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Gassing mechanisms in lithium-ion battery – a review

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Keywords : Lithium-ion battery, gassing, electrolyte degradation, gas generation mechanisms

Abstract

This paper provides a holistic view of the different studies related to gassing in NMC/graphite lithium-ion batteries over the past couple of decades of scientific development. It underlines the difficulty of predicting the concentration and the proportion of gas released upon cycling and storage and to get a clear mechanistic insight into the reduction and oxidation pathways of electrolyte solvents, the thermal electrolyte degradation, as well as the reactions that involve secondary sources such as water, NMC surface species and cross-talk reactions. Though many relevant experiments such as operando gas analysis using isotope-labeled solvents or two-compartment cells have been conducted, they failed, for instance, to determine the exact mechanism leading to the generation of CO and CO₂ gas. Last but not least, this paper discusses different strategies that are currently proposed to reduce or eliminate gassing such as the use of electrolyte additives that enable singlet oxygen quenching or scavenging, NMC coatings that limit the contact with electrolyte and different lithium salts to prevent thermal electrolyte degradation.

1. Introduction and context

In 1799-1800, the Italian physicist Alessandro Volta invented the first electrochemical battery, the voltaic pile. He could not imagine the impact of his invention on human society as nowadays Li-

ion rechargeable batteries are an integral part of our lives with the use of powering watches, computers, mobile phones, electric cars, portable tools, flashlights... and the list is still long.

However, this technology could be further developed to improve its lifespan. Indeed, during its operation (cycling or storage), the battery suffers from multiple deleterious phenomena: chemical evolution of the electrolyte [1], structural change of the cathode material [2], exfoliation of the graphite anode [3] and consumption of lithium inventory. These degradations lead to a decrease in electrochemical performance (increase in internal resistance, loss of capacity, and reduction in ionic conductivity). Meanwhile, tremendous efforts are directed at the increase of their energy density and power to support the deployment of renewable energies with stationary mass storage and electric vehicles by increasing their autonomy. This is achieved by extending the operating voltage window and by modifying the composition of the electrodes and electrolytes. Unfortunately, in most cases, the improvement in energy density and power is accompanied by increased degradation of the electrolyte, leading to harmful phenomena such as gas production in the battery.

Gases are not only detrimental to battery performance (increase in internal resistance [4], reduced cycle lifetime[4]), but they also induce mechanical stresses [5], [6] on cell packaging (swelling[7]). Gases originate from the degradation of the electrolyte at both electrodes, impurities, or structural changes on the cathode surface. Hydrogen [8], carbon monoxide [9] and dioxide [10], methane [11], ethane [11], and ethylene [12] are the main permanent gases released, and other gases such as singlet oxygen [13] or phosphoryl fluoride [14] act as intermediaries. The plurality of the emitted gases proves the complexity of the reaction mechanisms which can sometimes involve both electrodes through crosstalk reactions. A detailed understanding is therefore critical to finding appropriate electrochemical countermeasures to prevent their production. Some solutions already exist, such as the addition of electrolyte additives or the coating of positive materials, but they must constantly adapt to rapidly evolving state-of-the-art technologies.

This review aims to discuss the complexity of electrochemical and chemical gas generation processes. For the sake of a better understanding, we have focused only on an NMC-graphite battery containing a classical additive-free electrolyte composed of the LiPF_6 salt dissolved in a mixture of the carbonate solvents, ethylene (EC), and dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and/or diethyl carbonate (DEC). The first part deals with the main source of gas release: the electrolyte. Then, the secondary sources such as moisture, NMC surface species or SEI compounds, and the cross-talk effect are addressed. Finally, after reporting on the mechanisms, the currently proposed countermeasures are discussed. With regard to gas detection and quantification methods, the reader is referred to the work of Rowden et al [15] for detailed information.

Before going further into the underlying mechanisms responsible for gas generation, it is worth recalling the main sources. The electrochemical stability window of carbonate-based electrolytes often restricts the operating conditions of Li-ion cells. As a major electrolyte degradation process, beyond the 1-4.5V vs. Li/Li^+ potential range [15], [16], solvents endure electrochemical reduction below HOMO (Highest occupied molecular orbital) or oxidation above LUMO (lowest unoccupied molecular orbital) and release gaseous products. It should be noted that the LiPF_6 salt also causes a degradation of the electrolyte with a temperature increase [17], [18].

On the other hand, structural instability of delithiated NMC at a high State Of Charge (SOC) results in the release of singlet oxygen that can chemically oxidize carbonate solvents [19], [20]. In addition, its naturally present surface impurities [21] (proportional to the nickel content) can contribute to the degradation. Finally, water molecules from electrochemical cells electrochemically reduce or lead to adverse reactions as solvents and LiPF_6 hydrolysis. All those phenomena, summarized in Fig. 1, entail the generation of gas.

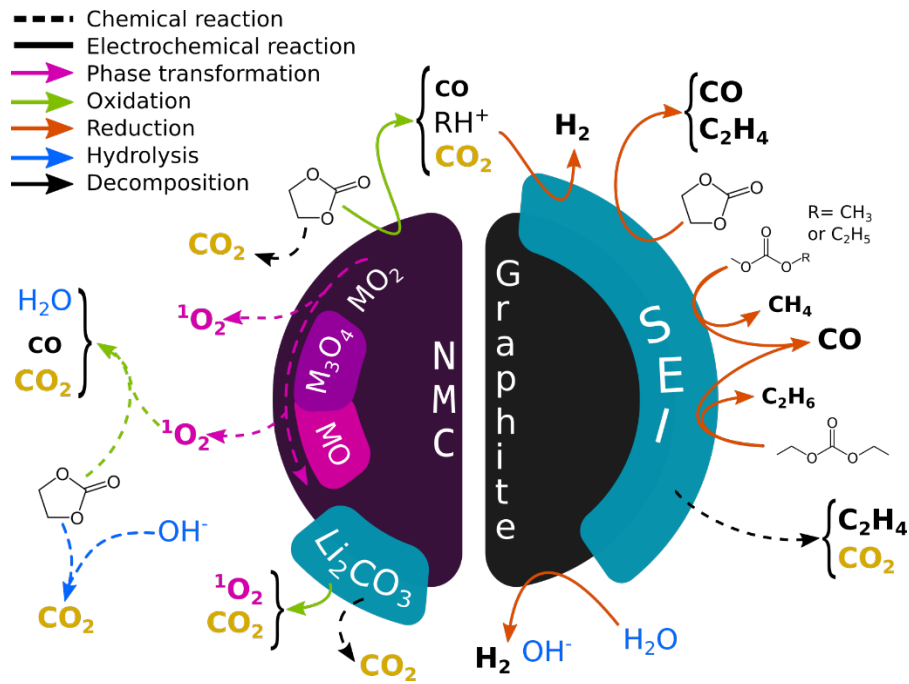


Figure 1: Main degradation mechanisms leading to gas evolution.

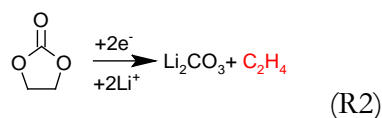
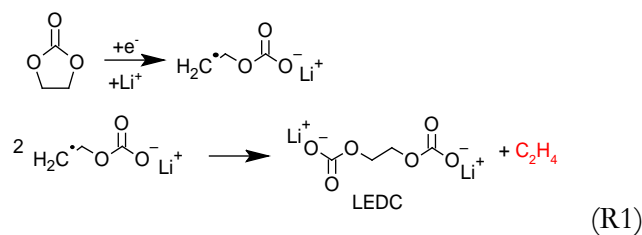
2. Main source: electrolyte degradation

2.1 Electrolyte reduction

As a prerequisite for battery operation, during the first charges, the negative electrode witnesses an electrolyte solvents reduction. This electrochemical reaction brings about the formation of a passivation layer commonly called SEI (Solid Electrolyte Interphase) [22] that is essential to enable graphite (de)lithiation processes. During this process, the following gases, CO, CH₄, C₂H₄, C₂H₆ and C₃H₈ are generally released from an additive-free electrolyte. Ethylene can only come from cyclic carbonate (EC), alkanes only from linear carbonates (DMC, EMC, DEC) and carbon monoxide from both cyclic and linear carbonates.

2.1.1 C₂H₄ formation

Ethylene is the most common emitted gas, its formation can take place according to the following EC reduction reactions (R1 and R2) [12]:



It should be noted that the lithium salts formed, namely lithium ethyl di-carbonate (LEDC) and lithium carbonate (Li_2CO_3), are the major SEI compounds, and as we shall see thereafter, can react to form gases.

The EC reduction process starts at ca. 1 V vs. Li/Li^+ , and a maximum ethylene concentration is observed at ca. 0.5 V vs. Li/Li^+ . It seems difficult to determine which of the two reaction mechanisms R1 and R2 is predominantly responsible for the production of this ethylene gas, but:

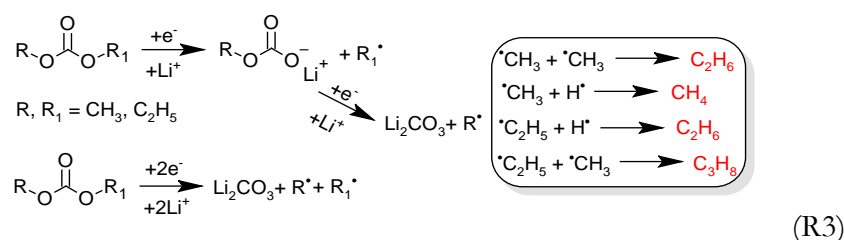
1. Formation of Li_2CO_3 would occur at potentials in the 1 – 0.8 V range vs. Li/Li^+ , followed by the formation of lithium ethylene dicarbonate (LEDC). [23]
2. Formation of Li_2CO_3 would be slightly more favourable at low EC concentrations (EC/DMC 1:5 vol.%), whereas LEDC would be favoured at high EC concentrations (volume ratio > 1/3). [24], [25]

After the formation of the SEI, EC is no longer reduced at the anode except after the occurrence of phenomena related to aging or abnormal cycling conditions, such as dissolution or cracking of the SEI. Thus, from the second charge, there is almost no ethylene release [26].

