Uncertainties in the use of oxygen consumption calorimetry for heat release measurements in lithium-ion battery fires

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A R T I C L E   I N F O

Keywords:
Li-ion battery
Thermal runaway
Heat release rate
Total heat released
Fire tests
Oxygen consumption calorimetry
Carbon dioxide generation calorimetry

A B S T R A C T

Accurate measurement of the heat release from a battery fire is vital for risk management, product development and construction of accurate models. Oxygen consumption calorimetry is the most common method for heat release measurements in experimental fire tests. The strength of the method is that it can be applied to unknown compositions of fuel with sufficient accuracy. Despite that this method is used to estimate heat release from battery fires, the method is subject to discussion. In this work, the method is studied in-depth, and potential errors are structured and quantified. Uncertainties associated with self-generated oxygen and internal heat generation, total gas release from the battery and impact on the heat release calculations, as well as the assumed E-factor (i.e., heat release per unit mass of oxygen consumed), are thoroughly discussed. For a Li-ion battery fire, it is concluded that oxygen consumption calorimetry will exclude internal heat generation and underestimate the total heat released from the external flaming fire by up to 10%. In addition, high rate of combustion reactions can result in that the measured peak heat release rate is underestimated much more, up to 100%.

1. Introduction

Oxygen consumption calorimetry (OCC) is the most widespread method for the measurement of the heat release rate (HRR) from fire tests. It is based on Thornton’s rule, who already in 1917 stated that heat release is proportional to oxygen consumption for complete combustion of liquid and gaseous organic fuels. First in the late 1970’s, the concept of oxygen consumption calorimetry was developed further. While it was Dr. William Parker that was awarded the 2016 DiNenno Prize for his contributions in the 70’s and 80’s, several researchers have been recognized for the development of the OCC experimental methodology over the years [1]. For example, Huggett showed in 1980 that Thornton’s rule is applicable also for organic solids. Since then, the tabulated list of known fuels and their heat release per unit mass of oxygen consumed during complete combustion have increased [2].

The strength of OCC is the assumption that it can be applied to unknown compositions of fuel using the average of tabulated values from known fuels. Huggett’s average of 13.1 MJ/kg consumed O2 is most often used with an assumed uncertainty of ±5% [3,4]. From a more extensive list of organic fuels, the average becomes 12.8 MJ/kg (±7%) [2]. However, the average value is highly affected by the number of low molecular weight hydrocarbons in relation to more complex fuels, why a more extensive list of fuels does not necessarily correspond to a more accurate average.

The relatively small variations in heat release per unit mass of oxygen consumed for different fuels make this method widely accepted for measurements of the HRR in fire tests. A similar method, carbon dioxide generation calorimetry (CDG), is based on the production of CO2 instead of the consumption of O2. However, the heat release per unit mass of CO2 produced varies comparatively more between different fuels [2]. Other methods sometimes used for HRR measurements are thermo-chemistry or mass loss calorimetry, which usually needs detailed knowledge about the fuel, or energy balance methods such as the Sensible Enthalpy Rise Method [5].

The increasing use of Li-ion batteries (LIBs) make their safety and fire hazard characteristics more vital to understand. The combustion of a LIB not only include the usually unknown and various composition of materials, but also the complex nature of thermal runaway events. Thermal runaway is the accelerating rate of exothermic reactions that take place during thermal decomposition of the battery materials, where the generation of oxygen within the cell is part of that process [6]. The potential effect from self-generated oxygen from the battery cell on the HRR...
measurements using OCC has been discussed in several contributions [7–16], but the conclusions have been different and there exists no consensus. Some argue that since no or limited amount of oxygen is typically measured in the off-gases from LIB thermal runaway, this will have limited impact on the OCC measurements [14–16]. This conclusion neglects that other gases will also impact the measurements, which is discussed further in this paper, as well as that the OCC measurement neglect internal heat generation (IHG) in the cell. Two papers [10,15] propose that an initial negative HRR is due to self-generated oxygen in the cell, which implies that the generated oxygen reaches the analyser, sampling gas from the smoke exhaust duct placed above the LIB. Mikolajczyk et al. [11], in turn, argue that CO₂ production within the cell can either be generated from O₂ reactions (typical combustion reactions) or from thermal degradation processes with less energy release. With the assumption in OCC that all reactions products in the exhaust duct originate from combustion, their conclusion was that OCC therefore would overestimate the total heat released (THR). On the contrary, most agree that OCC instead underestimates the THR since it does not account for IHG in the cell, which partly originate from the combustion reactions by self-generated oxygen. Liu et al. [14] stated that OCC only provides the heat release from the flaming fire outside of the battery cell, and used another method, Copper Slug Battery Calorimetry (CSBC), to estimate the cell internal generated heat. Chen et al. [7] instead added a theoretical term to the measured OCC based on the estimated oxygen release from the cathode material during decomposition. The estimation was related to the degree of Li intercalation in the material and thereby dependent on the battery state of charge (SOC). A similar approach was used by Vendra et al. [13]. These methods where a theoretical term is added typically need specific knowledge about the total weight of material in the cell and the decomposition characteristics.

Ribiére et al. [17] concluded that the theoretical THR from complete combustion of a LIB cell’s organic materials correlates well with the measured THR by OCC. For the cell tested, the organic materials comprised of the electrolyte (about 50 %) and polymers in separator, binders, and packaging. There are some studies where combustion of LIB electrolytes (carbonate solvent with dissolved lithium salt, typically LiPF₆) have been analysed by both OCC and thermochemistry methods [18–20], all with the conclusion that OCC results are accurate. In thermochemistry measurements, a mixture of, e.g., different carbonates are normalized as a single C₆H₇O₄ compound, and a theoretical heat release can be calculated based on only CO₂ and H₂O reaction products. Continuous measurement of CO₂ gives the HRR, and including CO makes it possible to also consider incomplete combustion. Moreover, Eshetu et al. [20] concluded, based on good correlations between OCC and CDG measurements, that the CO₂ is mainly generated from O₂ reactions during electrolyte heating and combustion. There is, however, a significant difference between combustion of pure electrolyte and combustion of a complete cell. For a 2.1Ah pouch cell, Somandepalli et al. [8] measured a 35 % difference in peak HRR when comparing OCC with CDG, originating from the production of CO₂ within the cell.

