



Evaluation of combustion properties of vent gases from Li-ion batteries

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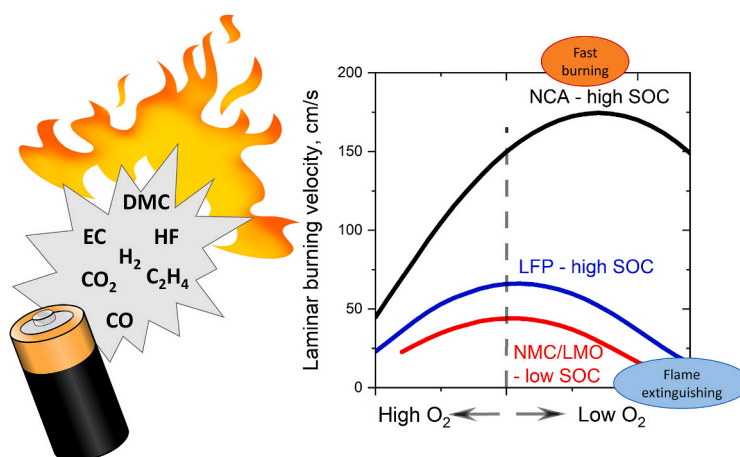
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HIGHLIGHTS

- A chemical kinetic model for Li-ion battery gases including carbonates and fluorine.
- Presence of fluorine compounds does not affect the ignition or flame propagation.
- Ignition is not sensitive to oxygen content, but may occur in O₂-depleted conditions.
- The laminar burning velocity of vent gases at same temperature vary by a factor of 4.
- Flame characteristics of a battery gas is dependent on the battery chemistry and SOC.

GRAPHICAL ABSTRACT



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ABSTRACT

Fire incidents involving Li-ion batteries is an increasing concern as the use of battery electric vehicles is increasing. Abuse conditions such as heating can result in ejection of flammable and toxic gases, presenting a health risk and risk of explosion or fire. The purpose of the present work is to increase the understanding of combustion of gas mixtures vented from Li-ion batteries. The investigation uses a new merged kinetic mechanism including hydrocarbons, hydrogen, carbon oxides, carbonates and fluorinated compounds. Seven typical Li-ion vent gas mixtures were selected based on published studies, and ignition and laminar flames were simulated. Modeling reveal a large variation in laminar burning velocity, flame temperature and heat release. Determining factors for laminar flames are the relative content of the carbonates and hydrogen gas, and the inert carbon dioxide. Gases from highly charged battery cells have the shortest ignition time at high temperatures and the fastest laminar burning velocity. The results can be used as input in computational fluid dynamics or safety engineering modeling. In addition, the versatile kinetic model can be used for fundamental studies of the combustion process and for generation of combustion characteristics such as laminar burning velocities for other vent gas mixtures.

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1. Introduction

Internal cell failure is the dominating safety concern of lithium-ion (Li-ion) batteries. In addition to mechanical, electrical and thermal abuse, latent manufacturing defects from cell production can trigger these failures to occur, thus initiating electrochemical and chemical reactions in the cell materials. These processes produce gases, leading to an overpressure in the battery cell, which can result in controlled venting or uncontrolled cell rupture. The severity of the gas production depends on battery chemistry [1], state of charge (SOC) [2], external temperature [2] and state of health (SOH), i.e. the aging status [3] of the battery. The worst case scenario is when the battery cell enters a state called thermal runaway (TR), when an uncontrolled sequence of exothermic chemical reactions results in rapid temperature increase and extensive gas production, as explained in detail by, among others, Wang et al. [4]. The TR process may cause enough heat and gas to initiate a gas explosion and increase the risk of fire. In mid- and large-scale, multi-cell battery installations, e.g. electric vehicle traction batteries and stationary energy storage systems, the TR can propagate from cell to cell within the battery, thus aggravating the situation. Gassing in Li-ion cells is researched extensively due to the flammability and toxicity of the species formed.

The gas mixture vented from a battery cell experiencing thermal runaway commonly contain CO_2 , CO , H_2 , CH_4 , C_2H_4 , C_2H_6 , carbonates and fluorinated compounds like HF and CH_3F . The relative amounts of the gas phase constituents vary significantly depending on cell chemistry, SOC and temperature. Reports differ on the carbonate content in the gas phase, which is likely highly sensitive to the external condition with respect to temperature and the extent of chemical transformation of battery material before the cell is vented or ruptured. The electrolyte in a Li-ion battery consist of carbonates and Li-salt, commonly LiPF_6 , which already at moderate over-temperatures can react and produce gas phase fluorinated compounds and carbonate decomposition products like CO_2 and hydrocarbons [5,6]. The published literature on battery vent gases include a number of studies where the equipment was not calibrated for measurements of carbonates and fluorinated compounds. It is important to point out that the presence of those compounds cannot be ruled out in some of these studies.

Gassing from Li-ion battery cells has been studied experimentally by applying different types of abuse to cells and batteries. Experimental work on gassing from Li-ion batteries can broadly be divided into two groups: studies of the properties of the vented gas mixture (amount, temperature, composition), and studies of the fire event where the vented gases are transformed in the combustion process. For both categories most of the studies focus on thermal abuse, i.e. external heating. An illustrative overview of studies on vent gas composition, prior to 2017, was presented by Fernandes et al. [7]. Since then there has been a series of publications on the topic by Essl et al. [2,3,8]. In 2023 a meta-analysis by Rappsilber et al. [9] covering research in the period 2000 to 2021 was published. The analysis addressed the effects of thermal runaway on Li-ion batteries, and it was concluded that experimental studies have been performed with diverse test methods and that the results are to a low extent mutually comparable.