2.1.2 $\text{CH}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ formation

Linear carbonates also contribute to SEI formation (carbonates are reduced below 0.9V vs. Li/Li^+ at the anode) and release gas during reduction (R3). Unlike cyclic carbonates, gas production

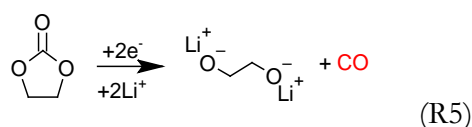
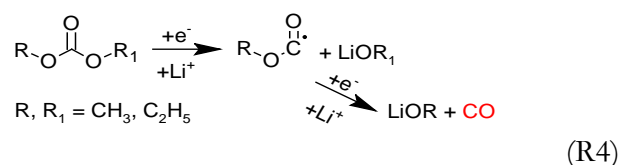
requires a recombination reaction between two alkyl radicals or with a hydrogen radical that may come from a water reduction reaction.



Pure DMC-based electrolyte gives CH₄ and trace of C₂H₆ [11], [27], whereas DEC gives C₂H₆. However, Yoshida et al. [11] found traces of CH₄ in pure DEC electrolyte, and Shin et al. [27] CH₄ and C₃H₈ in an EC/DEC mixture, which suggests another mechanism. Finally, though EMC reduction should form CH₄, C₂H₄ and C₃H₈, only CH₄ has been detected [11].

2.1.3 CO formation

As mentioned above, CO can be a reduction product [11] of both cyclic and linear carbonates (R4 and R5).



However, Leißing et al. [9] found, by using isotope-labeled EC solvent, that CO originated more from the decomposition of EC than from the linear carbonates (DMC, EMC or DEC); 2/3 of the total CO content was assigned to cyclic carbonate (Fig. 2). Conversely, Onuki et al. [12] did similar experiments with labeled solvents but did not find any CO from DEC reduction.

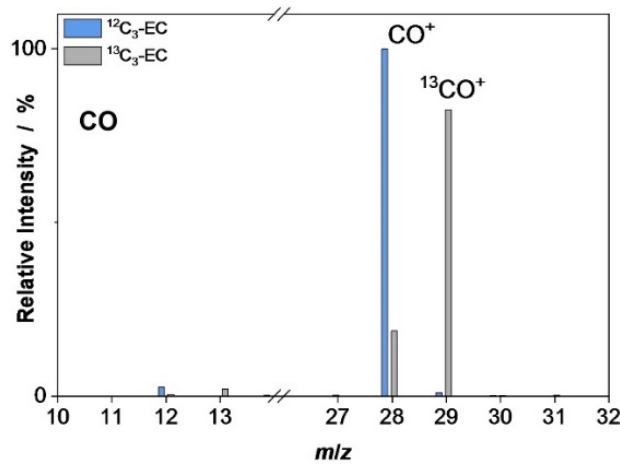


Figure 2: Mass spectrometry (MS) spectra of CO obtained from cells after formation with 1 M LiPF₆ in ¹³C₃-EC/DEC (grey) and EC/DEC (blue) 3:7 (wt.%), showing CO mainly originates from EC. From reference [9] under CC BY 4.0.

Overall, even if the formation of these gaseous products ensuing from electrolyte reduction upon first SEI formation, growth or repair upon prolonged cycling, is literature-known, their concentration and proportion seem difficult to predict (Fig. 3) as they depend on the electrolyte composition, cycling conditions (potential range, temperature, rate), surface morphology, entities and conspicuously on cross-talk reactions between both electrodes. Indeed, by comparing several studies [28]–[31], the quantity of gas released from a first charge up to 4.2V of an NMC/Gr cell varies from 9 to 23 $\mu\text{mol}/\text{m}^2_{\text{Gr+C}}$. During the second charge this quantity drops to 1 to 6 $\mu\text{mol}/\text{m}^2_{\text{Gr+C}}$.

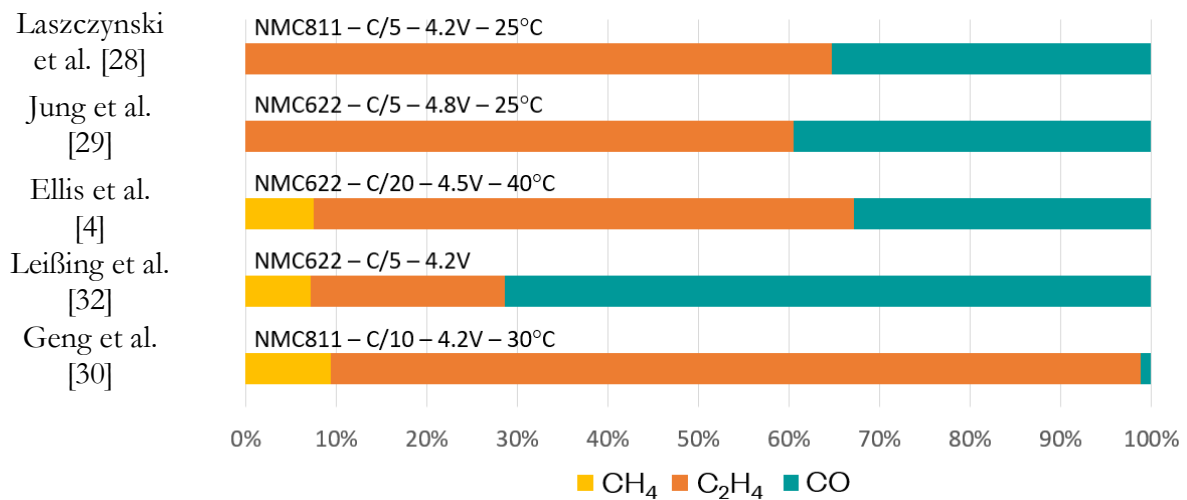


Figure 3: Proportions of CH₄, C₂H₄ and CO released during the first charge of NMC/Gr cells containing 1 M LiPF₆ in EC/EMC (3:7 wt.%) extracted from on-line electrochemical mass spectrometry (OEMS) analysis data from [29]–[31] and gas chromatography (GC) analysis data from [4], [33]. Traces of C₂H₆ were measured by [4], [31], [33] but are not shown here.

2.2 Electrolyte oxidation

Upon charge, the cathode potential rises, fostering two types of solvent oxidation: (i) electrochemical oxidation on the surface of the cathode and (ii) chemical oxidation due to the release of singlet oxygen coming from the cathode.

2.2.1 Electrochemical oxidation

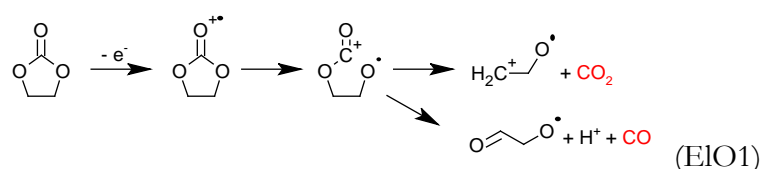
As aforementioned, electrolytes suffer electrochemical oxidation when the cathode potential exceeds its HOMO energy. However, it is difficult to determine this value as many parameters are considered (see Table 1), such as electrolyte, electrode composition, salt and current density. Table 1 reveals a large variation of the onset oxidation potentials as a function of the LiPF₆-based electrolyte solvents composition (from 3.8 to 6 V with LiMn₂O₄); DEC turns out to be less stable than DMC in contact with LiMn₂O₄ cathode and the onset oxidation potential is a little higher with graphite material than LiMn₂O₄.

Table 1 Onset oxidation potential depending on several parameters. Data extracted from [16] and adapted from [33].