If OCC does not fully capture the THR during LIB thermal runaway, it is important to know how much heat that is not measured within relation to the THR generated in a battery fire. Chen et al. [7] estimated the heat energy from self-generated oxygen to be 30 % of the measured THR at 100 % SOC. This self-generated heat was approximately 25 % higher than the stored electrical energy. Vendra et al. [13] estimated the heat from self-generated oxygen to be 30–60 % of the measured THR. Liu et al. [14], in turn, estimated the internal generated heat by CSBC measurements and mass loss correction to be 60–80 % of the THR measured by OCC (maximum THR measured at 75 % SOC). CSBC measurements were conducted both in ambient air and inert atmosphere with the conclusion that no heat feedback from the flames in ambient air affected the measurements. The measured internally generated heat was twice the stored electrical energy. Similar results were found by Lyon and Walters [21] using a nitrogen bomb calorimeter and the cone calorimeter (OCC). Finally, Voigt et al. [12] compared OCC with the

Sensible Enthalpy Rise Approach (SERA) for a complete battery pack and concluded that the SERA method gave approximately 30–70 % higher THR as compared to OCC.

The scientific literature in the area thus shows that the OCC method potentially underestimates the THR from a LIB fire by 30–80 %, because it does not capture internally generated heat. However, no consensus exists regarding how well OCC capture the HRR from the external flaming fire and how the method is affected by self-generated oxygen and gas release from the battery. Therefore, we are, in this present study, setting out to quantify the uncertainties associated with self-generated oxygen and total gas released from the battery and the potential impact on the heat release calculations.

2. Theory

To understand how a LIB thermal runaway, gas release, and burning characteristics affect the HRR measurements, it is important to understand the underlying equations used in the measurements. Both OCC and CDG are therefore described below, as well as a brief discussion of the associated uncertainties encountered in standard fire tests using these methods.

2.1. Oxygen consumption calorimetry

For complete combustion, the OCC method relies on the assumption that the HRR (q) is proportional to the amount of oxygen consumed. If the mass flow rate of oxygen in the intake air is \( m_{O_2} \) and the mass flow rate of oxygen in the exhaust gas is \( m_{O_2} \), the HRR follows as

\[
q = E \left( m_{O_2} - m_{O_2} \right)
\]  

(1)

For unknown compositions of fuel, Huggett’s average of 13.1 MJ/kg is most often used for the value of \( E \). However, the mass flow rate of oxygen cannot be measured directly, why other equations have been derived based on measurements of the exhaust gas mass flow rate as well as gas concentrations in the exhaust gas duct. There are different equations used based on the type of gas analyser and whether CO₂, CO and water vapor are measured or not, following the derivations of Janssens [3]. A common equation used in standard fire tests to calculate HRR based on O₂ and CO₂ concentration measurements in the exhaust gas is:

\[
q = E n_i M_{O_2} \left( 1 - X_{O_2}^{H_0} \right) \left( \frac{1 - \frac{X_{O_2}}{X_{O_2} \left( 1 - X_{O_2} \right)}}{X_{O_2} \left( 1 - X_{O_2} \right)} \right) \]

(2)

where:

\( m_e \) = measured mass flow rate of the exhaust gas (kg/s)
\( M_{O_2} \) = molecular weight of oxygen (32 g/mol)
\( M_a \) = molecular weight of intake air (=M_{dry air} ≈ 29 g/mol)
\( X_{O_2}^{H_0} \) = mole fraction of water vapor in the intake air (calculated based on relative humidity and air temperature and pressure)
\( X_{O_2} \) = measured mole fraction of oxygen in the intake air
\( X_{CO_2} \) = measured mole fraction of carbon dioxide in the intake air
\( X_{O_2} \) = measured mole fraction of oxygen in the exhaust gas
\( X_{CO_2} \) = measured mole fraction of carbon dioxide in the exhaust gas

The measured mole fractions of O₂ and CO₂ are measured on dry gas, i.e. with water vapor removed prior to analyser. The expansion factor \( \alpha \) is defined as the ratio between the molar quantity of combustion products (including inert gases involved) and the molar quantity of air involved in the combustion. Complete combustion of carbon (C + O₂ →
CO₂ results in \( \alpha = 1 \), while combustion of hydrogen (2H₂ + O₂ \rightarrow 2H₂O) results in \( \alpha = 2.1 \). Usually, an average value of \( \alpha = 1.105 \) is used for unknown compositions of hydrocarbon fuels. Sometimes, Eq. (2) is also written [3]:
\[
\dot{q} = \frac{E \dot{n}_a M_a}{M_g} \left( 1 - X_{H_2O} \right) \frac{X_0 (1 - X_{CO})}{1 + \phi (\alpha - 1)} \]  
(3)

\[
\dot{q} = \frac{X_0 (1 - X_{CO})}{X_0 (1 - X_{H_2O})} \]  
(4)

Here introducing the oxygen depletion factor \( \phi \), defined as the fraction of the intake air that is fully depleted of its oxygen. Note that the CO analyser is only used to determine the oxygen depletion, but that removal of CO₂ from the gas before measuring the O₂ concentrations would also work (using a modified equation, see Janssens [3]).