Thermal abuse is of particular importance to understand since the heat release by the thermal runaway process will result in high-temperature conditions independently on whether this is the initial trigger or not. If the initial trigger is mechanical or electrical abuse, the resulting high temperatures will further induce processes in the cell, and the heat release may act as a trigger to start failure processes in nearby cells. In most experimental studies there is first an initial limited venting rich in carbonates, which occur for all cells independent of battery chemistry and SOC. This can mark the endpoint of the cell failure, for example when the gassing is caused solely by aging of the materials, and results in loss of function of the cell or battery. However, in cases where a significant temperature increase occurs, which characterizes a thermal runaway, there is a violent second venting where a larger amount of gas

is ejected. This major vent commonly has high concentrations of CO_2 , CO , H_2 , and small hydrocarbons produced in decomposition of the carbonates.

The processes in a battery cell experiencing a thermal event include a sequence of material degradation steps starting with electrolyte vaporization and salt decomposition at 70–120 °C, inducing chemical reactions between salt and solvent or SEI (Solid Electrolyte Interphase). Above about 120 °C, the vaporization of solvent is sufficient to create overpressure, the separator is also melting and a first venting of the cell occurs. This first venting usually has a high carbonate content. Above about 160 °C the cell enters the TR state, and further heating is rapid, resulting in extensive venting with significant ejection of gases and often also liquid droplets and solid particles from the cell. At this stage, cell surface temperatures can become as high as 800 °C or more. For more detail on the sequence of physical and chemical processes, we refer to the review by Wang et al. [4].

Vented flammable gases may ignite inside or outside the battery depending on conditions such as gas temperature, pressure, gas flow speed, the composition of the gas mixture and convection as it enters the air outside the battery. Ignition can occur due to an external triggering source such as a spark or the gas mixture can auto ignite as a result of heating. In addition, heated particles have been suggested as potential ignition sources [10]. Ignition of typical vent gas mixtures has been investigated by Li et al. [11] based on thermal ignition theory, to reveal ignition limits depending on temperature and concentrations of gas and oxidizer.

If the gas mixture does ignite, but the resulting flame has a low burning velocity due to low temperature or a lack of oxygen, it will immediately extinguish, and no fire will occur. This means that for a battery fire to develop, both requirements for an ignition event and flame propagation must be met, and the gas chemistry mechanisms underlying these are studied in the present work. To enable efficient fire suppression and development of methods to prevent fires, understanding of the ignition and combustion of the vent gases is needed.

The combustion characteristics of the single gas components in the gas mixtures vented from Li-ion batteries have been researched quite extensively in the combustion research community, including studies of single component ignition properties, flame propagation speed and formation of toxic pollutants. However, the mixtures of relevance to battery vent gases have not been targeted by the combustion community. Thus, combustion research provides the building blocks for an increased understanding of battery fires, but further research applying the combustion research tools on battery vent gases is necessary. Already in 2009, Harris et al. [12] outlined a methodology for applying combustion chemistry modeling tools on an important battery electrolyte solvent, dimethyl carbonate (DMC). Harris et al. suggested that combustion characteristics, ignition energy, laminar burning velocity (LBV), flame temperature and heat release rate- (HRR) are relevant for understanding Li-ion battery vent gas fires. In addition, they pointed out that by using modeling it is possible to understand radical production in the flame, and this information can be used to evaluate or design flame inhibition methods. Unfortunately, too few researchers have listened to this call for action and the field has not been explored extensively. Some modeling work was done by Fernandes et al. [7] and Baird et al. [13], but their analyses are hampered by use of chemical mechanisms with limited capacity. Nevertheless, the University of South-Eastern Norway has published several papers applying both experimental and modeling strategies to understand the combustion of battery vent gases [14–19]. Among these is a study where Henriksen et al. [17] performed an experimental and modeling study of laminar burning velocities of typical Li-ion vent gas mixtures, including CO_2 , CO , H_2 , CH_4 , C_2H_4 and C_2H_6 , but neglecting carbonates and fluorinated compounds. Their motivation was to produce representative gas mixtures suitable for well-defined experimental and modeling studies. They selected three mixtures representing fast burning, slow burning and a generic case.

Laminar burning velocities are important parameters to use as input

in Computational Fluid Dynamics (CFD) simulations of explosion or combustion events and for safety engineering simulations. Henriksen et al. [15,16] present CFD simulation results where they used LBVs as input, based on the validated results from their experimental study [17]. LBVs are routinely determined using established experimental methodologies in the field of combustion research. It is, however, not feasible to perform experiments covering all gas mixtures that may be released from Li-ion batteries. Instead, it is helpful to use chemical kinetics modeling of the mixtures, provided that the kinetic mechanisms include the relevant combustible substances. Recent advances in multi scale modeling of thermal runaway in Li-ion batteries have been made by Kong and co-workers in a series of papers on a single battery cell [20], a battery pack [21], and in an approach where CFD was coupled with a conjugate heat transfer model [22]. In the single cell study [20] combustion of vented gases were modelled using a global combustion scheme. While incorporation of chemical kinetics is computationally demanding, motivating the use of global schemes, the general trend in the CFD research community is faster solvers and development of better kinetic models. It is therefore expected that more advanced chemical kinetics models will soon be needed to allow more accurate prediction of the combustion process following a thermal event, and to quantify production of toxic substances.