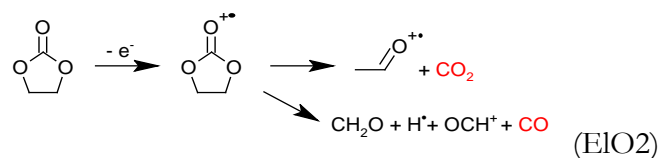
| Authors | Method | Electrolyte composition 1 M LiPF ₆ in | Electrode | Onset Oxidation potential vs Li/Li ⁺ |
|----------------------------|---------------------------------------|---|----------------------------------|---|
| Tarascon and Guyomard [33] | Galvanostatic Constant current at C/5 | EC/DMC 1:1 | LiMn ₂ O ₄ | 5.1 V |
| | | EC/DEC 1:1 | | 4.8 V |
| | | DMC | | 5.1 V |
| | | DEC | | 3.8 V |
| Xu et al. [16] | linear sweep voltammetry at 0.1 mV/s | EC/DMC 1:1 | LiMn ₂ O ₄ | 6 V |
| | | | Graphite | 6.5 V |
| | | DMC or EMC | LiMn ₂ O ₄ | 4.2 V |
| | | | Graphite | 6 – 6.5 V |

In the literature, Eggert and Heitbaum [34] were the first, in 1986, to study the oxidation of alkyl carbonate solutions (0.2 M LiClO₄ in PC). They revealed a CO₂ generation as an oxidation product

of PC, at 4.4 V vs. Li/Li⁺ on Pt electrode, by using a differential electrochemical mass spectrometry (DEMS). A decade later, Arakawa and Yamaki [35] detected CO₂ and other unidentified products coming from EC oxidation (2 M LiClO₄ in EC) at 5.5 V vs. Li/Li⁺ on a graphite electrode. They suggested a reaction caused by the catalytic effect of anion-intercalated graphite. A bit later, Imhof and Novák [10] found a CO₂ generation at 4.2 vs. Li/Li⁺ on the LiNiO₂ electrode, but nothing on LiMn₂O₄ and LiCoO₂, despite a charge to 5.5 V vs. Li/Li⁺, in an EC/DMC mixture with 1M LiTFSI salt. By using in-situ FTIR, Moshkovich et al. [36] identified CO₂ as well as CO, with alkyl carbonate solutions of commonly used lithium salts on metal electrodes. From their results, they proposed a possible EC oxidation pattern leading to these carbon oxides (EIO1):



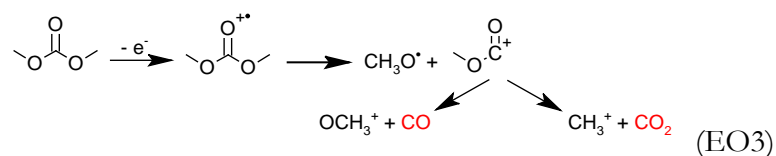
From theoretical investigations on EC oxidative decomposition mechanism, Xing et al. [37] proposed a different pathway (EIO2):



Experimentally, it has been reported that CO is released in amounts 6 times smaller than CO₂ [14], [38]. This is explained by the high activation energy required during the initial decomposition of EC^{•+} [37]. Interestingly, Metzger et al. observed that the CO/CO₂ ratio decreases in presence of water [39], [40] or at elevated temperatures [39].

Linear carbonates can also be oxidized but they do not release CO₂ as observed on in-situ FTIR spectra for 1 M LiPF₆ in DMC electrolyte according to Joho and Novák's works [41]. This finding is in contradiction with those of Moshkovich et al. [36] who used both in-situ FTIR and NMR

techniques. They observed the release of CO and CO₂ (LiAsF₆ 1M in DMC) and proposed the following mechanisms (EO3):



Most authors point out that the EC oxidation is favoured over that of linear carbonates. For [37], the dielectric constant of EC is much higher than DMC (≈ 90 vs. 3) and its acceptor number is 18.3 [42]. Thus, the PF₆⁻ anions will coordinate more strongly with EC, forming an EC-PF₆⁻ complex. Thereby, as during charging, the negative charges tend to migrate toward the cathode, the EC concentration increases near the cathode, favoring EC oxidation. Furthermore, lithium salt anion would reduce the onset oxidation potential of EC according to the calculations of Li et al. [43].

2.2.2 Chemical oxidation

In the 90s, a curious phenomenon was observed when charging cathodes at high voltage. During charging, the extraction of Li⁺ ions is normally accompanied with oxidation of the transition metal ion. However, with lithium manganese-based oxides (Li₂MnO₃ or LiMnO₂), it was possible to extract lithium even though all Mn were in 4+ oxidation state. For example, Richard et al. [44] observed an irreversible plateau above 4.3 V with Li_{4/3}Mn_{5/3}O₄. So, they suggested a simultaneous extraction of oxygen with lithium. A few years later, Lu and Dahn [45] corroborated this hypothesis via an in situ XRD study and in 2006, Armstrong et al. [46] proved the oxygen release by DEMS at high voltage for a Li[Ni_{0.2}Li_{0.2}Mn_{0.6}]O₂ cathode.

Obviously, this oxygen release can trigger consecutive oxidation reactions. A few years later, La Mantia et al. [47] and Holzappel et al. [48] performed similar DEMS analysis and noticed that CO₂ was generated along with oxygen, and thus suggested a reaction of oxygen with the electrolyte.

2.2.2.1 Layered metal oxide type structure instability

Before studying the mechanisms, let us take a close look at the processes leading to the oxygen formation. NMC cathode material, $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$, is a layered oxide with the general formula LiMO_2 . M can be Mn, Co, Ni.

The structure of LiMO_2 consists of a stack of MO_6 octahedra layers forming a trigonal crystal system (rhombohedral type lattice, same type of structure as $\alpha\text{-NaFeO}_4$). The octahedral sites are occupied by Ni, Mn and Co. The valence state for Mn and Co is 4+ and 3+ respectively. Hence, Ni valence state can be 2+ and 3+ depending on the Ni/Mn ratio ($\text{Ni/Mn} > 1$ implies the presence of Ni with a valence state of 3+). The inter-sheet space is occupied by lithium ions which can move through the 2D lattice. Lithium ion deintercalation leads to transition metal cation oxidation and therefore induces structural and chemical changes.

When charging, the order of oxidations of transition metals depends on the filling of electron shells and the energy levels of the atomic orbitals as qualitatively illustrated in Fig. 4.

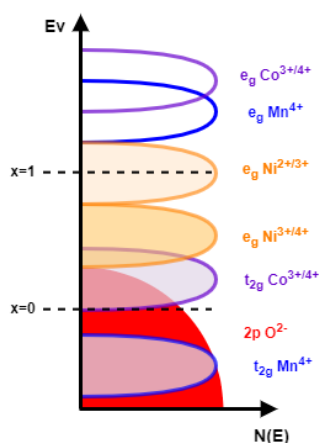


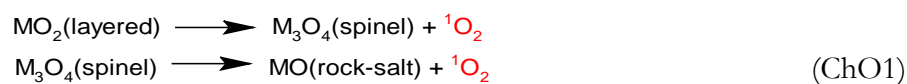
Figure 4: Representative scheme of energy level for NMC

The dashed lines correspond to the Fermi level for $\text{LiNi}_{1-y-z}\text{Mn}_y\text{Co}_z\text{O}_2$ in lithiated ($x=1$) and delithiated ($x=0$) states. Within this energy gap, the t_{2g} band of $\text{Co}^{3+/4+}$ overlaps the $2p$ O^{2-} band which implies a possible competition between the oxidation of Co^{3+} and O^{2-} . That is the reason why the raw materials delithiation is limited ($x=0.5$ in [49] and $x=0.65$ in [50] for LiCoO_2 , and NMC111, respectively). On the other hand, the lowest $\text{Ni}^{3+/4+}$ band barely touches the $2p$ O^{2-} band

[51]. Therefore, one could theoretically oxidize all Ni³⁺ without removing electrons from O²⁻. Yet, studies [13], [52], [53] have shown oxygen release with increased Ni content.

Dixit et al. [54] have shown, by calculating the oxygen binding energy, that this value decreases with the increase in nickel content in NMC, and with lithium deintercalation. Since the oxygen binding energy is an indicator of the strength of the M-O bonds, it is conceivable that structural changes will be facilitated for Ni-rich NMCs or for delithiated states [54]. Furthermore, when delithiated, Ni-O bond becomes more covalent (a better orbitals overlap) explained by closer energy levels for Ni⁴⁺ and O²⁻ than for Ni²⁺ and O²⁻, favouring electrons delocalization along the Ni-O bonds [54]. During oxidation, the extraction of these electrons weakens or breaks these bonds. These two aspects allow an easier oxygen release or reaction with the electrolyte.

On the other hand, the increase of Ni content implies the increase of Ni³⁺. It turns out that NiO₆ octahedra show Jahn-Teller distortions due to the non-pairing of its last single electron [55]. This local distortion is assumed to play a role during the lithium deintercalation process, and lead to the structural transformation from layered to spinel and from spinel to rock-salt type structure (ChO1).



The released oxygen is reported to be in an excited state (¹O₂, often called singlet oxygen) rather than stable state (³O₂ called triplet oxygen or simply O₂) [52]. Indeed, at room temperature, ³O₂ does not react with EC and could not form CO and CO₂ (cf. 2.2.2.3). Although the singlet oxygen is extremely reactive and has a short lifetime (10⁻⁶ to 10⁻³ s), it could have been evidenced from NMC structural transformation processes [52].

2.2.2.2 Oxygen release

Oxygen stemming from ¹O₂ relaxation has been detected through on-line electrochemical mass spectrometry (OEMS) technique. Streich et al. [52], through studying different NMC compositions, observed an O₂ release from potentials higher than 4.3 V vs. Li/Li⁺ and a linear concentration

increase with the Ni/Co ratio. The same trend was also found by Jung et al. [43, 44] (Fig. 5). Furthermore, it emerges from [13], [20], [30], [54] and [57] that during the first charge (≥ 4.8 V) of a polycrystalline Ni-rich NMC ($\geq 60\%$ Ni), the oxygen level varies from 5 to 20 $\mu\text{mol}/\text{m}^2_{\text{NMC}}$. Note that these values do not consider the part of the singlet oxygen reacting with electrolyte solvents (as shown below).