For open systems with good supply of air to the fire, it can be noted that a good estimation of the HRR can be calculated ignoring the CO₂ measurements, air humidity, expansion factor etc. using
\[
\dot{q} \approx \frac{E \dot{n}_a M_a}{M_g} \left( X_{H_2O} - X_{CO} \right) \]  
(5)

When the supply of air is limited, however, the assumption of complete combustion results in great errors and corrections for CO production might be needed. When including the CO production, Eqs. (3) and (4) become
\[
\dot{q} = \frac{E \dot{n}_a M_a}{M_g} \left( 1 - X_{H_2O} \right) \frac{X_0 (1 - X_{CO})}{1 + \phi (\alpha - 1)} \]  
(6)

\[
\dot{q} = \frac{X_0 (1 - X_{CO})}{X_0 (1 - X_{H_2O})} \]  
(7)

where:
\[ X_{CO} = \text{measured mole fraction of carbon monoxide in the exhaust gas} \]
\[ E_{CO} = \text{heat release per kilogram oxygen consumed during complete combustion of CO} (\approx 17.6 \text{ MJ/kg of O}_2) \]

Theoretically, if the oxygen concentration in the exhaust gas is above 14 % and the CO concentration is below 1 %, the percentage error of neglecting CO production is below 5 % [22]. In fact, the O₂ and CO concentrations in most open fire tests are far from these limits, why CO production can indeed generally be neglected. For the coming discussion, it can be noted that UL 9540A (4th ed., 2019), a standard for battery fire testing, specifies that Eqs. (6) and (7) shall be used for HRR calculations.

For all equations discussed above, it should be emphasised that several simplifying assumptions are attained in the derivation. Apart from the original assumption that the heat release per unit mass of oxygen consumed is a constant, the following main assumptions are also made:
- All gases are considered ideal gases
- Intake air consists of only O₂, CO₂, H₂O, and inert gases not involved in the combustion reactions
- The molecular weight of the exhaust gas is constant, i.e. \( M_g \approx M_a \).

2.2. Carbon dioxide generation calorimetry

The CDG method is very similar to the OCC method, but relies on the assumption that the HRR (\( \dot{q} \)) is proportional to the amount of carbon dioxide and carbon monoxide produced, i.e.
\[
\dot{q} = E_{CO} (m_{CO} - m_{CO}^0) + E_{CO} (m_{CO} - m_{CO}^0) \]  
(8)

where \( E_{CO} \) and \( E_{CO} \) are the net heat release per kilogram of CO₂ and CO produced, respectively. An average value of 13.3 MJ/kg for \( E_{CO} \) [2] is typically used for unknown compositions of fuel. In that case
\[
E_{CO} = \frac{M_{CO} \dot{E}_{CO} - \Delta H_{CO}}{M_{CO}} \approx 10.8 \text{ MJ/kg} \]  
(9)

With similar derivation as for the OCC method (see Ref. [23]) the counterpart to Eq. (6) becomes
\[
\dot{q} = \frac{m_a M_a}{M_g} \left( 1 - X_{H_2O} \right) \left( E_{CO} X_{CO} + E_{CO} X_{CO} - \frac{E_{CO} X_{CO} + E_{CO} X_{CO}}{1 + \phi (\alpha - 1)} \right) \]  
(10)

where \( E_{CO} = M_{CO} E_{CO}, E_{CO} = M_{CO} E_{CO}, \) and \( \phi \) is calculated according to Eq. (7). Furthermore, simplifying the equation by ignoring air humidity, expansion factor etc. (as in Eq. (5) for the OCC method), the CDG equation can be written as
\[
\dot{q} = \frac{m_a M_a}{M_g} \left[ E_{CO} (X_{CO} - X_{CO}^0) + E_{CO} (X_{CO} - X_{CO}^0) \right] \]  
(11)

The simplified Eq. (11) is used in some standard test methods and the errors induced are a few percentages at maximum in open and well-ventilated systems [23].

2.3. General uncertainties

The general uncertainties for the OCC and CDG methods are similar. Sources of errors include mass flow rate measurements in the exhaust duct, species concentrations measurements, the E-factors, the expansion factor \( \alpha \), humidity, and molecular weight of the exhaust gas. For OCC, in open system setups, the E-factor (i.e., heat release per unit mass of oxygen consumed), O₂ concentrations measurements, and mass flow rate measurements are those that contribute most to the uncertainty, e.g. when Eq. (2) is used [24,25]. Usually, regular calibration tests with a fire source of known heat output are conducted to adjust a calibration factor in the mass flow rate measurements [26]. Despite that, the combined expanded relative standard uncertainty for OCC is typically considered to be at least 10 % [24,25]. Single value uncertainties can however be lowered if averages are considered, as in many standard fire tests [25].

The uncertainty varies with the experimental setup and protocol used. Axelsson et al. [25] evaluated the uncertainty in the standardised test methods: Room/Corner Test (ISO 9705) and Single Burning Item, SBI (EN 13823). For example, the expansion factor \( \alpha \) mainly contributed to the uncertainty for a relatively large fire in the Room/Corner Test, while the uncertainty of the oxygen analyser was the largest for smaller fires in the SBI setup. The same conclusion was found by Brohez [24], who used the Fire Propagation Apparatus [27], a bench-scale setup where the fuel-to-air ratio can be controlled. The individual uncertainty of the oxygen analyser will increase rapidly at very low oxygen depletion levels, while at high oxygen depletion levels the uncertainty of the expansion factor \( \alpha \) as well as uncertainties from incomplete combustion will dominate. A depletion level where \( X_{CO}^0 - X_{CO} \approx 1–2 \% \) is typically desirable [24].