In the present work, a versatile chemical kinetic mechanism incorporating the common hydrocarbon compounds in vent gases, two carbonates and several fluorinated compounds is constructed from mechanism for the components, validated and used to increase understanding of combustion characteristics of Li-ion battery vent gas mixtures. The kinetic mechanism is the only existing mechanism including all classes of molecular components that are common in Li-ion battery vent gases. This mechanism is useful as a tool for determining macroscopic properties like ignition propensity and HRR from different gas mixture compositions and for revealing detailed information about the chemical interactions between the components. This paper outlines the model construction and presents validation of the performance of the model. Then the model is used to calculate ignition characteristics and properties of premixed and non-premixed flames for seven gas mixture cases selected to be representative of different vent gas scenarios prior to combustion.

The significance of this work is that it provides an analysis of combustion properties of Li-ion battery vent gases at a level that was not previously possible.

2. Method

2.1. Modeling approach

In combustion research, it is common practice to perform 0D and 1D modeling of ignition, flame propagation and extinction for a fuel to evaluate these fundamental combustion properties and allow assessment of its potential to burn efficiently in dedicated applications or to evaluate pollutant emission formation. While the CFD simulations mentioned in the introduction involve complex physical flow and heat transfer and are very time-consuming, the 0D and 1D simulations can be performed in minutes or hours on a regular desktop computer. To compute the combustion properties, a chemical kinetic mechanism containing the relevant chemical reactions and their associated reaction rate constants is needed. For the 1D flame simulations, it is also necessary to include thermodynamic and transport properties of each species involved in the chemical reactions. Kinetic mechanisms have widely been compiled for single fuels or groups of fuels of relevance for combustion studies, as described in detail by Curran [23]. As outlined in that work kinetic mechanisms are routinely validated towards a broad range of experimental data (ignition, flame propagation and species concentrations) which ensure the accuracy for a mechanism over a stated range of conditions. A unique aspect of the present work is that kinetic mechanisms for several hydrocarbon fuels were merged with a

mechanism for fluorine combustion, to give the first kinetic mechanism including the main groups of gas phase compounds expelled from malfunctioning Li-ion batteries.

Simulations were performed using commercial software Chemkin PRO release 15151 [24]. The opposed flow flame simulator OPPDIF was used for the non-premixed flames, with a fuel flow counter flowing an oxidizer flow at a distance of 1.0 cm. Calculations of the burning velocities of freely propagating premixed flames were performed using the PREMIX module. Transport properties for both OPPDIF and PREMIX simulations were considered using the mixture averaging approach. For PREMIX simulations, curvature and gradient parameters were set to 0.05 and 0.05, respectively, resulting in a grid of 300–450 points. Homogeneous ignition was simulated as a constant volume case using the SENKIN code in Chemkin.

In line with the standard in combustion science, the concept “equivalence ratio” is used as a metric for fuel to oxidizer ratio in a premixed combustion case. For the reader, it is important to know that at an equivalence ratio of 1.0 there is exactly the right amount of oxygen to completely oxidize the fuel mixture constituents. Lower equivalence ratios mean excess oxygen content, while higher means that there is insufficient oxygen to completely oxidize the gases.

2.2. Chemical kinetics model

None of the chemical kinetics models in the open literature includes all the different types of fuels that are present in the Li-ion battery vent gases. Henriksen et al. [17] performed an analysis of different kinetic models in relation to their performance on simplified Li-ion battery vent gases, and apart from the fact that no mechanism cover all relevant components they found a significant weakness in that the mechanisms showed variation in performance depending on CO₂ concentration. To achieve a versatile mechanism that can be used for a range of vent gases and for all CO₂ concentrations, several kinetic mechanisms were merged in the present work. Regarding the carbonates, validated mechanisms exist for DMC and diethyl carbonate (DEC). These two carbonates are representative of carbonates commonly used in Li-ion batteries since DEC has carbon-carbon bonds, while DMC does not. The base mechanism for hydrocarbon combustion used in the present work is the mechanism by Alexandrino et al. [25], developed for DMC combustion with the highly detailed Aramco mechanism for hydrocarbons, by Zhang et al. [26]. DEC chemistry is represented by a subset of reactions from Nakamura et al. [27] with updates by Sun et al. [28]. The fluorinated hydrocarbon combustion mechanism was taken from Linteris et al. [29]. The mechanisms have all been validated for the performance of the separate components by the respective authors, further information on this can be found in the reference to each mechanism. During the merging of mechanisms, it is important to check for consistent use of nomenclature and inclusion of relevant isomers. The carbonate mechanisms build on the same base chemistry and are thus compatible. In the fluorinated hydrocarbon mechanism, one modification had to be made to make it compatible with the hydrocarbon mechanism: only one propane radical, C₃H₇, was included, which was replaced by n-C₃H₇ in the merged mechanism. The full mechanism is available as supplementary material.

To test the performance of the merged model, LBV simulations were performed for components DMC [18,30], DEC [31], CH₄ [32] and C₂H₄ [33], at initial gas mixture temperatures of 25, 85 and 120 °C for which experimental data exist. The results are presented in Fig. 1, and it is seen that agreement with experimental data is good. This indicates that the chemistry is accurately treated by the model, and no errors were introduced in the merging process. The simulation results at 25 °C in Fig. 1 are illustrative to show the difference in flame propagation between the common vent gas constituents CH₄, C₂H₄, DMC and DEC, with C₂H₄ burning much more rapidly than the others. The hydrocarbons CH₄ and C₂H₄, were included in previous vent gas simulation studies by Baird et al. [13] and Henriksen et al. [17] using the mechanisms