Other factors play an important role in the release of singlet oxygen:

- **Temperature:** Jung et al. showed a decreasing onset potential due to reduced polarization and a rising oxygen release with increasing temperature (a two-fold increase from 25 to 50°C). Further, the higher the nickel concentration, the lower the thermal stability temperature of the NMC [57].
- **Water content:** Castel et al. [58] found 30% more oxygen when multiplying the water concentration by 10, from 80 to 870 ppm, (for $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ (M = Ni, Co, and Mn)).
- **Current rate:** Castel et al. [58] showed that low rates favour oxygen production.
- **NMC morphology:** The amount of oxygen decreases when using uncoated single crystals instead of polycrystalline particles, due to a higher morphological stability upon cycling (less cracking and volume change) [53], [59]. For example, Oswald et al. [53] observed an 80% reduction of oxygen amount for $\text{LiNi}_{0.85}\text{Mn}_{0.10}\text{Co}_{0.05}\text{O}_2$ single crystals.
- **Solvent composition:** Dose et al. [60] revealed an impact of the electrolyte composition on the release of oxygen. For NMC811, a LiPF_6 -electrolyte containing pure EC solvent leads to (i) more CO_2 and O_2 generation, (ii) a thicker rock-salt layer observed by TEM, and (iii) a higher impedance, than with an electrolyte containing only EMC.

This oxygen release is due to the phase transformation occurring mainly from the outermost surface of the NMC particles (as shown above). The oxygen release decreases as the oxygen-depleted surface layer grows [61].

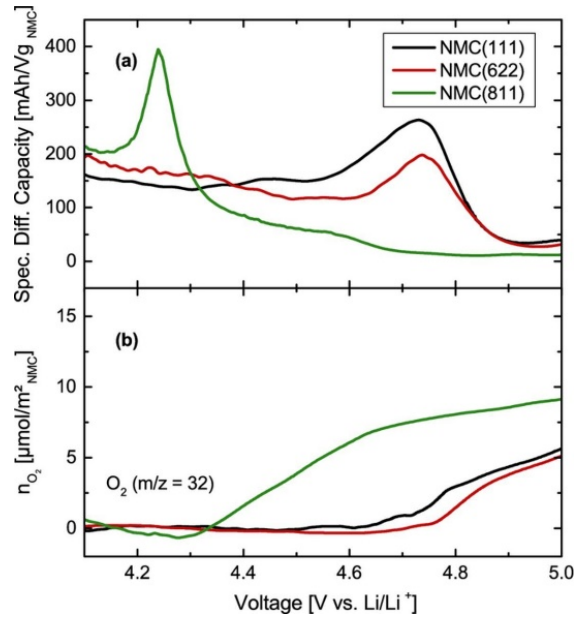
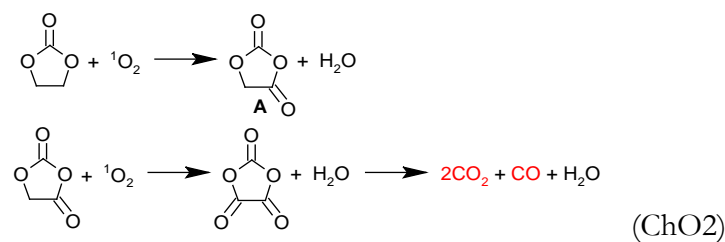


Figure 5: (a) Specific differential capacity vs. cell voltage of the NMC-Li cells. (b) Evolution of O₂ as a function of the cell voltage showing an O₂ release from potentials higher than 4.3 V. From reference [19] under CC BY-NC-ND 4.0.

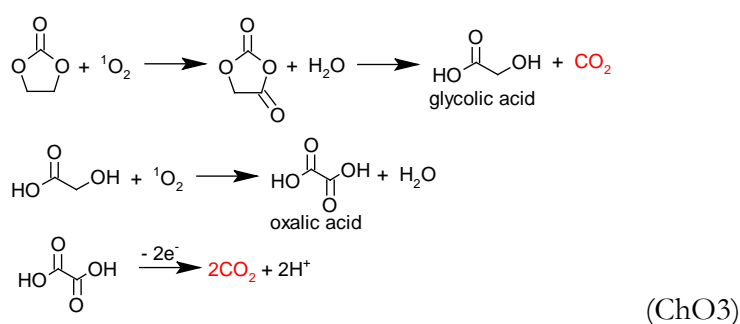
2.2.2.3 Oxygen reactivity and mechanisms

Released in the singlet state, the oxygen is likely to immediately react with the electrolyte, mainly with the solvent EC. Four mechanisms are reported in the literature, each requiring two oxygen singlets to generate CO₂ or CO₂/CO mixture.

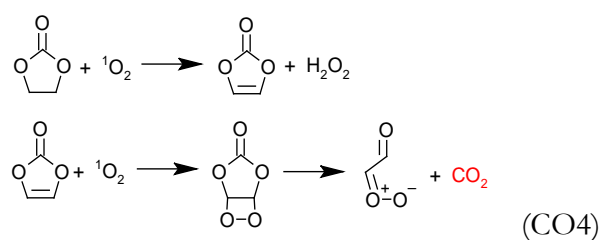
Jung et al. [62] observed that CO₂ and CO generation occurs, from an NMC-Gr cell with 1.5 M LiPF₆ in EC electrolyte, charged up to 4.8V, when ¹O₂ is generated. (no CO₂ and CO are generated with LiNi_{0.5}Mn_{1.5}O₂ which is known not to release oxygen). Furthermore, by using labelled solvent, they demonstrated that CO and CO₂ originated from EC and suggested an EC oxidation reaction mechanism following equations ChO₂. After undergoing two attacks of ¹O₂, the reaction yields H₂O, CO₂ and CO with a CO₂/CO ratio equal to 2 as observed experimentally [19], the global reaction being: EC + 2 ¹O₂ → 2CO₂ + CO + 2H₂O.



Conversely, based on NMR results, Rinkel et al. [63] proposed another mechanism for EC oxidation (ChO3) that forms glycolic acid. They suggested that the intermediate molecule in Eq. ChO2 (noted A in ChO2) was highly reactive and could quickly be hydrolyzed to form glycolic acid. The latter can endure a second chemical oxidation leading to oxalic acid. This acid is not detected by NMR and the authors propose that it could be oxidized to form CO₂ and protons. This would lead to the following overall reaction: $EC + 2 \text{}^1\text{O}_2 \rightarrow 3\text{CO}_2 + \text{H}_2\text{O} + 2\text{H}^+$. It can be noted that this mechanism does not account for the formation of CO.



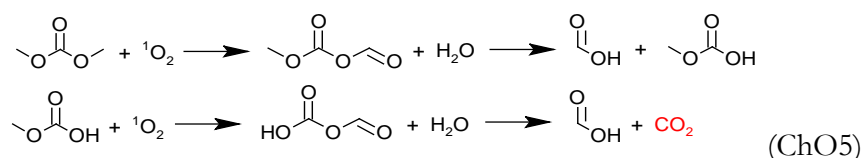
According to *ab initio* calculations, Freiberg et al. [20] suggested a mechanism involving VC as intermediate molecule and H₂O₂ (ChO4). The formation of H₂O₂ was proven experimentally by UV-spectroscopy through reaction of EC with a singlet oxygen-releasing dye under laser excitation (Rose Bengal dye). H₂O₂ seems to undergo a rapid decomposition reaction leading to water and oxygen. Unlike Jung et al., they did not observe any CO emission from EC oxidation.



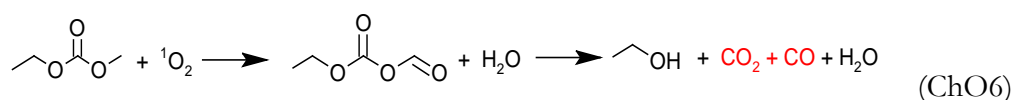
Recently, using NMR technique, Dose et al. [60] also found VC formation after charging a NMC811-LTO cell.

As aforesaid, EC is more prone to chemically oxidize than linear carbonates. For example, Freiberg et al. [20] did not observe any gas issuing from reaction between DMC and ¹O₂. Though, Rinkel

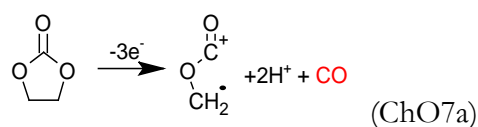
et al. [63] suggest a chemical oxidation of DMC following reactions (ChO5), after detecting, by using $^1\text{H-NMR}$, the presence of formic acid and hydrogen methyl carbonate in an electrolyte recovered from an LCO half-cell charged up to 4.6 V.



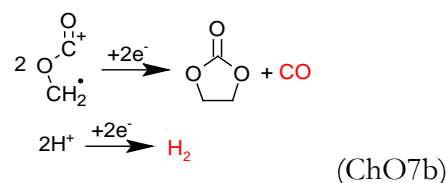
More recently, Dose et al. [60] proposed a chemical oxidation of EMC (1.5 M LiPF_6 in EMC) through reactions (ChO6), although the experimental CO_2/CO ratio value was found to be higher than the theoretical one (2.5 vs. 1).



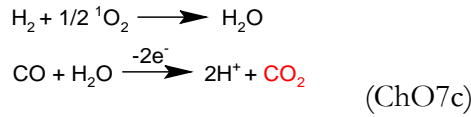
On the other hand, Galushkin et al. [31] proposed a different mechanism which does not imply a direct chemical reaction of singlet oxygen with carbonate molecules (EC in this case) but instead with H_2 resulting from multiple cross-talk reactions initiated by the electrochemical oxidation of EC. They proposed a CO-releasing electrochemical oxidation of EC, following reaction (ChO7a).



