lithium oxalate [12].

The magnitude of oxidative decomposition of electrolyte has been observed to increase with water content within the cell which has been proposed to be formed in reactions previously discussed such as Eq. (8). The increased water content supplies increased protons through oxidation and hydroxide ions through reduction at the negative electrode, both products instigate additional oxidative electrolyte decomposition at the respective electrode–electrolyte interfaces [29].

The combination of anode and cathode used in lithium ion batteries has been demonstrated to impact significantly on the gassing of the cell. Cells containing an LNMO positive electrode were observed to evolve gas at a higher

volume when coupled with a graphite counter electrode rather than LTO [44]. The authors attributed this finding to the impact on metal dissolution in the cell, with transition metals deposited on and damaging the graphite SEI surface inducing elevated rates of electrolyte reduction at the negative electrode leading to further SEI formation reactions the increase in SEI formation has also been observed from manganese dissolution from NMC electrode [50]. Gassing after formation cycling has been completed is more significant when LTO is used as the negative electrode as the higher redox potential of the material hinders its ability to react with gaseous products generated at the positive electrode [48]. Comparatively, by switching the cathode from LNMO to lithium iron phosphate (LFP) gas evolution can be minimised.

Delithiated lithium iron phosphate is a candidate for use as the counter electrode whilst testing the gas evolution of cathode materials [28]. As LiFePO_4 (LFP) electrodes do not partake in gas consumption or formation reactions they could provide a more conclusive study of the gas evolution products of working electrodes. This is corroborated through the work of Michalak et al. who found the gas evolution associated with LFP/LTO cells was minimal whilst the gas evolution of LFP/graphite cells predominantly occurred during the first cycle and was attributed to SEI formation on the graphite surface [44].

Conclusions

Techniques used for ex-situ and in situ analysis of gas evolution within lithium ion batteries have been discussed. The majority of which rely on the combination of techniques to maximise the information determined due to each technique's limitations. The literature findings from the use of these techniques highlight the complexity of gas evolution mechanisms present during the operation of lithium ion batteries. Gas evolution has been attributed to processes such as:

- Water reduction at the anode forming H_2 below 2 V vs. Li/Li^+
- Electrolyte reduction at the anode onset at an anode potential of 0.8 V vs. Li/Li^+ forming ethylene related to the formation of a solid electrolyte interphase
- Decomposition of lithium carbonate surface contaminants from the lithium nickel manganese cobalt oxide electrode at a potential of 3.82 V vs. Li/Li^+ forming CO_2
- Chemical oxidation of ethylene carbonate following the state of charge dependent release of singlet oxygen from the lithium nickel manganese cobalt oxide electrode

However, this only covers a small section of the mechanisms through literature with no major consensus on the dominant pathways for gas evolution.

Through experimental data it is clear that the magnitude of gas evolution of gas within the first cycle is of great interest as it is when the gas evolution rate is at its highest due to it being the only cycle when all of the gas evolution mechanisms stated above are likely to occur. The quantities and constituents of the gas produced during cycling is highly dependent on the choice of anode and cathode with the varying effect of cross talk between the electrodes depending on the material used.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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