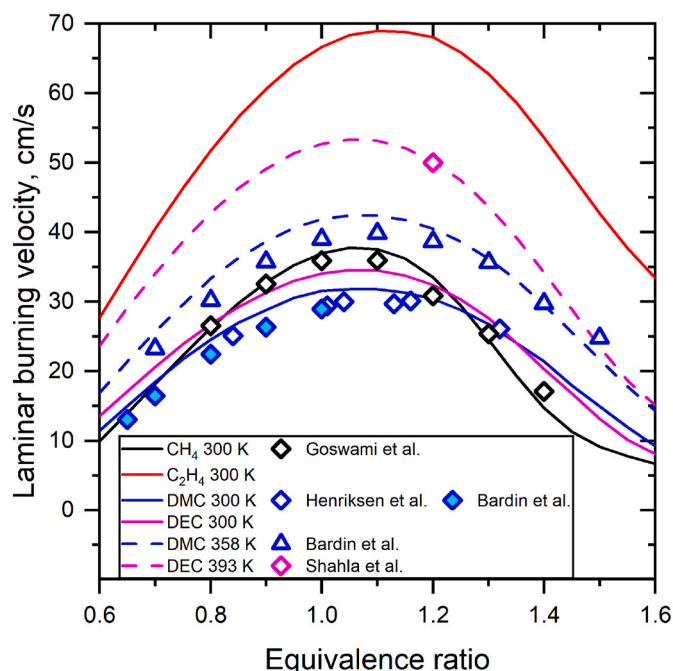


Fig. 1. Laminar burning velocities for single components, at initial gas mixture temperature 25 °C for all components and additional temperatures for DMC and DEC, simulations performed using the full mechanism compiled in the present work. Lines represent modelling and symbols experimental data [18,30–34].

GRI-Mech 3.0 and San Diego, respectively, and the results of the present mechanism is in agreement with these.

The mechanism was also tested for LBVs of multi-component vent gas mixtures determined experimentally by Henriksen et al. [17]. Fig. 2 presents the modeling results together with the experimental data, showing good agreement. The “high” case is based on the composition of vent gas from an NCA (Nickel Cobalt Aluminum) battery, originally studied by Lammer et al. [35], and the “low” case is typical gases from an LFP (Lithium Iron Phosphate) battery studied by Golubkov et al. [36]. These cases were by Henriksen et al. [17] modelled using several common combustion research models, including GRI-Mech 3.0 that was previously used by Baird et al. [13], with good agreement for all models at oxygen rich conditions. However, at oxygen depleted conditions several mechanisms, including GRI-Mech 3.0 either over- or underestimated the experimental results by up to ten percent. As explained by Henriksen et al. the GRI-Mech 3.0 is known to overestimate laminar burning velocities at high CO₂ conditions, and is therefore not suitable for many vent gas mixtures.

The two cases presented in Fig. 2 are selected for further study in the present work and correspond to Case 6 and 7 presented in Tables 1 and 2. The ability of the mechanism to accurately reproduce these experimental data confirms that it is suitable for modeling typical Li-ion battery gas mixture compositions.

2.3. Selected cases

As outlined in the introduction, a large number of published studies present the composition of vent gases from malfunctioning Li-ion batteries, but as pointed out by Rappsilber et al. [9] the use of different experimental approaches limit the potential for intercomparing between the studies. In the present work, seven cases were selected to represent a broad span of potential vent gas mixtures. The cases are selected from experimental studies where the gas composition was determined before onset of combustion. The cases are outlined in Table 1, and the detailed composition is given in Table 2. Below some details on the different cases are outlined, for further details the reader is referred to the cited

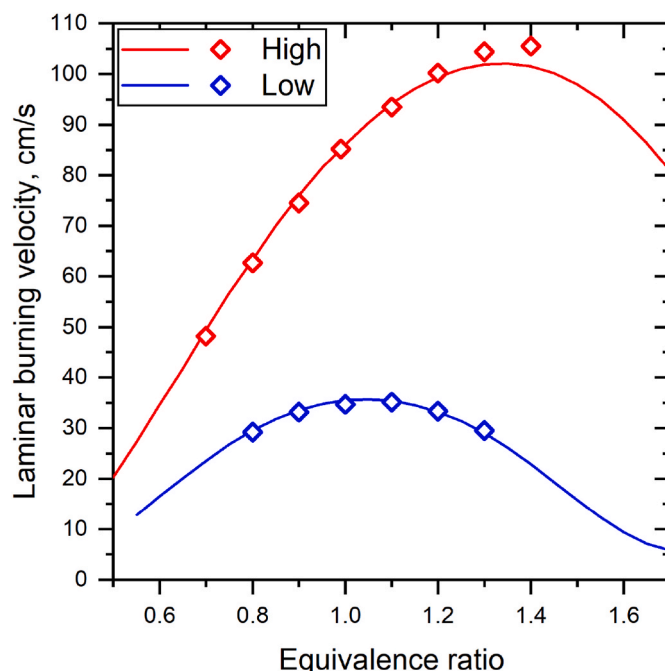


Fig. 2. Laminar burning velocities at initial gas mixture temperatures 25 °C for gas mixtures studied experimentally (symbols) by Henriksen et al. [17]. Modelling (lines) was performed using the full mechanism developed in the present work.

Table 1

Outline of selected cases based on literature.

Case	Battery chem.	SOC	Case description	Reference
1	–	–	Only carbonate, DMC/DEC	
2	LFP	135	Overcharge. Including all types of vent gases	[7]
3	LFP	135	Same as Case 2 but without F-compounds	[7]
4	NMC/LMO ^a	30	Low SOC, no TR	[2]
5	NMC/LMO ^a	100	High SOC	[2]
6	NCA	100	Early TR onset. High LBV	[17,35]
7	LFP	100	TR onset at high temperature. Low LBV	[17,36]

^a The NCM/LMO is a composite electrode material.

references.

