Fire behavior of Li-ion batteries - working paper

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Li-ion batteries show special fire behavior, in particular they are difficult to extinguish. The observation that the batteries apparently still burn relatively well and for a long time in an oxygen-reduced atmosphere led to the widespread statement that the batteries themselves release oxygen, which nourishes the fire, due to chemical processes during the fire:

Lithium-ion battery fires do not require oxygen to burn and can be considered by nature a chemical fire. [1].

Weil die lithiumhaltigen Energiespeicher bei einem Brand den für das Feuer nötigen Sauerstoff selbst herstellen, bleibt fast nur die Kühlung der Umgebung als Brandschutz übrig. [2]

Hinzu kommt, dass einige der eingesetzten Kathodenmaterialien bei hohen Temperaturen zerfallen. Diese Reaktion ist ebenfalls wärmeproduzierend (exotherm) und setzt zudem den gebundenen Sauerstoff frei, der im Falle einer Feuerentwicklung einen Brand nur sehr schwer beherrschbar macht. [3]

Thermal runaway occurs when a cell has reached the temperature at which the temperature will continue to increase on its own and it becomes self-sustaining as it creates oxygen which feeds the fire (literally). [4]

One major shortcoming of these batteries is that they can overheat at relatively low temperatures of as little as 150 degrees Celsius (302 Fahrenheit). The biggest problem with any battery that has Cobalt within its chemistry is that when it catches fire, the battery 'feeds' itself the oxygen it requires to continue burning. [5]

There are hundreds of such statements to be found on the Internet, including on internationally relevant sites. Scientific test series have confirmed that a reduction in oxygen tends to reduce the fire behavior [6], but not to the extent that gas extinguishing systems are recommended as a good method for fighting fire from Li-ion batteries. A lot of water is therefore still the method of choice [7].

The lithium mixed oxides lithium cobalt oxide (LCO), lithium nickel manganese cobalt oxide (NMC) and lithium nickel cobalt aluminum oxide (NCA), which are frequently used as cathode material, can release oxygen because of internal structural rearrangements. The oxygen reacts immediately with the other components of the battery, especially the electrolyte, which over time leads to a loss of performance, as the electrolyte, for example, becomes locally solid. This process always runs at a low level, even at normal battery operation, and is one reason for the aging of batteries [8].

When the temperature is increased, the release of oxygen is accelerated. In tests with different Li-ion mixed oxide powders, an oxygen-based weight loss of 9-11 mass percent has been determined [9]. In this case, too, the resulting oxygen reacts immediately (with the electrolyte) and there is a significant production of carbon dioxide or carbon monoxide.

Prior to addressing the oxidation of the electrolyte and vapors in air we address reactions between the cathode and the electrolyte. As temperatures rise, the metal oxide can undergo phase transformations that release oxygen,

$$\begin{aligned} \mathrm{Li_xCoO_2} &\rightarrow \mathrm{xLiCoO_2} + \frac{1-\mathrm{x}}{3}\mathrm{Co_3O_4} + \frac{1-\mathrm{x}}{3}\mathrm{O_2} \\ \mathrm{Co_3O_4} &\rightarrow \mathrm{CoO} + \frac{1}{2}\mathrm{O_2} \end{aligned} \quad (4)$$

and this oxygen can react with the electrolyte at the particle surface.

$$\mathrm{C_3H_4O_3(EC)} + \frac{5}{2}\mathrm{O_2} \rightarrow 3\mathrm{CO_2} + 2\mathrm{H_2O}. \quad (5)$$

These reactions are strongly exothermic, being typical combustion oxidation. However, the amount of oxygen released by the cathode is only sufficient to oxidize a small fraction of the electrolyte, so that the direct electrolyte flammability is a significant issue.

Extract from [10] - note the last sentence.

In other words, oxygen is actually released, which, however, is always immediately consumed by chemical reactions with other cell materials. In terms of chemistry, these reactions are combustion reactions, but can take place in a Li-ion cell as catalytic combustion without an open fire, since the substances (metals) present can have a catalytic effect. The reaction is clearly exothermic, so that the thermal runaway itself can be explained well, i.e. the continuous supply of heat with each spread to a new cell nearby. (Other exothermic reactions also take place in parallel):

The third group of the exothermic reactions proceeds in the temperature range from beginning of oxygen release from a cathode, approximately at Tox≈200–250◦C till the end of the thermal run-away process. In this temperature range, a cathode thermal decomposition is accompanied with release of oxygen, which reacts afterwards with electrolyte. The exothermic reactions of electrolyte burning on a cathode are dominant in the course of the thermal runaway of lithium-ion cells.

