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Gas explosions and thermal runaways during external heating abuse of commercial lithium-ion graphite-$LiCoO_2$ cells at different levels of ageing

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HIGHLIGHTS

- Gas explosions due to delayed ignition of battery emitted gases in air mixture.
- Three separate vents were detected, two vents before thermal runaway.
- Gas emissions of HF and POF_3 detected in 3rd vent with and without fire.
- Dead cells significantly less thermally reactive than working cells.
- Dead cells still undergo thermal runaway.

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ABSTRACT

Commercial 6.8 Ah lithium-ion cells with different ageing/status have been abused by external heating in an oven. Prior to the abuse test, selected cells were aged either by C/2 cycling up to 300 cycles or stored at 60 °C. Gas emissions were measured by FTIR and three separate vents were identified, two well before the thermal runaway while the third occurred simultaneously with the thermal runaway releasing heavy smoke and gas. Emissions of toxic carbon monoxide (CO), hydrogen fluoride (HF) and phosphorous oxyfluoride (POF_3) were detected in the third vent, regardless if there was a fire or not. All abused cells went into thermal runaway and emitted smoke and gas, the working cells also released flames as well as sparks. The dead cells were however less reactive but still underwent thermal runaway. For about half of the working cells, for all levels of cycle ageing, ignition of the accumulated battery released gases occurred about 15 s after the thermal runaway resulting in a gas explosion. The thermal runaway temperature, about 190 °C, varied somewhat for the different cell ageing/status where a weak local minimum was found for cells cycled between 100 and 200 times.

1. Introduction

Lithium-ion batteries have revolutionized many products since they have a high energy density combined with several other attractive properties. Li-ion cells are used in very high numbers in e.g. cell phones, laptop computers and power tools. Besides, they are being rapidly introduced in large systems and are found in kWh to MWh energy capacity applications used in e.g. electrified vehicles, ships and stationary grid storage plants.

The use of Li-ion batteries is, however, associated with more pronounced/different risks of developed heat, gas emissions, explosions and fire compared to other battery types. These risks are yet far from being fully understood and there is a potential for increased safety through research studies as well as from the analysis of incidents. The type and the severity of the risks depend on different applications and battery system sizes. Failure consequences can be significantly increased with increasing battery system size due to cell and module failure propagation [1–3].

The Li-ion cell contains all three parts of the fire triangle that are necessary to have a fire; heat/igniter, combustible material and oxygen. Furthermore, upon overtemperatures, starting from typically 70–120 °C, the Li-ion battery starts to swell and can release gases (venting). The vented gases are flammable and toxic [4]. If the temperature is high enough, of the order of 150–200 °C, an accelerated

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self-supporting rapid temperature increase, a thermal runaway (TR), can also occur [5,6]. The term onset temperature of a thermal runaway is referring to the temperature where the exothermic reactions starts and eventually lead to thermal runaway, while the term thermal runaway temperature refers to the very rapid temperature increase of the thermal runaway. The thermal runaway is typically associated with a release of large quantities of smoke and gas, a possible cell case rupture/explosion, fire or a gas explosion. There are thus two main types of explosions, an internal cell case explosion and a gas explosion of the flammable vented gases mixed with air. Cylindrical and hard prismatic cells can build high internal pressures and are therefore designed to release the gases via a built-in cell safety vent, however in case of e.g. a vent malfunction, extreme pressures can build up inside the battery cell, resulting in a cell case explosion. A gas explosion, on the other hand, occurs by a delayed ignition of vented combustible battery gases mixed with air accumulated in a confined or semiconfined enclosure. The consequences of a gas explosion can be significantly more severe than those of a cell case explosion.

The vented gases can contain both evaporated solvents and decomposition products, e.g. CO, CO_2, H_2, CH_4 [7–9]. Beside CO, a large number of different toxic compounds can be released [10–12] including fluoride gases. Hydrogen fluoride (HF) has caused most attention and is very toxic [13–15]. Few studies have been published that report measurements of released HF amounts from commercial Li-ion battery cells during abuse [16–20] and HF release during electrolyte fire tests [21]. The fluorine in the cells comes from the Li-salt, e.g. $LiPF_6$, but also from electrode binders, e.g. PVdF, electrode materials and coatings, e.g. fluorophosphates [22,23] and AlF_3-coated cathodes [5,24,25], as well as from fluorine containing additives, e.g. flame retardants. Battery safety is complex and a holistic perspective is essential, for example by introducing AlF_3-coatings the risk for a thermal runaway to occur can decrease while the risk for emission of toxic fluoride gases as well as for gas explosion might increase. The overall safety is therefore difficult to evaluate, it depends on battery size and scenarios, and an improvement of one parameter might actually worsen the overall safety.

