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Comprehensive gas analysis on large scale automotive lithium-ion cells in thermal runaway

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HIGHLIGHTS

- Seven gas species (CO2, CO, H2, C2H4, CH4, C2H6 and C3H6) found to be most common.
- Gas composition is independent on emitted gas volume.
- Energy density and cell capacity affect venting gas volume, onset temp. and mass loss.
- Hard case cells ejecting more solid mass during thermal runaway than pouch cells.

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ABSTRACT

Measurements on 51 lithium-ion cells undergoing thermal runaway reactions within an autoclave setup are conducted in order to examine venting gas volume, composition and cell mass loss as well as to identify influencing factors on related parameters. A new method to calculate the volume of released gas during thermal runaway is proposed. Comprehensive examination of the gas analysis is done and compared to literature. Seven gas species (CO_2, CO, H_2, C_2H_4, CH_4, C_2H_6 and C_3H_6) are determined to be the most common within venting gas and an independence of gas composition from venting gas volume can be shown. Furthermore, energy density and cell capacity are found to be an influencing factor of venting gas volume, thermal runaway onset temperature and mass loss, thus severity. Finally a difference for pouch and hard case cell formats in solid to gaseous mass loss proportion is discovered and explained.

1. Introduction

Battery electric vehicles (BEVs) [1,2], plug-in hybrid vehicles (PHEVs) [3] and hybrid electric vehicles (HEVs) [4,5] offer an emission free or reduced emission transportation possibility in times of rising concern for global warming and smog loaded mega cities. With lithium-ion cells entering the transportation market as promising power sources and energy storage for those vehicles [6], worries about safety arise [7]. Several trigger mechanisms can lead lithium-ion cells into thermal runaway [8] what may further result in severe thermal propagation reactions [9]. In order to improve cell safety, additives for lithium-ion cells have been developed [10,11], but it is also important to understand thermal runaway and propagation impacts to ensure passenger safety. Thermal propagation is the chain reaction like spreading of a single cell thermal runaway throughout the battery system. Besides huge amounts of excess heat [12] many hundred liters of hot, toxic and flammable gas, so called venting gas are the outcome of a thermal runaway or propagation within a lithium-ion battery system. With an ongoing increase in energy density and cell capacity, efforts for thermal propagation prevention rise beyond reasonable limits. For passenger safety of electric vehicles it is crucial to understand the volume and composition of venting gas, as well as influencing factors of venting gas for counter measures and detection systems [13] on a battery level, as it was proposed for example by the UN ECE [14].

This article focuses on determinating the mentioned gas and ejection composition as well as influencing factors with the help of autoclave measurements and a newly introduced method to calculate gas compositions from these measurements.

The remainder of this article is organized as follows: Section 2 describes the autoclave setup, its function and used sample cells as well as the newly introduced method to calculate gas volume and gas mass. Evaluation of sample cells and measurment setup, conducted gas analysis, possible influencing factors and the ejection composition are presented successively in section 3 followed by a conclusion in section

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2. Experiment and methods

In order to investigate the venting behavior and venting gas properties of lithium-ion cells a total number of 51 cells were brought into thermal runaway. Before each test the physical dimensions of the cell cavity is measured as well as its weight and capacity. A constant current constant voltage (CCCV) charging method as it is described in Refs. [15] [16], and [17] is used for the capacity measurements as well as for charging the sample cells up to a state of charge of $SOC = 100$ % prior to the autoclave test. Triggered by heat plates the different cells then subsequently undergo a thermal runaway within an autoclave. The generated venting gas is analyzed and quantified by calculations. The cells weight after the thermal runaway is measured again to determine the mass loss.

2.1. Autoclave setup

A gas tight and stable container, called an autoclave was used to evaluate gas composition and volume of released venting gas during a thermal runaway process of a lithium-ion cell. Such a container allows not only to take gas samples of the released venting gas but also to have a safe environment to conduct thermal abuse tests on large scale lithium-ion cells with energies of up to $E_{\text{cell}} \approx 300$ Wh.

Fig. 1 shows a schematic cross section of an autoclave. The container is made out of steel and consists of a cylindric base (1) and a lid (2). Bolts (3) hold the lid to its base and guarantee, together with a seal, a gas tight enclosure. Different gas tight feed though openings (4) allow necessary wires for measurement and operating equipment to go into the autoclave and provide an interface for gas analysis. Within the autoclave a lithium-ion cell (6) is held between jigs (5) which also act as heat plates to trigger a thermal runaway reaction. In Fig. 1 only one of two jigs (5) is shown for better visibility of the cell.