Extract from [11]

Cooling extinguishing agents are therefore generally very useful.

In contrast to the oxides, the cathode material lithium iron phosphate (LFP) shows hardly any thermal effects up to 300 ° C and is therefore beyond competition in terms of safety. [12]

The considerations above are supported by the fact that in the meanwhile quite numerous gas investigations of cells during a thermal runaway no or only very little released oxygen has been measured, but carbon dioxide and carbon monoxide were always clearly detectable [13], [14], regardless of the used cathode material. More recent studies have shown that the CO or CO_2 concentration increased in parallel to the (brief) occurrence of oxygen in the cell:

The simultaneous occurrence of $^1O_2$ and CO_2 supports the hypothesis that the formation of the latter gas is mainly caused by a chemical oxidation of the electrolyte by the $^1O_2$ released from the layered oxide materials, rather than by a simple electrochemical electrolyte oxidation.

Extract from [15]

The instability of the cathode layer increases with a higher state of charge. The release of oxygen then occurs at lower temperatures and to a greater extent. Ultimately, greater electrical energy is converted into greater chemical energy (heat release).

In gas measurements during a thermal runaway, significant amounts of released hydrogen were usually measured [12], [16], [17]. Now there are also theories and experiments according to where this hydrogen comes from - the electrolysis processes taking place in the cell create more and more atomic hydrogen over time, which can be stored in the graphite of the anode. At elevated temperatures, this atomic hydrogen is recombined into molecular hydrogen ($H + H \rightarrow H_2$), releasing heat.

The conducted experiments in ARC-calorimeter show that during cycling of lithium-ion cells in anode graphite, there is accumulated hydrogen, which exists inside of graphite in atomic form. Upon cell heat-ing up to the temperature, at which mass release starts of atomic hydrogen from graphite, the powerful exothermic reaction of recombination of atomic hydrogen with heat release 436 kJ/mole starts. …. Thus, the first exothermic reaction at a thermal runaway in aged cells is the exothermic reaction of recombination of atomic hydrogen accumulated in anode graphite. It increases considerably a heat release in a beginning of a thermal runaway.

Extract from [11]

This reaction apparently takes place at an early stage of a thermal runaway, which could very well explain why hydrogen can usually be measured very early when a thermal runaway starts. The dependence of the accumulated hydrogen on the service life of the battery has to be examined in more detail.

The fact that larger amounts of free hydrogen can be measured well after a thermal runaway supports the conclusion that oxygen is not released at the same time. In any case, an advanced thermal runaway would have sufficient energy to initiate an oxyhydrogen reaction.

Hydrogen is a gas that can burn up to an oxygen concentration of about 5 vol% - an unusual behavior compared to most other substances, which require at least 12-14% oxygen for combustion [18]. The special fire behavior of Li-ion batteries possibly is not due to the fact that oxygen is released from the batteries, but to the fact that the hydrogen emitted when heated can burn for a long time even in an oxygen-poor environment [19].

Summary:

- During a thermal runaway, oxygen is released internally from the cathode material, which immediately reacts chemically with the electrolyte and above all generates CO and CO_2. The gases generated cause the cell to burst. The gases then blown off contain little or no oxygen. This may also explain that batteries in a thermal runaway are sometimes difficult to ignite - especially if the gases released contain a great amount of carbon dioxide. Local self-inerting effects could be the cause.
- The internal exothermic reaction of the oxygen maintains the permanent release of heat and thus the progress of the thermal runaway.

- At the beginning of the thermal runaway of every cell, hydrogen is released, later mainly unburned electrolyte. Hence, the thermal runaway does not release the oxidizing agent, but permanently new fuel. Since hydrogen is still flammable even at very low oxygen concentrations, inerting measures must be carried out very consistently in order to actually prevent open combustion.

Conclusions:

Early gas detection measures should focus on hydrogen. Since the hydrogen, in contrast to the produced oxygen, is not used up immediately in the cell, the question arises as to whether hydrogen detection should not take place directly in the cell.

The combination of intensive cooling and inerting (oxygen content < 5 vol%) appears to be promising in combating current lithium-ion battery fires.

Hazardous situations with regard to fire and explosion occur above all when fresh oxygen is supplied from the outside.

The development of new materials that do not show the reactions mentioned is the most important step towards safe battery technology.

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