Including corrections for CO production, as in Eq. (6), or even
corrections for soot production, introduce other E-factors with their own individual uncertainties if an unknown composition of fuel is considered. Brohez [24] illustrated one example where the expanded relative standard uncertainty of the CO and soot corrections were 29 % and 157 %, respectively. Based on that result, the recommendation was to use the simplest OCC procedure, without corrections for CO and soot production, in case of unknown composition of the fuel.

Comparing OCC and CDG, the main differences relating to uncertainties is the estimations of the E-factors. Huggett’s average of $E$ (13.1 MJ/kg) is usually considered to have an uncertainty of $\pm 5 \%$ [3, 4], but considers only the most common organic fuels. Averages from a more extensive list of organic fuels are associated with uncertainties of $\pm 7 \%$ for $E$, $\pm 11 \%$ for $E_{CO_2}$, and $\pm 18 \%$ for $E_{CO}$ [2]. Furthermore, Biteau et al. [28] calculated the mean and standard deviation of the different E-factors for an even more extensive list including various and more complex materials from the literature and found them to be 13.1 ($\pm 14 \%$) for $E$, 13.1 ($\pm 16.5 \%$) for $E_{CO_2}$, and 10.7 ($\pm 31.7 \%$) for $E_{CO}$. The slightly higher uncertainties associated with the production of CO2 and CO, as compared to the consumption of $O_2$, is probably why the OCC method is most widely used. However, as pointed out by Biteau et al. [28], for non-standard materials where these methods show diverging results, it is not possible to assume the correctness of one method above the other.

3. Measured heat release from battery tests

As part of the analysis in the present paper, literature data was collected on the measured THR from various LIB tests; see Fig. 1. Part of this data has previously been published by RISE [29]. The THR in kJ is presented based on the calorimetric method used. IHG-methods include the Fractional Thermal Runaway Calorimeter (FTRC) developed by NASA [30], Copper Slug Battery Calorimetry (CSBC) [14, 31, 32], Accelerating Rate Calorimetry (ARC) [33, 34], different bomb calorimeters [21, 35], and enthalpy change methods [36, 37]. Tests where OCC or CDG have been used are categorized into (i) tests on a single cell or on a bundle of cells without additional packaging material (red dots), and (ii) tests on module, pack or at complete rack level (blue dots).

From the linear trend lines in Fig. 1, it is clearly seen that most of the heat energy comes from the flaming fire outside of the battery, captured by the OCC and CDG methods. Furthermore, it can be suggested, based on the difference between red and blue coloured trend lines, that a significant portion of the THR comes from combustion of the packaging materials and surrounding components in larger battery systems. The variance is however substantial, and the observed differences can also be due to different types of cells, different test methodologies, and differences in combustion efficiency. The mean and standard deviation of the ratio between the measured THR and the available electrical energy is presented in Table 1 for the data showed in Fig. 1. Based on this data, the internally generated heat is expected to be 1–2 times the available electrical energy, and the heat energy measured with OCC/CDG in battery fires a factor 5–10 more. Mikolajczak et al. [11] estimated that the stored chemical energy of an average 18650 cell would be approximately 7–11 times the electrical energy excluding packaging material, which agrees well with the data in Table 1.

4. Experimental work

There are several test series conducted by some of the authors, both previously published and ones recently carried out that will be analysed and discussed. These test series are summarized in Table 2, where test series 1 constitute the most recent one and the others are presented in descending order according when they were conducted. Detailed description of test series 3 and 4 are found in previous publications noted in Table 2. The open setup used in test series 1 is an improved but similar setup as in test series 3. A semi-open enclosure was built to ensure that all gases are collected by the hood and exhaust duct; see Fig. 2. Reference tests were conducted with a propane burner at different HRR outputs to ensure that enough air enters the enclosure along the floor to maintain open atmosphere conditions (the oxygen depletion, $X_{O_2}$, was at all times less than 2 %). The volume flow rate in the duct system was approximately 1.0 m$^3$/s in the tests, and an almost laminar flow was rendered by a set of guide vanes and by employing sufficient length of the duct ahead of measurements. Gases were analysed using an X-STREAM instrument including a paramagnetic oxygen analyser and a nondispersive infrared (NDIR) sensor for CO and CO$_2$. In addition, the remaining particulate matter in the enclosure after each test was collected and weighed.

In test series 2, the same closed setup was used as in test series 3 (see Fig. 3), which is thoroughly described in Ref. [43]. For the purpose of this present study, only the gas composition analysis is of interest. The gases were analysed by both an Agilent 490 Micro-GC gas analyser and the X-STREAM instrument including a paramagnetic oxygen analyser and a nondispersive infrared (NDIR) sensor for CO and CO$_2$. In addition, some gas bags were further analysed with regard to the different hydrocarbons, employing gas chromatography (GC) with flame ionization detector (FID) and mass spectrometer (MS). The TR (thermal runaway) trigger methods used in test series 1–3 are described in Ref. [43].

5. Analysis and discussion

The analysis focuses on uncertainties in the use of OCC, relating specifically to the measurement of heat release from LIB fires and thermal runaway scenarios. Topics covered include oxygen released and gas released from the battery, the E-factor, measurement of peak HRR and the effect of combustion efficiency on the measurements.