Case 1 is a mixture of carbonates DMC and DEC, which represents a situation with electrolyte leakage and evaporation at conditions (low temperature) where no other components are formed.

Case 2 is taken from the overcharge abuse study on a cylindrical 26650 cell with LFP cathode by Fernandes et al. [7]. The electrolyte consisted of LiPF₆ and four different carbonates, but the carbonate content used in the simulations in the present work is a simplified composition with only two constituents. A thermal event was triggered by overcharging the battery to 135% SOC, but the thermal event self-extinguished; no runaway temperature increase indicating a TR occurred. The maximum surface temperature reached was about 145 °C and the vent gas mixture has quite a large carbonate content which implies that chemical transformation inside the battery cell was not extensive. It is interesting to note that release of carbonates was observed after the battery cell started to cool down, thus occurring after the main thermal event. Fernandes et al. also detected fluorinated components, and these continued to be released after the carbonates ceased to be released in the cooling process. Case 2 is interesting since it includes all classes of potential vent gases, and since it is representative

Table 2

Compositions (mole fractions) used as input for the simulation study for the seven cases outlined in Table 1.

Case	DMC	DEC	CO ₂	CO	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	HF	C ₂ H ₅ F	CH ₃ F	H ₂ O
1	85	15										
2	53	8	18	2	9	1	4	0.6	2	2	0.4	
3	53	8	20	2	9	1.4	4	2.6				
4		21	48	5	4.5	0.5	3	0.5				17.5
5		3	38	17	23	4	6	1				8
6			10	37.1	42.8	7.1	3					
7			48.4	9	29.5	5.6	7	0.5				

for a battery that does not go into extensive thermal event.

Case 3 is essentially the same as Case 2, but without the F-compounds, and the aim of this case is to investigate whether the F-compounds affect the combustion properties.

Case 4 and 5 are taken from Essl et al. [2] and are gases from NMC/LMO (Nickel Manganese Cobalt/Lithium Manganese Oxide) pouch cells at low (30%) and high (100%) SOC exposed to external heating, where only the gases from the high SOC batteries are a result of TR. The purpose of including these cases is to compare the combustion properties of vent gases from identical batteries but with and without TR, where the low SOC case (4) has a significant amount of carbonate while the high SOC case (5) has significantly higher CO and H₂ content.

Finally, Cases 6 and 7 are adopted from Henriksen et al. [17] where they represent high LBV and low LBV cases, derived from studies by Lammer et al. [35] and Golubkov et al. [36] on cylindrical 18650 cells. Case 6 is an NCA battery, known for producing O₂ inside the battery and with a rather low onset temperature for exothermic reactions, exposed to heating as a trigger for TR. Case 7 has the more chemically stable LFP cathode that does not produce O₂ and was shown by Golubkov et al. to have a high onset temperature for TR, 195 °C.

3. Results and discussion

3.1. Auto ignition

Thermally driven ignition of a gas mixture in the absence of a spark or other triggering event is called auto ignition. The first step in an ignition event is the thermal decomposition of molecules. As this occurs, reactive radicals are produced, and these will, in turn, react with other molecules to form a runaway reaction sequence [37,38]. The temperature at which thermal decomposition occurs depends on stability, or bond strength, in the fuel molecule. For the Li-ion battery vent gases, it is relevant to understand whether or not they are likely to auto ignite at the conditions when they are ejected from the cell or battery enclosure. From experimental studies it is known that ejected gases can have

temperatures in the range from about 100 °C for the first vent to above 1000 °C for the main vent [8], while cell surface temperature of the Li-ion battery in TR can range from 400 °C to 900 °C [7,39]. The risk that auto ignition occurs is also related to the residence time of the gas in a heated region, which depends on the physical geometry and the rate at which the venting occurs.

Fig. 3 shows ignition delay time as a function of temperature at two different fuel-to-oxidizer ratios, a surplus of oxygen in Fig. 3a and an oxygen-depleted situation in Fig. 3b. Note that ignition does not require a high oxygen content but occurs at about the same delay time in the oxygen-depleted case.

At temperatures below about 550 °C, all gas mixtures ignite rather slow, from about 0.2 to 10 s and the mixtures with a high carbonate content (Case 1–3) ignite slightly faster than the others, while at high temperatures the H₂/CO rich mixtures ignite faster.

Comparing the ignition delay time for similar mixtures with (Case 2) and without (Case 3) fluorinated compounds, it is clear that the presence of F does not affect the ignition.

Cases 4 and 5, representing gases from identical NMC/LMO batteries at different SOC, show a longer ignition delay time for the low-SOC case where the fraction of carbonates is larger, compared to the ignition delay time for the high-SOC that has a higher fraction of reactive H₂ and CO. This is in line with expectations on the ignition characteristics of these compounds.