As the tests where originally designed as safety tests the autoclave contained ambient air to simulate realistic conditions such as in battery housings. During the test heat plates heat up the cell with a heat rate of $R_{\text{heater}} = 1\ \text{K min}^{-1}$ until it goes into thermal runaway, determined by a sudden rise in heat rate caused by the cell itself. During this process cell temperature is constantly monitored in order to detect the onset Temperature T_{onset} of the runaway process. After the ending of the thermal runaway reaction and after the internal pressure is stabilized, what determines the end of most exothermic reactions, a valve releases pressure from the autoclave down to $P_{\text{autoclave}} < 100$ kPa above ambient pressure and a gas sample is taken for further analysis. Gas analysis is conducted with a gas chromatograph (GC-WLD) in accordance to DIN 51872-04-A for nitrogen (N_2), hydrogen (H_2), carbon monoxide (CO) and carbon dioxide (CO_2) and with the method of headspace GC-FID for

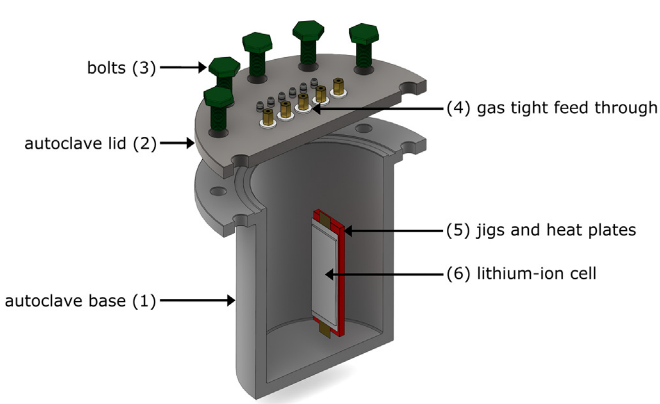

Fig. 1. Schematic cross section of an autoclave. Only one of two jigs/heat plates is displayed for better visibility of the lithium-ion cell.

methane (CH_4), ethane (C_2H_6), propane (C_3H_8), ethene (C_2H_4) and propene (C_3H_6).

2.2. Gas volume and mass calculation

Obtaining gas volumes with standardized test conditions (STP; temperature $T^\circ = 298.15$ K and pressure $p^\circ = 100$ kPa [18]) is important to compare results. STP can be calculated with the help of recorded temperature and pressure and by applying the ideal gas law

$$n = \frac{p \cdot V}{R_{\text{m}} \cdot T} \tag{1}$$

where n is the amount of substance in mole, p is the gas pressure, V is the gas volume and R_{m} is the ideal gas constant. This method was used for example by Golubkov et al. in their gas analysis [19]. However, while pressure is easily measured, the gas temperature can vary within the autoclave and is not easy to accurately determine without extensively stabilizing it beforehand. To cope with this challenge and by using the fact, that the autoclave is initially filled with ambient air, a different calculation approach is chosen. The composition of ambient air at the earths surface is well examined and contains a nitrogen volume concentration of $c_{\text{N}_2\text{Air}} = 78.084$ Vol-% [20]. This nitrogen is assumed to be inert and the molecular N_2 quantity will remain unchanged after the cell thermal runaway. Any thermal nitrogen oxides being formed as described by the extended Zeldovich mechanism [21] are neglectfully low at temperatures of $T < 1773{,}15$ K [22,23]. By comparing the N_2 concentrations in the autoclave before and after the thermal runaway, the volume of any generated gas specimen can be calculated by

$$V_{\text{gas}} = \frac{V_{void} \cdot c_{\text{N}_2\text{Air}}}{c_{\text{N}_2\text{Vent}}} c_{\text{gasVent}} \tag{2}$$

with V_{gas} being the volume of generated gas specimen, V_{void} the void volume in the autoclave, $c_{\text{N}_2\text{Vent}}$ the N_2 concentration and c_{gasVent} the concentration of the desired gas specimen in the venting gas filled atmosphere within the autoclave after the thermal runaway reaction. This equation assumes that all gases have equal or similar compressibility, hence a change in pressure will not change the gas concentrations. The calculated gas volume is then given at STP, given the fact, that STP conditions were present when closing the autoclave lid.

The gas mass m_{gas} can then be calculated from gas volume by

$$m_{\text{gas}} = \frac{V_{\text{gas}} \cdot M_{\text{gas}}}{V_{\text{m0}}} \tag{3}$$

with M_{gas} being the molar mass of the specific gas type which can be calculated from the periodic table and V_{m0} being the molar volume of an ideal gas with $V_{\text{m0}} = 24{,}465\ \ell\ \text{mol}^{-1}$ at STP.

Using these calculation methods makes the results independent of local temperature variations during the test and referrers them back to the STP as they are present before the test. Small errors can occur due to the deviation of room temperature and pressure from STP before closing of the autoclave.

2.3. Sample cells

In order to achieve a wide range in different cell properties a total number of 51 cells, 41 pouch cells and 10 hard case cells, are tested in the autoclave setup described in sec. 2.1. All examined cells had a graphite anode and a $LiNi_xMn_yCo_zO_2$ (NMC) cathode combined with an electrolyte consisting of lithium hexafluorophosphate (LiPF6) conducting salt and varying solvent concentrations of ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC). Table 1 gives an overview over the different property ranges of the tested cells. Capacity and electrical energy has been measured before each test. The bandwidth of tested cells goes from small low energy high power cells to big high energy low power