Then, cation radicals and protons cross the separator to get reduced at the anode according reactions (ChO7b), giving EC, CO and H_2 .



The latter goes to the cathode side and react with singlet oxygen to form water. Finally, CO oxidizes into CO_2 , following (ChO7c).



This overall pathway (ChO7) is based on the fact that cation radicals and protons must cross the separator to form CO_2 , which is not in line with the work of Metzger et al. [38]. Indeed, by using a ceramic separator to suppress cross-diffusion between the anode and the cathode electrodes (Fig. 6), they demonstrated that both CO_2 and CO were produced at the positive electrode.

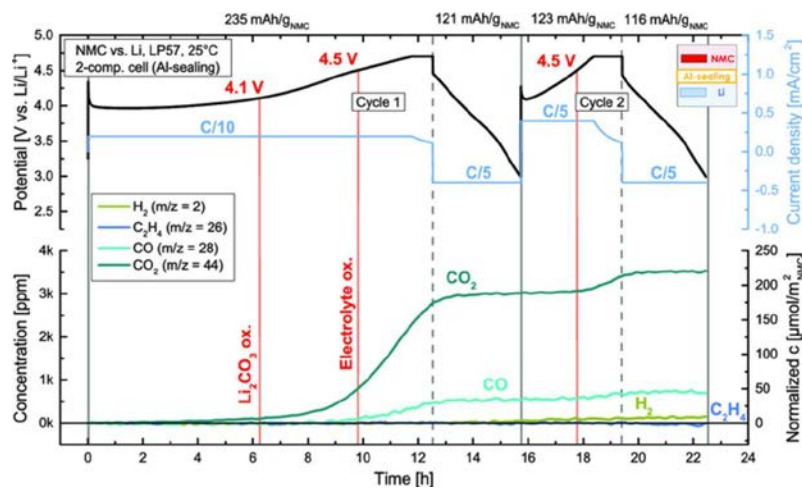
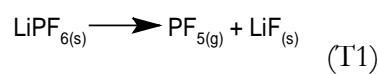


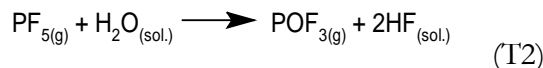
Figure 6: First two cycles of an Al-sealed two-compartment NMC-Li half-cell and gas evolution from the NMC working-electrode compartment. From reference [38] CC BY-NC-ND 4.0.

2.3 Thermal electrolyte degradation

Lithium salts play a crucial role in the thermal stability of electrolytes. Sloop et al [64] performed electrolyte storage experiments at 85°C and showed that EC is consumed in presence of certain salts; while no degradation is observed in the case of a salt-free EC/DMC mixture. In fact, the addition of Lewis acid salts triggers chemical reactions. The authors demonstrated, by thermogravimetric analysis, that 30% of a LiPF_6 salt powder decomposed after being stored for 3h at 50°C , following reaction (T1).

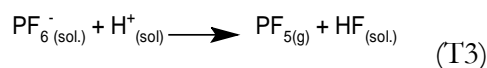


PF_5 is a strong Lewis acid [65] ($\text{PF}_5 > \text{BF}_3 > \text{HF}$) which reacts rapidly with molecules such as traces of water in the battery to form POF_3 according to reaction (T2).



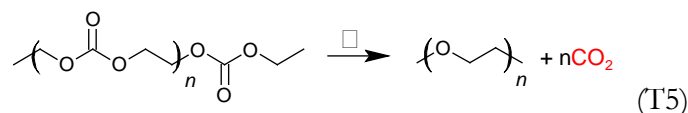
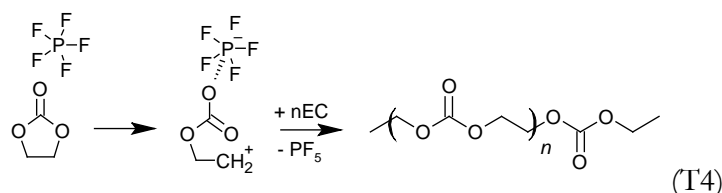
Both PF_5 and POF_3 gases are highly reactive toward electrolyte solvents [18] or act as catalysts [64] (see below). They are considered key undesirable elements in the degradation processes.

Interestingly, Solchenbach et al [14] demonstrated that the presence of protons in the 1.5M LiPF_6 in EC electrolyte favored the formation of PF_5 at temperatures as low as 25°C , following reaction (T3). This salt decomposition is much less pronounced when the same amount of water is added to the same electrolyte.



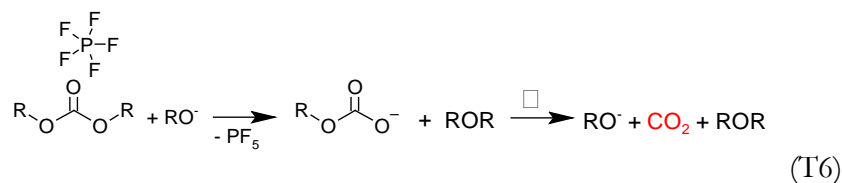
PF₅ as catalyst

Upon electrolyte storage at 85°C , Sloop et al. suggested [64] in 2003, that EC reacts through a ring-opening polymerization in the presence of PF_5 to form ether carbonate oligomers (reaction T4). They assumed that a decarboxylation process occurred to form the CO_2 detected gas (reaction T5).



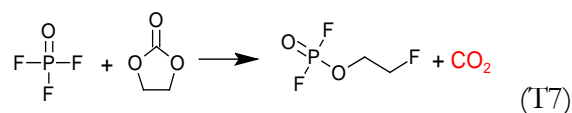
In their publications, they did not mention whether the linear carbonate (DMC in their case) could also react through a PF_5 catalyst process. This was addressed by Ravdel et al. in 2003 [66]. They analyzed the thermal degradation products from mixtures of LiPF_6 in DMC, DEC or EMC, after storage at 85°C . By means of GC-MS and NMR spectroscopy, they were able to identify CO_2 , ethers and fluorophosphates. To account for the formation of ethers, the authors proposed that

the transient alkoxide anions formed during the linear carbonates transesterification reaction (catalyzed by PF_5) attack the alkyl group of the linear carbonates to produce carbonate anions and ethers. The carbonate anions would undergo a decarboxylation process (reaction T6) to form gas.

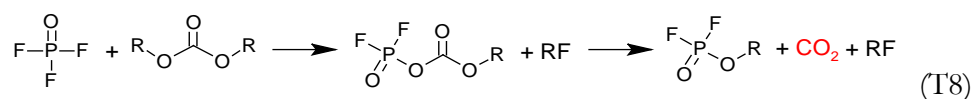


Reaction with POF_3

Campion et al. proposed reactions between carbonates and POF_3 , from EC [18] according to reaction T7:



And from linear carbonates [67] according to reaction T8:



In this case, subsequent nucleophilic substitutions of fluorine may occur to form phosphates. It can be noted these two reaction mechanisms are widely agreed upon (T7 and T8).

Investigations of Sloop, Ravdel, Campion and co-workers were carried out at a storage temperature of 85°C . The question arises as to whether such degradation can occur at lower temperatures. Since 2015, Nowak' group did substantial work on electrolyte degradation characterization. In [68], the storage of 1M LiPF_6 in EC/EMC (1:1 wt.%) was investigated at 20, 40, 60 and 80°C . It was shown that from 20°C , fluorophosphate species were formed. Although CO_2 was not measured, it can be assumed that it is also produced at such low temperatures.

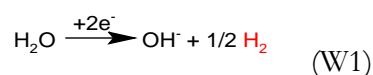
3. Secondary sources

As reported above, the electrolyte is the source of many reactions leading to gas generation. However, gas release may have other, less obvious origins that involve impurities namely water, electrolyte degradation products, NMC surface species or dissolved transition metal ions. Although varying from one battery to another (materials supplying, assembling and cycling procedures), their concentrations should be as low as possible, making their impact difficult to assess.

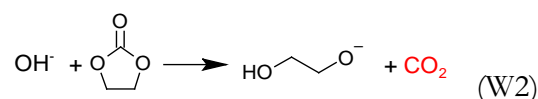
3.1 Water

Omnipresent in cells, as impurity and solvents chemical oxidation by-product, water is detrimental to electrochemical performances. It is prone to react with the electrolyte components, such as LiPF_6 and carbonate solvents, but also with the SEI compounds or the conductive carbon, generating gas via electrochemical or chemical processes.

Since 1998, researchers have been interested in determining the exact mechanisms of degradation related to water. Imhof et al. [8] detected hydrogen as a sub-product of the electrochemical reduction of water contained in an electrolyte, taking place at a potential of about 1.3 V vs Li/Li^+ (reaction W1).