5.1. Oxygen released from the battery cell

During thermal runaway and thermal decomposition of the battery materials, oxygen is generated within the cell. There are, however, few
studies where oxygen has been reported as part of the gas composition analysis performed outside of the cell. If reported, usually the concentration is very low (<1 %) [14, 36, 52, 53], and it has been argued that this will have limited impact on the OCC measurements [14–16]. On the other hand, there are also some studies where up to 6 % oxygen have been reported [39, 54, 55]. Note that the oxygen release within the cell is much higher, but most oxygen will react further inside the cell contributing to the IHG. In test series 2 of the experimental work, a specific focus was put on the analysis of oxygen generation. Two separate analysis techniques were used on separate gas bags taken from the pressure vessel after each test. The results from the 8 tests conducted are presented in Fig. 4 (corrected by subtracting the background nitrogen concentration). Two different sizes of the same type of LIB cell (NMC811/C) were tested at two different SOC levels, 75 % and 100 %. Cells denoted as “pre-heated” were triggered by a slow heating ramp (1 °C/min) while the others were forced into TR within a few minutes using a local heater device. Several conclusions can be drawn from the tests:

- The oxygen concentration measurements are reliable due to the agreement between the two different analysis techniques.
- Due to measurements of almost zero oxygen (<0.1 %) in two of the tests, it can be assumed that any air left behind in the vessel before the test, or any air contamination in the gas bags or in the analysers, are negligible.

<table>
<thead>
<tr>
<th>Test series</th>
<th>Number of tests</th>
<th>Test object(s)</th>
<th>Setup</th>
<th>SOC [%]</th>
<th>TR trigger method(s)</th>
<th>Prev. publ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>3 different cells, 55, 70, 157 Ah</td>
<td>Open</td>
<td>75–100</td>
<td>Nail penetration</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>2 different cells, 70 &amp; 157 Ah</td>
<td>Closed</td>
<td>75–100</td>
<td>Fast &amp; slow heating ramp</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>37</td>
<td>1 cell, 157 Ah</td>
<td>Open &amp; closed</td>
<td>25–100</td>
<td>Fast &amp; slow heating ramp, external fire, nail penetration, overcharge</td>
<td>[43]</td>
</tr>
<tr>
<td>4</td>
<td>6 + 10</td>
<td>6 vehicles, + 10 battery tests at different scales</td>
<td>Open</td>
<td>80–90</td>
<td>External fire</td>
<td>[29, 51]</td>
</tr>
</tbody>
</table>

Fig. 2. The open setup used in test series 1. The door was closed during tests and fresh air enters along the opening between the insulation wall and the floor.

Fig. 3. The closed and inert pressure vessel setup used in test series 2 and 3.

Fig. 4. Oxygen volume concentration measured in 8 different tests in test series 2 by two different analysis techniques.
As shown in Ref. [43], the more violent TR and higher gas production rates associated with both higher SOC and pre-heating of the cell also have an impact on the oxygen released to the outside of the cell.  

The cell size has an effect on the oxygen concentration, suggesting higher internal temperatures for a larger cell.

It should be emphasised that any oxygen released to the outside of the cell is expected to be involved in further combustion reactions in case of normal atmospheric with external flames present. In that case, it can be seen as if the total amount of other gases (CO and CO$_2$) consists of, on average, about 25% hydrogen (H$_2$).  

Additionally, the most likely scenario is that all oxygen is consumed, with as high oxygen concentration as up to 6% in the battery gases. Released from the battery and reaching the exhaust duct is limited, also corresponds to an error of 2%. It is seen that the effect of having oxygen from having the battery gases reaching the exhaust duct. Therefore, it is unlikely that self-generated oxygen would result in negative HRR, contrary to what was suggested in two papers [10,15].

Assuming a partly flaming fire from the battery cell, the measured THR will be much higher. For example, comparing the contribution from having 6% oxygen reaching the analyser (−0.4 L/Wh) with the measured OCC data in Fig. 1 for single cells (trendline at 18 kJ/Wh), this corresponds to an error of 2%. It is seen that the effect of having oxygen released from the battery and reaching the exhaust duct is limited, also with as high oxygen concentration as up to 6% in the battery gases. Additionally, the most likely scenario is that all oxygen is consumed, either already inside the battery cells or in case of a flaming battery fire.  

5.2. CO$_2$ and CO released from the battery cell

Battery gases released during thermal runaway at 100% SOC consists of, on average, about 25% hydrogen (H$_2$), 20% total hydrocarbons (THC), and 55% CO$_2$ and CO [43]. As mentioned previously, without external flames these gases will displace air in the exhaust duct and thereby give rise to the measured THR. Conservatively estimated, the amount of gas released might reach 1.0 L/Wh, but around 0.5 L/Wh at 100% SOC is more likely based on literature data [43]. Using Eq. (3) in the same way as in previous section, and assuming 0.5 L/Wh of gas release, gives that the measured THR, normalized to electrical energy of the cell, would be about 1.8 kJ/Wh ± 0.5 kJ/Wh. However, in a battery fire it is more likely that the released gases are combusted before measured. This might affect the E-factor in the OCC calculations, which is discussed below. Disregarding the effect of the combustion reactions, the released CO$_2$ from the battery will still be unaffected and displace some of the air in the exhaust duct. Considering 0.5 L/Wh gas release with 30% CO$_2$, a realistic added THR to the measurements would be approximately $E(0.3 \times 0.5 \times \rho_a)/(M_{O_2}/M_a)(0.21) \approx 0.5$ kJ/Wh. With the assumption that OCC only measure the external flaming fire, and this is around 18 kJ/Wh (see Fig. 1), the CO$_2$ release from the battery would add a systematic error of about 3%, based on the above calculations. The expected measurements or contributions to the measured THR by CO$_2$ and O$_2$ release from the battery are summarized in Table 3. Note that the time evolution of the different gaseous emissions might not be identical, giving rise to a time dependent gas composition, however, it is estimated that this will have a limited impact on the analysis of the THR using average gas composition data.

Displacement of air in the exhaust duct is not the only effect caused by the battery gases. Released CO$_2$ and CO will also directly affect continuous measurements of $X_{O_2}$ and $X_{CO}$ in Eqs. (2), (6) and (7). The additional CO$_2$ and CO violate one of the basic assumptions for these equations: that the incoming air/gas to the combustion region is constant with regards to CO$_2$ and CO concentrations ($X_{O_2}$, $X_{CO}$). The added CO is expected to result in a lower estimated HRR due to the assumption that some of the consumed oxygen was part of incomplete combustion (Eq. (6)).