There are many different types of abuse tests [26], a common one is external heating. There are several types of external heating methods for Li-ion battery cells, e.g. heating in an oven [6,26], by IR radiation [19,20,27–29], by cartridge or other heaters [30–32], in a closed chamber using e.g. accelerated rate calorimeter (ARC) [5,33] or other types [8,34,35]. So far, in most studies new/fresh cells, i.e. non-aged cells, have been tested and few studies are available investigating the influence of ageing on safety. Still it is essential to have a high battery safety level over the complete battery life time, since properties of the components may change during ageing. Ageing is typically seen in terms of calendar and cycle ageing. In order to shorten test time, storing and cycling the cells are often performed at increased temperatures, e.g. 35–55 °C, however, the results measured at these temperatures will differ from those obtained during use at ambient temperature, e.g. 20 °C, since other side and decomposition reactions may occur. The ageing processes of Li-ion cells are non-linear and complex [36–38] and not yet fully understood. For example, during ageing the solid electrolyte interphase (SEI) layer is changed and SEI plays an important role in the early stage of the thermal runaway. Abraham et al. [9] described the evolution of such modified SEI using calorimetric techniques and by quenching the temperature, described three main stages of the thermal runaway analysing the surfaces with XRD, XPS, SEM and Raman spectroscopy.

Roth and Doughty [39] studied the thermal stability of calendar aged Sony 18650 cells by ARC-tests and found that aged cells, up to 70 °C, showed higher exothermic onset temperatures. Wu et al. [40] studied 0.75 Ah non-commercial graphite/lithium cobalt oxide (LCO) Li-ion cells after 10 and 200 cycles and found that in nail penetration abuse tests the thermal safety decreased after 200 cycles. Röder et al. [41] studied 2 Ah graphite/LMO-NMC Li-ion 18650 cells stored at 60 °C up to 36 weeks and found in ARC-tests that exothermic reactions and thermal runaway onset temperatures are lower for cells aged 36 weeks. In contrast, Zhang et al. [42] studied 4.6 Ah graphite/LMO Li-ion cells stored at 55 °C for a duration between 10 and 90 days and found that the onset temperature of self-heating and thermal runaway increased for increased ageing. Fleischhammar et al. [43] studied the influence of cycle ageing on the thermal response in ARC tests for 1.5 Ah graphite/LMO-NMC high-power Li-ion 18650 cells and found significantly lower onset temperatures for first exothermic response as well as for the thermal runaway, with starting temperatures as low as 30.7 °C, and also found lithium plating on the anode for cells undergoing 1C cycling at −10 °C. Friesen et al. [44] studied safety in ARC tests of graphite/NMC 18650 fresh and cycle aged cells using 1C at 0 °C down to 70% state of health (SOH). Cells showed decreased thermal safety, aged cells had onset temperatures as low as 30 °C as well as earlier thermal runaway. The same authors also studied safety by nail penetration abuse tests and found that aged cells have a delayed but more reactive thermal runaway. In general, formation of lithium metal-plating on the anode at low temperature cycling and/or at too high charging currents poses increased risks for Li-ion batteries [43–46].

In this work Li-ion cell safety is studied for non-cycled cells stored at 20 °C and 60 °C as well as for cells aged by 100, 200 or 300 deep C/2 cycles, all cells are of the same cell type, a commercial 6.8 Ah graphite/$LiCoO_2$ Li-ion cell. The safety is assessed by abuse testing in form of external heating (oven) accompanied with FTIR gas measurements. One ARC test is performed for comparison of the safety evaluation methods.

2. Experimental

2.1. Cells tested

The cells, all from the same batch of commercially available lithium-ion cells, had nominal capacity and voltage of 6.8 Ah and 3.75 V, respectively, a LCO cathode, a graphite anode, a polymeric separator and prismatic packaging, see Table 1 for detailed cell specifications. The cells contained fluorine due to the presence of $LiPF_6$ salt in the electrolyte, however, other parts in the cell might also contain fluorine, see examples in the introduction section. Anyhow, the cell was not analyzed for other potential sources of fluorine.

2.2. Electrical characterization

Four-wire electrochemical impedance spectroscopy (EIS) in the frequency range 100 kHz - 5 mHz, with 60 points logarithmically distributed, was performed using a *Metrohm Autolab PGSTAT302N* and the *Metrohm Nova v1.11 software* in the galvanostatic mode with an

Table 1
Specification of the commercial Li-ion cell, from cell datasheet, electrolyte from TG-FTIR analysis [47] and separator from DSC-analysis [48].

Parameter	Value
Nominal voltage	3.75 V
Nominal capacity	6.8 Ah (20 °C, C/5 to 2.5 V cut-off)
Packaging	Jellyroll in aluminum hard prismatic can
Weight	140.2 g
Cycle life according to datasheet	> 70% capacity after 600 cycles with C/2 and 100% depth of discharge (DOD) at 20 °C
Max continuous discharge current	14 A
Max recommended continuous charge current	7 A
Anode	Graphite
Cathode	Lithium cobalt oxide, $LiCoO_2$
Electrolyte	Salt: lithium hexafluorophosphate, $LiPF_6$ Organic solvents: EC, DMC, EA Additives found: VC, presumable low molecular weight ketone
Separator	Shutdown separator, PE-PP