Fig. 4 presents the data at one temperature, 730 °C, where it is clearly seen that the carbonate-containing mixtures (Case 1–3) ignite as much as an order of magnitude slower than the most reactive mixtures, among which Case 6 where the reactants consist of almost fifty per cent hydrogen gas ignite the fastest. Here it can be noted that from the bulk of the literature it is evident that at high temperatures like 730 °C the vented gas mixtures are significantly processed within the battery and commonly do not contain carbonates, but have a high H₂ and CO content. Carbonate rich vent gases like cases 1–3 are mainly ejected at a slow rate at lower temperatures, which potentially gives them a long residence time in the vicinity of for example a heated cell surface which

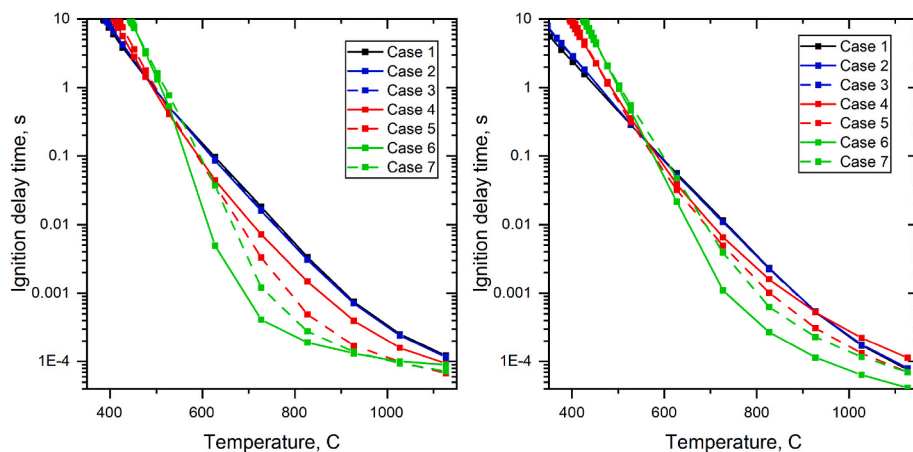


Fig. 3. Ignition delay time for gas mixtures well mixed with air, at conditions with high oxygen content, equivalence ratio $\phi = 0.5$, (left) and low oxygen content, $\phi = 2.0$ (right).

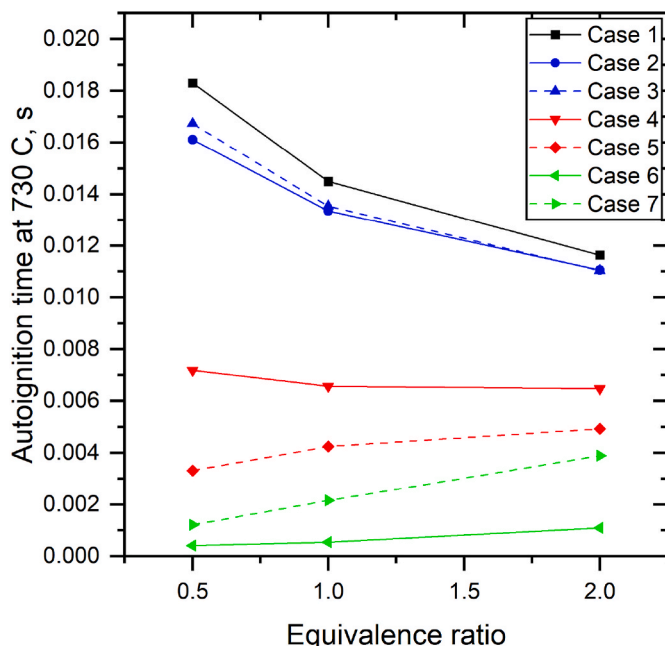


Fig. 4. Auto ignition time for gas mixtures at 730 °C, for fuel to oxidizer ratios where the oxygen rich is to the left ($\phi = 0.5$) and oxygen depleted to the right ($\phi = 2.0$).

may on the timescale of seconds trigger an ignition at temperatures in the range 400–600 °C.

3.2. Flame

3.2.1. Premixed laminar flame

LBV can be used as a metric for flame extinction since flames propagating slower than about 5 cm/s will be extinguished. The LBV will also indicate how rapidly a flame will propagate through a vented gas mixture and is a useful metric for comparing the ability of different mixtures to sustain a flame. The laminar flame simulations also provide temperature and HRR that can be compared between the investigated cases.

The seven cases were modelled at an initial gas temperature of 150 °C (423 K) since gas temperatures close to this was measured in several studies [1,8,36,39,40]. The results are presented in Fig. 5, where it is seen that Case 6, i.e. the “high” case presented by Henriksen et al. [17], indeed burns much faster than the other mixtures. It is also seen that the peak velocity for this gas mixture is shifted to gas compositions with lower oxygen content. The reason for the high reactivity of these oxygen-depleted flames is that the combustion chemistry is driven by H atoms instead of OH radicals that dominate at higher oxygen levels.

In Fig. 5, it is seen that the laminar burning velocity for Case 5 (SOC 100%) is about 50% higher than that for Case 4 (SOC 30%), which clearly shows that the combustion properties of gases from a given battery are highly dependent on the SOC during the thermal event leading up to the gas production.

Fig. 6 presents adiabatic flame temperatures, T_{ad} , and HRR from chemical reactions, for the seven cases for which LBVs were presented in Fig. 5. T_{ad} is the theoretically highest temperature that can be achieved for combustion of a certain gas mixture, based on neglecting heat losses. As can be seen in Fig. 6, the trends in HRR are not directly proportional to the trends in temperature. Heat released from the exothermic combustion reactions is used to heat the gas but also to activate species in chemical reactions. The energy in the system is thus transformed both to heat, resulting in temperature increase and to chemical energy, accelerating the production of reactive radicals, supporting rapid flame propagation. Using Case 6 as an example, the HRR is high compared to