The effect on the oxygen depletion factor $\phi$ is however less intuitive, why the overall effect has been investigated experimentally here. Fig. 5 shows the result from two of the tests in test series 1 on a 55 Ah cell. The combustion efficiency, defined here as the ratio between the total mass of CO and CO$_2$ detected in the exhaust duct ($m_{CO}/m_{CO_2}$), was the highest for a low CO/CO$_2$ ratio (Fig. 5a) and the lowest for a high CO/CO$_2$ ratio (Fig. 5b). It is seen that the CO release from the battery, if reaching the exhaust duct, has a significant effect on the HRR when using Eq. (6). The THR, calculated by integrating the HRR curves in Fig. 5b, is for Eq. (6) 35% lower as compared to Eq. (2), which in turn is 5% lower as compared to Eq. (5), where CO$_2$ measurements have been neglected. For the scenario in Fig. 5a however, where all the CO is consumed in the external combustion, all equations give the same result. The combustion efficiency in battery tests will be discussed further below. It should be emphasised that very little CO is produced in the external fire in this test setup, which was validated by a reference propane burner up to 200 kW, where HRR calculated by Eqs. (2) and (6) were inseparable. This test is shown in Fig. 6. Here, the simplified Eq. (5) for OCC shows a lower HRR as compared to Eq. (2). That this is not seen in the battery tests shown in Fig. 5 could be due to the CO$_2$ release from the battery, compensating for this expected difference.

In the propane reference test shown in Fig. 6, the HRR based on CDG is lower as compared to the OCC result (Eq. (2)), especially when the average E-factors are used (Fig. 6b). When correct E-factors for propane are used, the result from both OCC and CDG is within expected general uncertainties as discussed in the Theory section (see also Fig. 6a). Note that the HRR based on the propane flow meter should not be seen as the true HRR, since this method is also associated with uncertainties.

Applying CDG and Eq. (10) to the battery test shown in Fig. 5a gives a much higher HRR, as seen in Fig. 7. This is due to the CO$_2$ release from the battery. Instead of violating the basic assumptions as for OCC, the extra CO$_2$ is seen as coming from combustion reactions, irrespective of whether they are external or internal of the battery. It can be speculated

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### Table 3

Summary of the expected measurements (first two scenarios) or contributions to the measured THR (last two scenarios) discussed as a consequence of air displacement by battery gases in the exhaust duct.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Measured THR (kJ/Wh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Battery fire (single cell)</td>
<td>18</td>
</tr>
<tr>
<td>Cell venting (no fire)</td>
<td>1.8</td>
</tr>
<tr>
<td>30% CO$_2$ from the battery</td>
<td>0.5</td>
</tr>
<tr>
<td>6% O$_2$ from the battery</td>
<td>−0.4</td>
</tr>
</tbody>
</table>
whether the CO₂ and CO released from the battery is primarily a result of combustion reactions. Mikolajczak et al. [11] described that CO₂ production within the cell can either be generated from O₂ release within the cell (typical combustion reactions) or from thermal degradation processes with less energy release. Table 4 presents the integrated IHG based on the measured difference between CDG and OCC (as seen in Fig. 7). The mean values from all battery tests correspond well with the literature data for IHG-methods listed in Table 1, and the test data indicate that the CDG measurements could be a good estimation of the total heat release rate, including both internal and external HRR. However, the literature data include IHG-methods where Joule heating from internal short circuit is captured, not possible to measure with CDG. This shortcoming might be partly compensated in the CDG measurements as a result of the assumption that all CO₂ and CO comes from combustion reactions, which is likely not the case.

Finally, the difference between CDG and OCC measurements due to the released CO₂ and CO from the battery can be described as large for single cell tests, but the effect from the battery gases is less evident in a full-scale vehicle test, as seen in Fig. 8 for one of the BEVs burned as part of test series 4. The difference in THR using CDG as compared to OCC is also presented in Table 4 for different tests. In general, the CDG measurements gives a lower HRR as compared to the OCC measurements for all vehicle tests, but it is also seen that the difference in HRR changes (see “Diff.” plot in Fig. 8, displaying the difference between OCC and CDG measurements) when the battery fire is observed to be most intense between 24 and 27 min in the full-scale vehicle test. Here, the relative difference changes from −20 % → +10 %. It is therefore recommended to use both CDG and OCC methods in large-scale battery fire tests to get the most information. But as mentioned in the Theory chapter, for any non-standard materials involved in the fire, it is not possible to assume the correctness of one method above the other (disregarding the effect of the battery gases).

5.3. The E-factor

For single battery cell tests, a major part of the external flaming fire is combustion of the released gases during thermal runaway. The main constituents that are combustible are, in general, H₂, CO, CH₄, and C₂H₄. For example, in test series 2, twelve different hydrocarbons were quantified by gas chromatographic analysis with flame ionization detector (FID) and mass spectrometer (MS), and CH₄ and C₂H₄ together constituted about 85 % of the THC. Tabulated lower heating values (LHV) or net calorific values are shown in Table 5 which are translated into net heats of complete combustion per unit mass of oxygen consumed. If the battery gases released consists of about 25 % hydrogen (H₂), 20 % total hydrocarbons (THC), and 25 % CO (average literature data at 100 % SOC [43]), and assuming that the THC consists of equal

![Image](Fig. 5. HRR calculated with three different equations for two different tests on a 55 Ah cell. a) Low CO/CO₂ ratio, and b) high CO/CO₂ ratio.)