Bernhard et al. [26] observed this reduction process at 1.6 V in presence of an electrolyte containing 4000 ppm of H_2O (see fig. 7). Interestingly, CO_2 gas was also released along with H_2 . To account for the CO_2 production, they proposed an OH^- -driven EC hydrolysis (reaction W2):



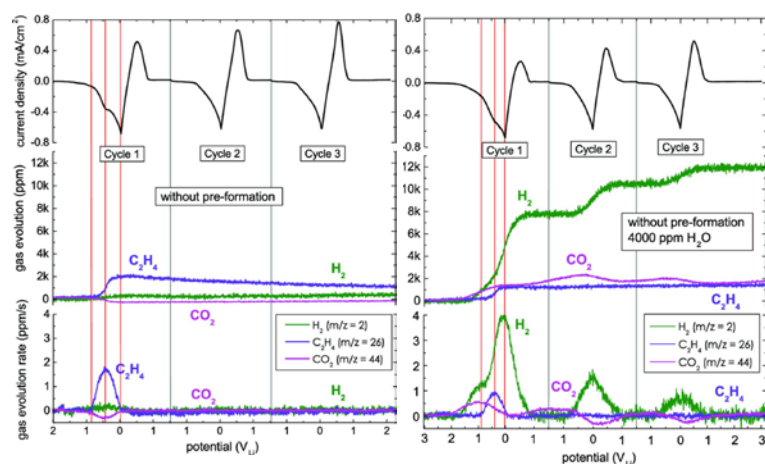
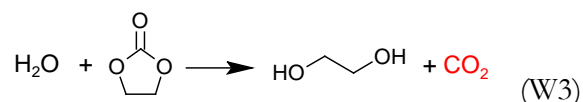
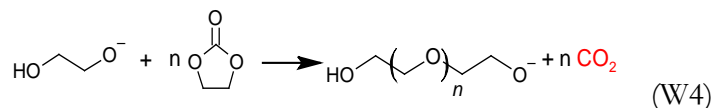


Figure 7: Gas evolution during the first three formation cycles of a pristine graphite working-electrode vs. a metallic lithium counter-electrode in 1 M LiTFSI in EC/EMC with less than 20 ppm H₂O (left) and 4000 ppm H₂O (right) showing the H₂ release along with CO₂. From reference [26] CC BY-NC-ND 4.0.

Metzger et al. [39], [69] investigated the hydrolysis reaction of EC with water or OH⁻ by varying respectively their concentration from 0 to 5000 ppm and 0 to 167 ppm. They also studied the influence of the temperature from 25 to 60°C. Both reactants produced CO₂ gas (reactions W2 and W3).

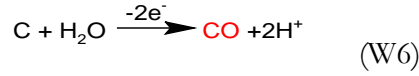
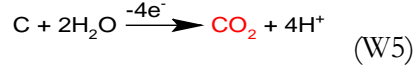


Note that OH⁻ is more reactive than H₂O as reaction W2 occurs at a temperature as low as 25°C against 40°C for reaction W3 with H₂O. Moreover, EC can undergo consecutive nucleophilic attacks by the alkyl di-alkoxide (reaction W2) and keep producing CO₂ (reaction W4).



It worth noting that H₂O-driven linear carbonates hydrolysis would not lead to the formation of CO₂ [63].

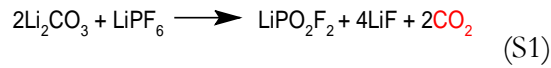
Finally, water was proved to be involved in the oxidation of conductive carbon [39], at potentials over 4.5 vs. Li/Li⁺, to produce CO₂ and CO (reaction W5 and W6).



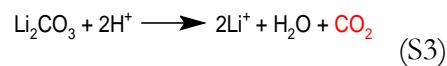
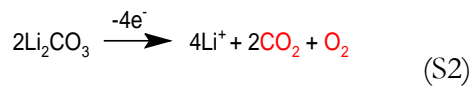
This study was undertaken with a LiClO₄ (2M) in EC electrolyte. However, Metzger et al. [70] demonstrated that conductive carbon is stable with LiPF₆ but not with LiClO₄-based solutions.

3.2 NMC surface species

Surface impurities form at the surface of NMC particles during both, synthesis and storage under ambient air [71], [72]. Li₂CO₃ and LiOH/Li₂O were the most widely reported surface species in the literature [21], [73], [74], representing less than 1 wt. % of NMC. Some researchers have focused on the fate of Li₂CO₃ in the cell and its impact on NMC electrochemical performances [21], [75]. Its decomposition always generates CO₂ gas. Once in the cell, Li₂CO₃ can chemically react with the electrolyte. [21] and [76] demonstrated that it could react with LiPF₆ to form LiPO₂F₂ following reaction S1:



Li₂CO₃ can also decompose upon oxidation, once a certain potential threshold is reached (3.8 V [77] – 4.5 V vs Li/Li⁺ [78]). However, the mechanism is controversial as Li₂CO₃ can be subjected to a direct electrochemical oxidation (reaction S2) [77], [79], [80] or chemically react with protic species formed upon the anodic oxidation of organic solvents (reaction S3) [78], both reactions leaving CO₂ gas.



With regard to the electrochemical process (reaction S2), intriguing observation was made that oxygen was not detected at the same time as carbon dioxide. Mahne et al. [77] explained that the oxygen was released under its very reactive singlet state ($^1\text{O}_2$). As discussed hereabove, $^1\text{O}_2$ would oxidize electrolyte solvents to yield CO_2 or CO_2/CO mixture.

It is worth noting that, to distinguish reaction S2 or S3 from other potential CO_2 releasing reactions (such as electrolyte solvents oxidation), most of the authors judiciously used ^{18}O [79] and/or ^{13}C [78], [81] isotopes to form $\text{Li}_2\text{C}^{18}\text{O}_3$ or $\text{Li}_2^{13}\text{CO}_3$ as illustrated in Fig. 8.

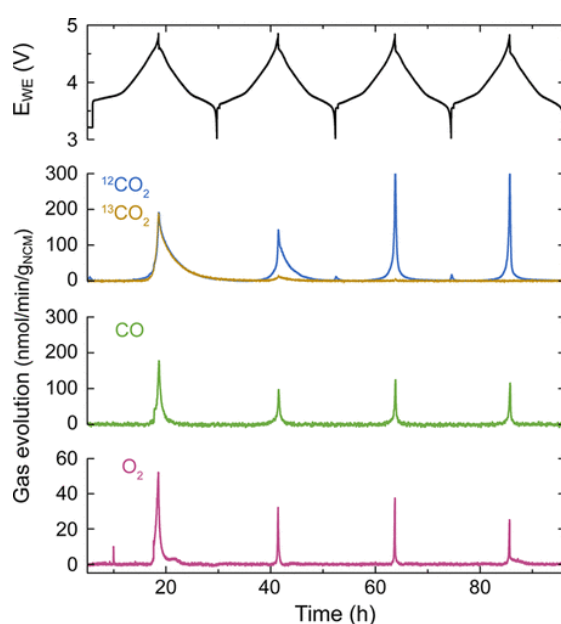


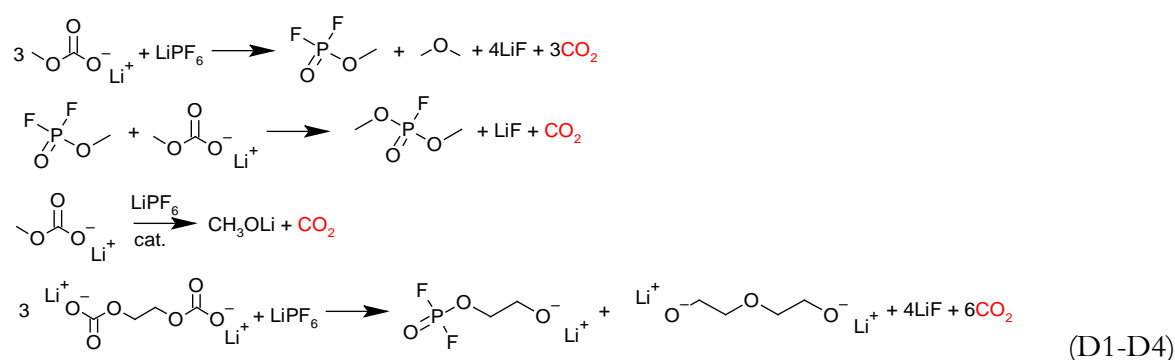
Figure 8: Evolution rates of CO_2 , CO , and O_2 during DEMS–DEIRS measurement for NMC/LFP cell containing 1M LiPF_6 in EC/EMC (3:7 wt.%). Reprinted with permission from [81] Copyright © 2018 American Chemical Society.

3.3 SEI degradation

As mentioned above, main SEI components are inorganic (Li_2CO_3) and organic ($\text{CH}_3\text{OCO}_2\text{Li}$, $\text{C}_2\text{H}_5\text{OCO}_2\text{Li}$, $(\text{CH}_2\text{OCO}_2\text{Li})_2$, $\text{HO}(\text{CH}_2)_2\text{OCO}_2\text{Li}$) lithium carbonate salts. They can undergo acid-base reactions when in presence of acidic species, like protons. In the case of Li_2CO_3 , the reaction can produce CO_2 .

They can also be thermally degraded. Parimalam et al. [76] investigated the thermal stability of Li_2CO_3 , $\text{CH}_3\text{OCO}_2\text{Li}$ and $(\text{CH}_2\text{OCO}_2\text{Li})_2$ upon storage in a 0.65 M LiPF_6 in DMC solution, at 55°C

for 2 days. CO₂ was produced in the three cases. For Li₂CO₃, the reaction generates LiPO₂F₂ and LiF as previously mentioned in reaction S1. Additional compounds such as fluorophosphates, LiF and dimethyl ether were detected in case of both organic carbonate lithium salts. However, the reaction mechanism is quite puzzling. The authors proposed the following reactions (reaction D1-D4) but were aware that a deeper mechanistic investigation was needed to account for the presence of fluorophosphates.