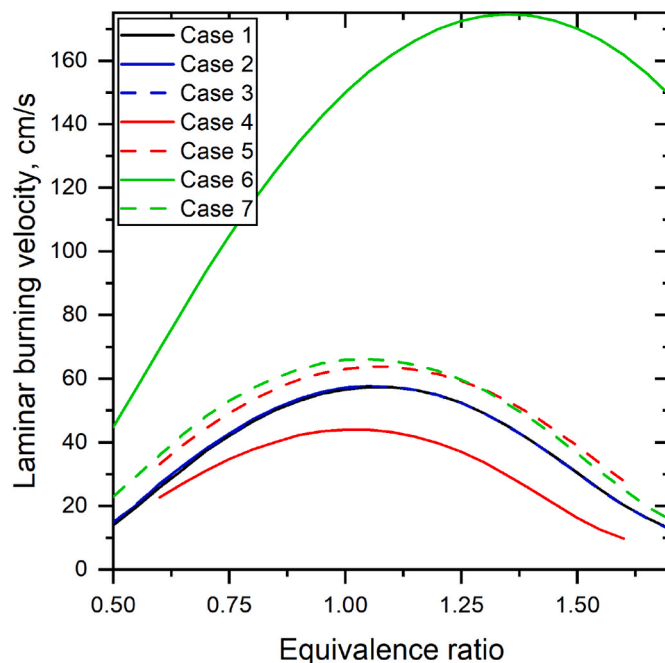


Fig. 5. Laminar burning velocities as a function of equivalence ratio for premixed flames, at initial gas mixture temperature 150 °C.

the other cases, while T_{ad} is, in comparison, not that high. This means that, in this case, a significant amount of energy produced in the system is boosting the chemical reactivity.

The lowest flame temperatures are for cases 4, 5 and 7, which have a common property of high CO_2 content. The energy required to heat the inert CO_2 leads to a comparably low gas temperature. From a comparison of Case 2 and Case 3, it is evident, just like for ignition delay time, that F-compounds do not have a distinguishable effect on the combustion.

3.2.2. Laminar diffusion flame

When the vent gas is ejected, it contains little or no O_2 , and it is likely that an emerging flame will not be of a premixed type but rather a diffusion flame where a flammable gas mixture meets an air stream. As proposed by Harris et al. [12], simulation of a laminar diffusion flame is a good description of the situation that may occur when a rapidly ejected vent gas flow meets the surrounding air. These simulations reveal the local environment at a given condition with respect to flame temperature, HRR and reactive radical composition. This information is valuable for the evaluation of the effects of potential flame quenching using chemical flame extinguishing methods where a quencher should catalytically destroy reactive OH and H radicals. Here simulations have been performed under identical flow and gas temperature conditions, for case 1, 3 and 6 in Table 1. Cases 1 and 3 have in this study been shown to have almost identical properties with respect to auto ignition and for premixed flames, even though case 1 is a pure carbonate gas mixture and Case 3 contain a range of typical vent gas constituents. Case 6 is the most extreme case which burn significantly faster than the other gas mixtures in premixed conditions.

Fig. 7 present the temperatures and HRR for the three cases and Fig. 8 show the distribution of the three main reacting radicals OH, H and O. Case 6 has a maximum temperature about 200 °C hotter than the other cases, and the position of the high temperature zone is shifted upstream. The heat release rates show peaks that correspond to the peaks of the reactive radicals. The concentration of reactive radicals is significantly higher in Case 6 with high H_2 and CO content. The high H radical concentration occur closest to the fuel stream, since this is the main radical in an oxygen depleted environment.

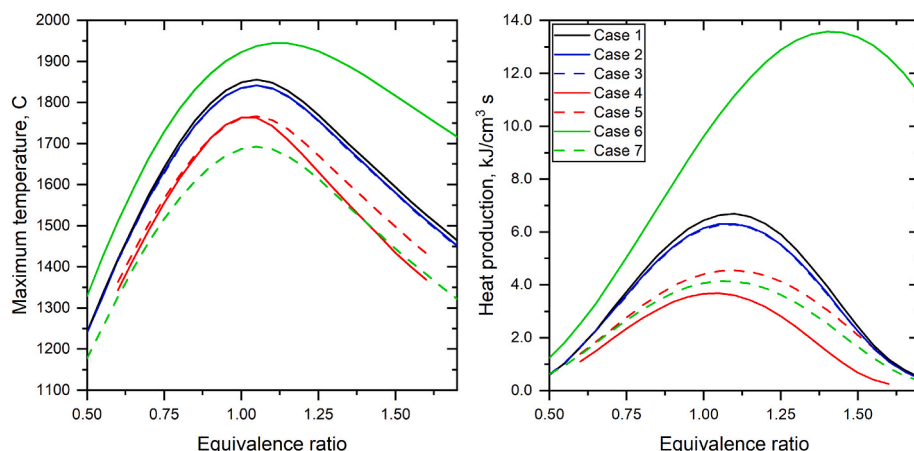


Fig. 6. Maximum flame temperature (left) and heat production (right) as a function of equivalence ratio for premixed flames, Case 1–7.

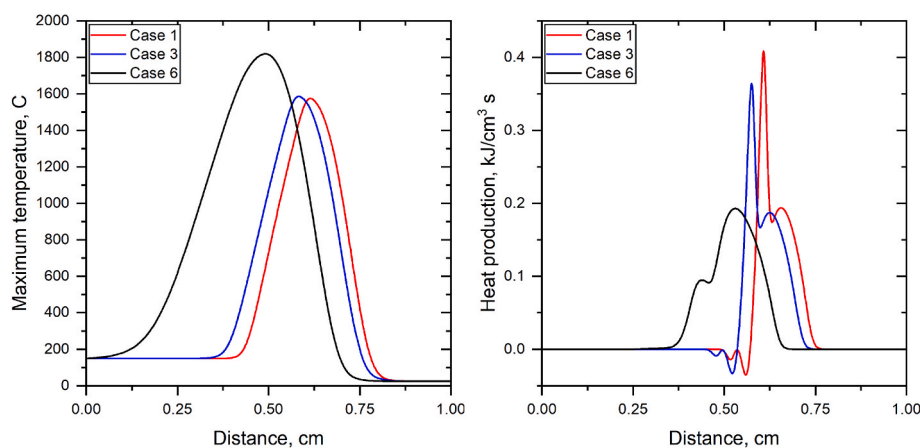


Fig. 7. Temperature (left) and HRR (right) for diffusion flames for the three selected cases.