![Image](Fig. 6. HRR calculated for different OCC and CDG equations for a propane reference test and compared with expected HRR based on the propane flow meter. Tabulated E-factors for propane is used in a), and average E-factors in b.).)
Table 4

<table>
<thead>
<tr>
<th>Test series</th>
<th>Test(s)</th>
<th>THR, CDG (kJ/kg)</th>
<th>IHG based on CDG (kJ/kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>All (10)</td>
<td>+47.134 %</td>
<td>1.5 (+0.25)</td>
</tr>
<tr>
<td>1</td>
<td>All’ (14)</td>
<td>+49.68 %</td>
<td>1.4 (+0.33)</td>
</tr>
<tr>
<td>3</td>
<td>ICEV</td>
<td>–12 %</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>BEV 1</td>
<td>–7 %</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>BEV 2</td>
<td>–7 %</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Module</td>
<td>+11–12 %</td>
<td>1.6 (+0.11)</td>
</tr>
<tr>
<td>3</td>
<td>Cell(s)</td>
<td>+15–24 %</td>
<td>1.8 (+0.26)</td>
</tr>
</tbody>
</table>

All tests with observed external flaming fire.

Table 5

<table>
<thead>
<tr>
<th>Fuel</th>
<th>LHV (MJ/kg)</th>
<th>MJ/kg of O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>12.0</td>
<td>15.1</td>
</tr>
<tr>
<td>CO</td>
<td>10.1</td>
<td>17.7</td>
</tr>
<tr>
<td>CH₄</td>
<td>50.0</td>
<td>12.5</td>
</tr>
<tr>
<td>C₆H₁₀</td>
<td>47.2</td>
<td>13.8</td>
</tr>
</tbody>
</table>

Tabulated lower heating values (LHV) \[5\] and corresponding net heats of complete combustion per unit mass of oxygen consumed.

5.4. Peak heat release rate

The nature of a thermal runaway typically creates very high gas productions rates and violent combustion. If the gas production rate is much higher than the gas flow rate in the exhaust duct and to the gas analysers, OCC and CDG methods will smear the HRR data over a longer time. In test series 3, for the open test setup, the cell was positioned on top of a scale during the tests for time-resolved mass loss data. The result from two tests, at 100 % SOC and using a slow TR trigger heating ramp in a), and 75 % SOC and a faster heating ramp in b). Both the SOC and the TR trigger method affect the gas production rate and combustion reactions rate. The mass loss data typically starts with a negative mass loss rate due to the force applied on the scale from the cell pressure release and high gas flow rate during the thermal runaway reactions. Therefore, it can be difficult to rely on the shape of this curve. However, estimating the duration of the event from the mass loss data is more accurate as compared to using the OCC data. Assuming a simple triangular or rectangular HRR shape, where the area is proportional to that the exact composition of the THCs is less important.

Considering the average gas composition mentioned above, 1 mol of battery gas would consume \((0.25 \times 0.5 + 0.25 \times 0.5 + 0.1 \times 2 + 0.1 \times 3)/0.7 = 1.07\) mol of O₂ in case of complete combustion. 0.5 L/Wh of battery gas would then consume about 0.70 g of O₂ per Wh, and using Huggett’s average E-factor it results in 9.2 kJ/Wh. Including the larger hydrocarbons detected in test series 2, the heat of combustion could theoretically extend up to 10 kJ/Wh, however, using the lower total value of hydrocarbons and higher value of CO detected for this specific cell \[43\], the theoretical heat of combustion would be around 7 kJ/Wh.

7–10 kJ/Wh in measured heat release is low compared to the measured THR shown in Fig. 1, which is due to that solid material is part of the combustion process as well. For this reason, ejected particulate matter was collected and weighed, both in the open setup used in test series 1 and in the inert setup in test series 3. Comparing the weights of the remaining cell as well as ejected particles for tests with the same type of cell and the same triggering method, reveals that the mass loss in the open setup was, on average, 6 %pt. higher, corresponding to 0.22 g/Wh.

If that would correspond to, for example, complete combustion of graphite the amount of oxygen consumed would be 0.22 \((M_{C} / M_{graphite}) \approx 0.6\) (g of O₂)/Wh, and using Huggett’s average E-factor, this becomes approximately 8 kJ/Wh. As seen, this is the same order of magnitude of heat released as from the theoretical combustion of the gases. In addition, adding both contributions from combustion of the released gases as well as from ejected particles matches well the 18 kJ/Wh trend line seen in Fig. 1. This means that on cell level, combustion of the released battery gases during thermal runaway is expected to account for approximately 50 % of the measured THR, and since the actual E-factor is estimated to be up to 20 % higher as compared to Huggett’s average for these gases, the systematic error might be in the order of 10 %.

The need for an adjustment of the E-factor is not unique for LIBs. Here the error is estimated based on average literature data and is in the same order of magnitude as the general uncertainties for any unknown compositions of fuel. However, note that this error only applies for the HRR from the external flaming fire. IHG will be neglected and is not easily adjusted for since there will be a variation between different LIBs.
the base times the height, maintaining the THR (same area under the curve) would mean that a $x\%$ shorter duration gives $y\%$ higher peak, where $(1 - x)(1 + y) = 1$. In Fig. 9a, the duration based on mass loss data is approximately 15 s, which is only about 50 % of the duration based on the OCC data. The actual peak HRR is then estimated to be 100 \% higher than what was measured with OCC. Similarly, in Fig. 9b the duration is about 25 \% shorter based on the mass loss data, and the peak HRR is then estimated to be about 30 \% higher than measured. The size of the error will be affected by the combustion reactions rate as well as the volume flow rate in the exhaust duct. However, it should be noted that increasing the volume flow rate too much might increase the uncertainties if the oxygen depletion factor gets too low.