3.4 Cross-talk reactions

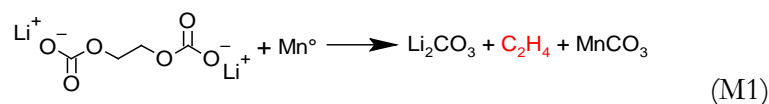
A cross-talk reaction involves a chemical or electrochemical process, occurring at one electrode, yielding a compound that crosses the separator to react chemically or electrochemically at the other electrode [82]. It can cause an impedance increasing and/or a capacity fade of the battery [83], [84].

3.4.1 Transition metal dissolution

Hydrofluoric acid [85]–[87] but also NMC surface structural evolutions [88] are responsible for the dissolution of transition metals (TMs) from cathodes. This phenomenon was evidenced by the use of the inductively coupled plasma (ICP) technique [87]–[89] or operando X-ray absorption spectroscopy [90]. TMs were found to dissolve nearly stoichiometrically at potentials > 4.3 and 4.6V for NMC 111 [87] and 622 [91], respectively, and to be in a 2+ oxidation state [88], [90] when detected at the surface graphite surface electrode.

Solchenbach et al. [92] investigated the impact of the presence of Mn²⁺ and Ni²⁺ ions in electrolyte towards degradation mechanisms taking place on graphite electrodes after performing an SEI with

a TM-free electrolyte. They found that only Mn^{2+} , and not Ni^{2+} , significantly increases the C_2H_4 evolution and thus the ethylene carbonate (EC) reduction. Based on [83], [93] studies, they proposed a mechanism where i. the Mn^{2+} ions diffuse through the SEI until they are close enough to the graphite electrode to be reduced (Mn^0), ii. Mn^0 reduces LEDC to form Li_2CO_3 and C_2H_4 through reaction M1:



This reaction induces creation of cracks within the SEI which allows fresh electrolyte reduction through (R1) and (R2) reactions.

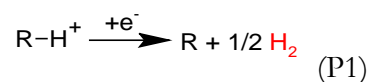
It is interesting to note that, unlike Mn^{2+} , neither Ni^{2+} nor Co^{2+} seem to cross the SEI to be reduced. This can be explained by the propensity of Mn^{2+} to exchange its ligands faster than Ni^{2+} and Co^{2+} , as evidenced through a higher rate constant for H_2O substitution in the inner ion coordination sphere [94]. This ability to change its environment endows Mn^{2+} with a higher mobility even in a solid phase like the SEI. It is of considerable interest in practice to see whether Mn-containing electrode materials can provide long cycle life in the presence of LiPF_6 or if alternative salts must be substituted.

3.4.2 Protic species reduction

Metzger et al [38] demonstrated that the protic species generated at the positive electrode upon charge could be involved in a crosstalk process. For that purpose, they performed OEMS analysis and made use of a two-compartment cell able to prevent diffusion/migration of any molecules (gas/liquid) or ions, except Li^+ ions.

An increase of hydrogen evolution (by a factor of about 3) was observed when the cut-off potential of a NMC111/Graphite cell impregnated with 1M LiPF_6 in EC/EMC (3:7 wt.%) electrolyte, was increased from 4.2 to 4.6 V vs. Li/Li^+ . Furthermore, this H_2 production was hindered when using

the two-compartment cell. This proved that the protic species generated by electrolyte oxidation at the cathode cross the separator to be reduced on graphite electrode. They proposed the following reduction reaction where RH^+ represents protic species:



They assume that $\text{OCH}_2\text{CH}_2^+$ is the protic species resulting for EC oxidation (see reaction E1O1).

It is worth noticing that, as aforementioned with solvent chemical oxidation (reactions ChO2 and ChO3), NMC can also release singlet oxygen upon charge. H_2O , which is believed to be formed from chemical oxidative reaction of EC with $^1\text{O}_2$ (ChO2), can be reduced at the negative electrode hence, taking part of crosstalk reactions.

Finally, it should be noted that Sloop et al. [64] have suggested another cross-talk reaction involving CO_2 gas as a shuttle. They proposed that CO_2 produced at the positive electrode could reduce at the graphite surface and form lithium oxalate. The latter could partially dissolve in the electrolyte and be oxidized to CO_2 at the positive electrode. However, sodium then lithium oxalate oxidations were found to occur at potential around 4.9 [64] and 4.4-4.6 V [95], [96], respectively. Since these potentials are beyond the standard charge cut-off voltages of the NMC/Gr cells, this cross-talk reaction is unlikely to occur. Interestingly, this statement raises the question of the CO_2 consumption which was observed by [97], [98]; the CO_2 reduction mechanisms are not fully understood leaving room for further investigations.

4. Discussions and perspectives

Table 2: Gas produced and their origins.

| Electrolyte | H ₂ | | CO ₂ | | | CO | | C ₂ H ₄ | | CH ₄ , C ₂ H ₆ , C ₃ H ₈ | |
|---------------------|-----------------|------------------|------------------|---------------------------------|-------|----|----|-------------------------------|----|--|---|
| | CC | LC | CC | LC | CC | LC | CC | LC | CC | LC | |
| Elec reduction | | | | | x | x | x | | | | x |
| Elec oxidation | | | x | | x | | | | | | |
| Chem oxidation | | | x | | x | | | | | | |
| Thermal degradation | | | x | | x | | | | | | |
| Secondary sources | RH ⁺ | H ₂ O | H ₂ O | Li ₂ CO ₃ | LiAlk | | | LEDC | | | |
| Elec reduction | x | x | | | | | | | | | |
| Chem reduction | | | | | | | | x | | | |
| Elec oxidation | | | | x | | | | | | | |
| Chemical reactivity | | | x | x | x | | | | | | |

CC: cyclic carbonate, LC: linear carbonate, Elec: electrochemical, Chem: chemical, RH⁺: protic species, LiAlk: lithium alkyl carbonates, LEDC: lithium ethyl decarbonate,

Table 2 summarizes the different gases produced according to the phenomena described above.

These phenomena can be grouped as follows:

- Processes limited by the low amount of reactant:

This concerns (i) Solvents chemical oxidation as well as NMC material-originating Li₂CO₃ oxidation and chemical reactivity. Solvents chemical oxidation relies on structural transformations that occur only at the extreme surface of particles through a 15 nm thick layer [60]. The Li₂CO₃ surface species-related processes are dependent on its quantity, which does not exceed ~3 mg/g of NMC [21]. (ii) Water reduction or its chemical reaction with solvent. Its origin comes from moisture or is a product of EC chemical oxidation. Its concentration within the battery is difficult to estimate but remains low (Metzger et al. [38] found 33 ppm of water in electrolyte after few cycles, compared to <20 ppm for a non-ageing electrolyte).

(iii) Singlet oxygen, ¹O₂, is the source of the chemical oxidation; its production is due to the NMC surface structural transformation or to the electrochemical oxidation of Li₂CO₃. One way to prevent its action is to trap it. Singlet oxygen scavengers (Fig. 9), such as 2,2,6,6-tetramethylpiperidine, 9,10-dimethylantracene or 9,10-diphenylantracene [99] have been studied within the Li-air battery field. Unfortunately, these molecules were found to suffer from a weak anodic stability < 4V. Recently, Petit and al. [100] have proposed an interesting ¹O₂ quencher (2,1-

pentyl-1,4-diazabicyclo[2.2.2]octan-1-ium bis(trifluoromethane)sulfonimide) with a high voltage stability ($> 4.5\text{V}$). We can also mention a surface modified fullerene additive (malonic acid grafting) [101] which is able to trap $^1\text{O}_2$ but also moisture. Despite all these studies, finding a singlet oxygen scavenger or quencher, suitable for Ni-rich NMC, remains a challenge to overcome.

An alternative approach to avoid chemical oxidation relies on the introduction of a buffer layer between the cathode and the electrolyte. Many studies [102] have focused on NMC surface coatings aimed at increasing the chemical stability of the interface and they successfully improved the NMC electrode performances. However, the origin of this improvement is rarely demonstrated as the different processes generating gas are intimately linked. Few of these studies have measured the effect on the gas production. LaPO_4 [103] and titanium-based coating [104] reduce gas production at potential over 4.4 V, whereas LiF and lanthanum titanium oxide coating reduces it when cells are stored at high temperature ($\geq 60^\circ\text{C}$), in the charged state. Jo and al. [105] have demonstrated that Li_3PO_4 coating scavenges HF, decreases the quantity of soluble bases on NMC 622 surface and reduces the transition metal solubilization during cycling.

Concerning the water scavengers, authors reported a positive effect of the presence of imidazole derived molecules [106], [107]. We can also mention the use of molecular sieves introduced within the positive electrode [108]. This shows that the harmful effect of water can be circumvented.