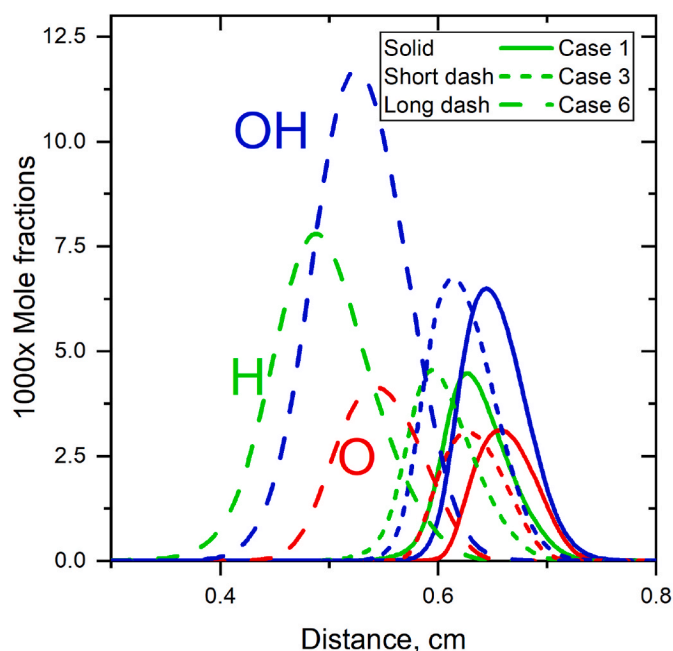


Fig. 8. Distribution of H, OH and O radicals in cases 1, 3 and 6.

4. Conclusions

This work is the first systematic modeling study of combustion characteristics of typical gas mixtures vented from Li-ion batteries, where carbonates, hydrogen, hydrocarbons and fluorinated compounds are included. The chemical kinetics mechanism presented in this work is unique in the sense that it includes the broad range of battery vent gas constituents. The mechanism can be used to model combustion properties of all relevant vent gas mixtures, and its use is therefore not limited to the cases selected for the present study.

Based on an in-depth review of the literature, seven gas mixtures were selected to represent a broad range of gas compositions vented from Li-ion batteries before onset of combustion. To evaluate the combustion behavior calculations of ignition and flame propagation were performed for the selected vent gas mixtures. Based on the modelling results the following is observed:

- Autoignition time in the temperature range 500–1000 °C is one to two orders of magnitude faster for the most reactive gas mixtures vented from high SOC cells, compared to the gas mixtures that have a larger fraction of unprocessed battery content, i.e. carbonates. Ignition is highly temperature dependent and at temperatures below about 550 °C ignition of the gas mixtures will require a long time or an external ignition source.
- Gas mixtures with high carbonate content, typical for a first vent during a thermal event in a battery cell, ignite and burn slowly but release a significant amount of heat.

- Ignition is not very sensitive to oxygen content and the investigated gas mixtures have close to the same ignition propensity in an oxygen depleted environment as at high oxygen availability.
- Fluorinated compounds in the amounts common in battery vent gases does not have any effects on the macroscopic combustion characteristics.
- There is a large variation in LBV, with the fastest burning mixture being the one with high H₂ content and the slowest with high carbonate content.
- The seven gas mixtures can be considered as either high in carbonates or high in H₂, among which the high-H₂ cases both ignite faster and have a higher LBV compared to the high-carbonate cases. However, the same trends are not seen for flame temperature, where the presence of large amounts of inert CO₂ that take up heat keep the temperature down.

The present analysis increases the fundamental understanding of combustion characteristics for Li-ion battery vent gases, which open up for improvements in battery design and mitigation strategies. As an example, by knowing the conditions for flame propagation, battery packs can potentially be designed to minimize the risk for the flame supporting conditions. Also, understanding of the ignition mechanism and early flame development, including information about governing radical species, can support development of early mitigation strategies.

Research on thermal runaway in Li-ion batteries have up until recent years mainly been performed using experimental methods, but as mentioned in the introduction section of this work advanced modeling is under development. Multi scale models may including a sequence of events including the thermal runaway, heat transfer in the battery pack, gas venting and combustion of the released gases. To accurately model the full process chemical kinetics models for combustion of the released gases will be needed. The kinetic model presented here is the first model including all relevant gas component types that will enable prediction of both hydrocarbon combustion and formation of toxic fluorinated compounds. To allow efficient use in multi scale and CFD models the kinetic scheme will need to be reduced in size, which is planned as a continuation of the present work.

CRediT authorship contribution statement

Elna J.K. Nilsson: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Validation, Visualization, Writing – original draft, Writing – review & editing. **Christian Brackmann:** Formal analysis, Validation, Writing – review & editing. **Annika Ahlberg Tidblad:** Conceptualization, Formal analysis, Funding acquisition, Writing – original draft, Writing – original draft, Writing – review & editing.

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

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jpowsour.2023.233638>.

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