5.5. Combustion efficiency

A thermal runaway is typically associated with violent and fast combustion. Due to the very high gas production rates and high gas flows, it is common that flames can be visible and extinguished alternately during the most intense gas generation, affecting the overall combustion efficiency. This have been seen in both test series 1 and 3, where the measured THR varied considerably due to this phenomenon. One way of defining the combustion efficiency is to study the ratio between the total mass of CO$_2$ ($m_{\text{CO}_2}$) and the total mass of CO ($m_{\text{CO}}$) measured in the exhaust duct. In Fig. 10, the THR measured by OCC (Eq. (2)), normalized to the available electrical energy in the cell, is plotted against combustion efficiency for tests conducted both in test series 1 and 3. Results from test series 1 include all three different sizes of cells, but one test is not seen in the graph where $m_{\text{CO}}/m_{\text{CO}_2}$ is as high as 0.7 (THR was around 3 kJ/Wh). The THR measured in test series 3 is, in general, somewhat lower as compared to measurements in test series 1. This is due to that the test setup was improved in test series 1 to ensure that all gases were collected by the hood and exhaust duct. The variation seen in the figure for similar $m_{\text{CO}}/m_{\text{CO}_2}$ ratio, especially for high combustion efficiency, might be a result of differences in the combustion of solid particles, since the ratio only refer to combustion of CO in the released gases. The number of ejected particles will, in turn, depend on e.g. SOC, TR triggering method and cell size. In addition, four tests of the 14 with external flaming fire in test series 3 have been excluded from the graph because the cells ventilated in other directions than upwards, resulting in large amount of gas not collected by the hood above the cells. Still, by observing the trend in Fig. 10, one can estimate a theoretical THR of at least 15 kJ/Wh for these cells at complete combustion of the CO from the battery. This correlates well with the theoretical discussion in section 5.3 where about 7 kJ/Wh is assumed to come from complete combustion of the released gases and about 8 kJ/Wh from combustion of lost particulate matter measured in these tests. The combustion efficiency has a very large impact on the measured HRR, especially at cell level, and it can be anticipated that the large variance from the literature data displayed in Fig. 1 depends as much on differences in combustion efficiency as on differences in cell type.

6. Conclusions

Based on literature data, the internally generated heat during thermal runaway is expected to be 1–2 times the available electrical energy, and the THR measured with OCC in large battery fires is expected to be 5–10 times higher. There are several theories in the literature about the uncertainties when using OCC for HRR measurements in LIB fires, but most agree that OCC will mainly measure the HRR from the external flaming fire, not IHG in the battery. Details are outlined concerning the
uncertainties associated with self-generated oxygen and IHG, the total gas released from the battery and impact on the HRR calculations. Further, different equations used in OCC or CDG methodology as well as the assumed E-factors, and differences in combustion efficiency and rate of combustion reactions are outlined and analysed. For a LIB fire test, it can be concluded that:

- Self-generated oxygen will only affect IHG. Although some self-generated oxygen might be consumed outside of the cell, this will still be neglected by the OCC measurements. If some of the oxygen reaches the exhaust duct, it is estimated that this will, at maximum, yield an error of ~2 % of the THR.
- Released carbon dioxide from the battery is estimated to give a systematic error of approximately +3 % of the THR.
- Using Eq. (6) with CO correction is not recommended, since carbon monoxide released from the battery might induce large errors.
- Using Huggett’s average E-factor is estimated to give a systematic error in the order of ~10 % of the THR.

It should be noted that the above approximate errors are valid for single cell tests. Including packaging materials and surrounding components in larger battery systems will probably decrease the size of the errors, because such materials are expected to be more similar to what the method was developed for originally. In addition, the LIB type will affect the amount of self-generated oxygen, the total gas production and gas composition. Above numbers are based on conservative values of oxygen release and total gas production, and average literature values for the gas composition. Overall, it can be assumed that OCC will underestimate the THR from the external flaming fire by up to 10 %, but since the general uncertainties of using OCC also are in the same order of magnitude it can be argued that this can be neglected, at least for larger battery fires. A summary of the general uncertainties of using OCC compared with the estimated systematic error in LIB fire tests is shown in Table 6.

Another uncertainty is connected to the rapid behaviour of thermal runway, high gas production rates and following violent combustion. In small scale tests, peak HRR measured by OCC is expected to be underestimated, in the tests performed here up to 100 %. In addition, partly incomplete combustion is expected of the battery gases, which partly incomplete combustion is expected of the battery gases, which in Table 6.

<table>
<thead>
<tr>
<th>Fire test with unknown fuel composition</th>
<th>LIB fire test (systematic error)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall E-factor (13.1 MJ/kg)</td>
<td>&gt;10 %&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>±5-14 %&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>&lt;10 %&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>– 10 %&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

<sup>a</sup> Can be lowered by looking at averages (and THR).
<sup>b</sup> Systematic error for THR from external flaming fire (can be higher for peak HRR).
<sup>c</sup> Based on different lists of tabulated fuels.
<sup>d</sup> Cell level tests.

Table 6

Summary of general uncertainties when using OCC for unknown compositions of fuel and additional systematic error for LIB fire test.

CRediT authorship contribution statement

Ola Willstrand: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. Mohit Pushp: Writing – review & editing, Investigation. Haukur Ingason: Writing – review & editing, Methodology. Daniel Brandell: Writing – review & editing, Supervision.

Declaration of competing interest

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

Data availability

The authors do not have permission to share data.

Acknowledgements

This work is part of a project funded by the Swedish Energy Agency (project no. 51787-1). Partners within the project comprise of RISE Research Institutes of Sweden, Northvolt, Scania, and Uppsala University. We also acknowledge support from Batteries Sweden (grant no. Vinnova-2019-00064), and STAndUp for Energy.

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