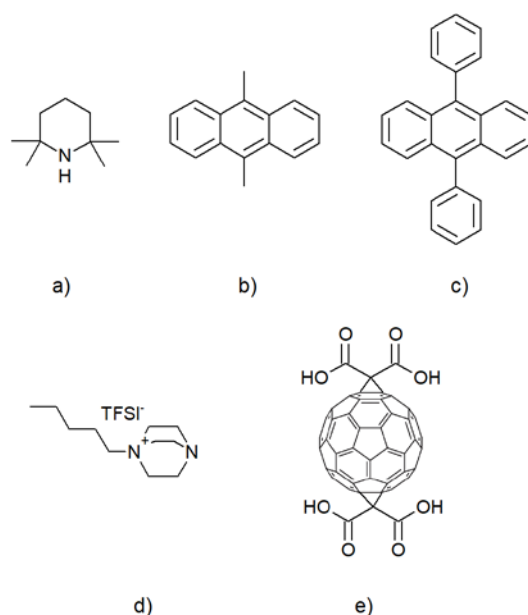


Figure 9: $^1\text{O}_2$ scavenger and quencher a) 2,2,6,6-tetramethylpiperidine, b) 9,10-dimethylantracene, c) 9,10-diphenylanthracene, d) 2,1-pentyl-1,4-diazabicyclo[2.2.2]octan-1-ium bis(trifluoromethane)sulfonimide and e) malonic acid-decorated fullerene.

- Processes involving SEI formation and degradation:

(i) Solvents are reduced to form the SEI; the gas produced are usually extracted from the battery after the “formation” process but can be re-formed during cycling. (ii) Lithium alkyl carbonates can reduce and both Lithium alkyl carbonates and Li_2CO_3 chemically react. In both cases, the gases formation will depend on the SEI quality. The impressive number of publications on SEI-reinforcing additives reflects the difficulty of finding the right recipe. Molecules (Fig. 10) such as prop-1-ene-1,3-sultone [109], 1,3-propane sultone and vinylene carbonate [110], methylene methanedisulfonate [111] or succinic anhydride [112] were found to reduce the amount of gas in the formation stage. Some of them reduce also gas production upon cells storage at 4.2V and 80°C [113]. It is worth noting that the measurement of the volume expansion is generally used, through ‘Archimedes’ principle, to evaluate the amount of gas produced. However, this does not give information about their origin. Designing experiments dedicated to evaluating the passivation properties of the SEI throughout the battery life remains challenging. The production of C_2H_4 and alkanes could be interesting to follow as SEI deterioration indicators.

Another possibility is the partial or complete substitution of the carbonate solvents. After detecting that C_2H_4 and CO were the major gas produced during the formation stage, Teng and al. [114] substituted EC by γ -butyrolactone. They demonstrated that the amount of gas was drastically reduced. Unfortunately, the use of γ -butyrolactone as a co-solvent does not meet the cells cyclability requirements. The replacement of carbonates by other families of solvents is still relevant but seems difficult to achieve.

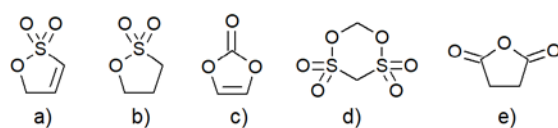


Figure 10: SEI-reinforcing additives a) prop-1-ene-1,3-sultone, b) 1,3-propane sultone, c) vinylene carbonate, d) methylene methanedisulfonate and e) succinic anhydride.

- Processes involving the electrochemical oxidation of solvents:

These processes mainly depend on the cut-off voltage of the cell and can entail subsequent processes such as the reduction of protic species to form H_2 . As discussed in the electrochemical oxidation section, knowing the potential at which carbonates oxidize is extremely complicated. In the case of NMCs, the determination of this value is further complicated by the superimposition of the chemical oxidation processes which produce identical gases. According to [19], this chemical oxidation was found to occur at around 80% of NMC delithiation. In order to study the anodic stability of solvents, it is interesting to use spinel active material-based electrodes. Indeed, unlike NMCs, the latter do not undergo any structural transformation on their surface. Xu et al. [115] showed that the onset oxidation potential of 1M $LiPF_6$ in EC/EMC (3:7 wt.%) electrolyte was 4.8 V vs Li/Li^+ with $LiNi_{0.5}Mn_{1.5}O_4$ spinel material. This indicates that, with a cut-off voltage of 4.3 V, no gas coming from solvent electrochemical oxidation is expected to be produced in current commercial batteries.

However, the question arises as to whether we could enlarge the electrochemical stability window of the electrolytes. For that, other solvent families are necessary. Sulfones [116], [117], nitriles

[118]–[120] and fluorinated [121] molecules seems to be the more appropriate solvents. Unfortunately, they suffer from high viscosity and low conductivities, which leads to envisage them as co-solvent or additive but improvements are still needed.

- Electrolyte thermal degradation:

This phenomenon occurs throughout the life of the battery, while in operation or at rest, which implies that it may generate significant amounts of gas. LiPF_6 , through its decomposition compounds (reaction T1 and T2), is the main culprit. Specific additives (Fig. 11) including salts, such as lithium benzimidazole [122], lithium fluorosulfonimide salts [123], lithium bisoxalatoborate [124] and lithium 4,5-dicyano-2-(trifluoromethyl)imidazole [125], or neutral molecules, such as diphenyldimethoxysilane [126] and 1-(2-cyanoethyl)pyrrole [127] are dedicated to trap PF_5 or HF, but they do not hinder the PF_6^- degradation. Their low concentration (few wt.% of additives) may not be sufficient to stop gas generation over the entire life of the battery. All of them improve high temperature cycling performances and some are reported to limit the transition metal dissolution [126]. It is worth mentioning that the efficiency of the additive to scavenge PF_5 or HF is usually demonstrated by making use of the NMR technique, however, to our knowledge, no one has measured the resulting gas production decrease.

Replacing LiPF_6 remains the ultimate solution. LiFSI ($\text{Li}(\text{SO}_2\text{F})_2\text{N}$) salt is reported to be the best candidate to replace LiPF_6 thanks to its higher ionic conductivity, better stability towards hydrolysis and lower fluorine content compared to LiPF_6 [128]. The main drawback of this imide salt is its inability to protect the aluminum current collector from corrosion beyond 4 V. However, it can be used in mixtures up to 30-50% with LiPF_6 without facing corrosion problem [123], [129]. Recently, Qiao et al [130] have synthesized a promising non-corrosive sulfonimide salt, lithium (difluoromethanesulfonyl)(trifluoromethanesulfonyl)imide ($\text{Li}(\text{SO}_2\text{CHF}_2)(\text{SO}_2\text{CF}_3)\text{N}$), with an acceptable ionic conductivity (3.7 mS cm^{-1} in EC/EMC 3:7 wt.%), that could replace LiPF_6 .

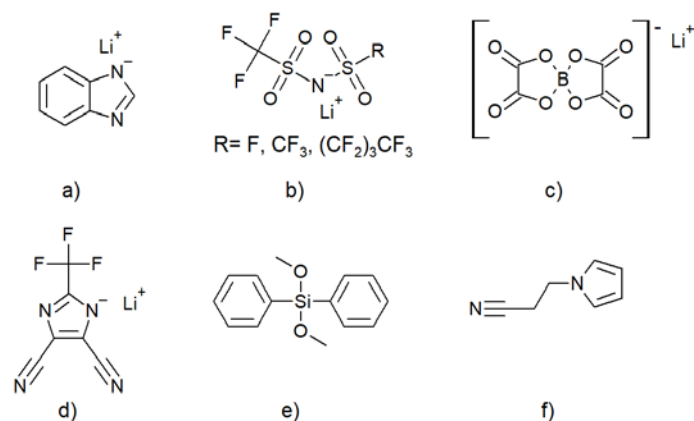


Figure 11: trapping molecules of PF_5 or HF a) lithium benzimidazole, b) lithium fluorosulfonimides, c) lithium bisoxalatoborate, d) lithium 4,5-dicyano-2-(trifluoromethyl)imidazole, e) diphenyldimethoxysilane and f) 1-(2-cyanoethyl)pyrrole.

4. Conclusions

In this review, we reported on the origin of the permanent gases produced during the entire life of the Li-ion battery, composed of NMC, graphite and a carbonate solvents-based electrolyte with LiPF_6 salt. All gases are detrimental for the lifespan of the battery, however, clear trends regarding the most prominent mechanism or most produced gas is difficult to extract from the literature, as their production depends on the operating conditions of the battery. While the number of gases, entailing carbon oxides, alkanes, ethylene, and hydrogen is limited, their origin may be multiple, from chemical, electrochemical and crosstalk reactions along with active material degradation. Most of the mechanisms reported in this review are generally accepted, which allows some gases to be used as indicators, such as ethylene and alkanes to evaluate the passivation properties of SEIs and thus the cycle life of the battery. However, some processes such as chemical and electrochemical oxidation are still subject to debate. Some reported studies have shown that further insight can be provided by the gas isolation system between the electrodes and the use of isotopic elements. Thus, the origin of each gas and solutions to mitigate their production could be investigated according to the type of reactions, active materials and electrolyte components such as EC, linear carbonates and lithium salts.

As discussed in this review, solutions to mitigate gas production exist but are not trivial. The above-mentioned analysis makes it possible to unveil two main routes. The first is the replacement of the LiPF_6 salt. Indeed, this salt is involved in the electrolyte thermal degradation, the chemical reactivity of SEI compounds and NMC surface species, and the transition metals dissolution phenomena. The second is the optimization of the morphology and coating composition of NMC materials. Although the release of carbon oxides, produced by the chemical oxidation of the solvent, is limited by the restricted thickness through which the phase transformation can occur (layered to rock-salt type structure), numerous publications indicate that NMC particles crack, which leads to an increase in surface area, and thus an increase in the production of these gases. Therefore, it is conceivable that an NMC/Gr cell with a positive electrode consisting of a single crystal NMC and comprising an electrolyte substituted with about 1/3 of the lithium salt by LiFSI could yield less gas.

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