Effect of cathode material and state of charge on the emissions of several LIB batteries

Nour Elsagan, Yoon Ko  
Fire safety unit, construction research center, National Research Council of Canada

Abstract:
Electric vehicles (EV) are considered as a greener alternative solution to the conventional internal combustion engine vehicles. They incorporate Lithium ion batteries (LIB) which are currently the main power source for EV and other devices. However, the use of LIB introduces new challenges to emergency responders and fire protection engineers due to their fire risk.

In this work, the emissions resulting from the burning of LIBs with different cathode materials (LiCoO$_2$ (LCO), NCA/NCM and LiFePO$_4$ (LFP)) and states of charge (SOC) (0%, 30%, 50%, 100%) were measured using the Fourier Transform InfraRed (FTIR) techniques. The batteries were burned in a cone calorimeter facility under 50 kW/m$^2$ heat flux. The following emissions were detected with significant concentrations; CO, CO$_2$, HF, POF$_3$, EMC, DMC, C$_3$H$_6$, CH$_4$, C$_2$H$_6$, C$_2$H$_4$, HCHO, NO.

Such data could be used in the early detection of LIB fires, which would assist first responders in scoping the hazards and stratifying mitigation measures.

Keywords: Lithium ion batteries, SOC, type of LIB cathode, fire emissions

Introduction
The number of Electric vehicles (EVs) is increasing. 2.5% of the newly registered cars in Canada were EV in 2020 [1]. LIBs offer high energy density, long life and reliability that suits the use in EVs, thanks to their advanced chemistry comprising a carbon anode, a metal oxide cathode and an organic liquid electrolyte. However, this composition raises the concern of potential fire hazard of LIBs since they already contain the fuel (organic electrolyte) and oxygen (metal oxide cathode) that can react together and release heat leading to thermal runaway. Risks pertaining to thermal runaway extends from thermal failure, mechanical failure, internal/external short circuiting, or electrochemical degradation.

In this work, the effect of the battery state of charge (SOC) and cathode materials on the burning behaviour of LIB is investigated. Measurements of heat release rate and emissions were conducted and presented herein.

Experimental setup
The burning of the LIB was conducted in Fire Testing Technology Cone Calorimeter attached to FTIR to analyze the emissions. Error! Reference source not found. shows a photo of the setup. The LIB was placed on a 10 x 10 cm$^2$ sample holder. The battery was then rolled into fibrefrax and placed in a hollow steel tube. This was used to keep the battery in an upright position during testing, as well as to mitigate risks if the battery were to blow out or vent from the side. The positive side of the battery was placed up towards the cone, as this is where the safety vents appeared and the most likely location for the jet flame to be produced.
Test Matrix
Seven batteries were tested to investigate the effect of different cathode materials and state of charge (SOC) on the fire behaviour and emissions of the LIB. The specifications of the batteries are listed in Table 1. In all tests, the heat flux was fixed at 50 kW/m², and emissions were measured. The HRR data were also calculated based on the cone calorimetry and normalized by dividing by the surface area of the battery for comparison. The observation of time to ignition and explosion were recorded.

Table 1. Specifications of the LIB tested

<table>
<thead>
<tr>
<th>LIB model</th>
<th>LCO</th>
<th>NCA, NMC</th>
<th>LFP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>Lithium cobalt oxide LiCoO₂</td>
<td>LiNiMnCoO₂, LiNiCoAlO₂</td>
<td>Lithium iron phosphate LiFePO₄</td>
</tr>
<tr>
<td>Anode</td>
<td>Carbon 11</td>
<td>carbon</td>
<td>carbon</td>
</tr>
<tr>
<td>Nominal capacity (mAh)</td>
<td>2600</td>
<td>3350</td>
<td>1550</td>
</tr>
<tr>
<td>Nominal voltage (V)</td>
<td>3.7</td>
<td>3.6</td>
<td>3.2</td>
</tr>
<tr>
<td>Mass (g)</td>
<td>45.4</td>
<td>45.5</td>
<td>42</td>
</tr>
</tbody>
</table>

Results and discussion
All batteries displayed two separate fire events which were seen as sudden spikes in the cone calorimeter and emissions data. The first fire event corresponded to the activation of the integrated safety vent. The second fire event occurred after the venting and varied greatly depending on the type of battery and the state of charge (SOC).

Effect of different cathodes
Figure 2 shows the HRRPUA of LIB batteries at 50% SOC with different cathode materials; NCA, NMC, LCO and LFP. The 2nd peak was higher than the 1st in case of LCO and NCA, NMC, while LFP showed the higher peak (8 MW/m²) first followed by another peak (1.5 MW/m²) at 1500s. This higher 1st peak might be attributed to the fact that, gases were released at higher temperatures in case of LFP which resulted in rigorous combustion and high HRRPUA.
Figure 2. HRRPUA of LIB batteries at 50% SOC with different cathode materials for 1200 s (left panel) and 1500 s (right panel- till the 2nd peak of LFP)

Table 2. Time to ignition and explosion for all tested batteries

<table>
<thead>
<tr>
<th>Battery cathode</th>
<th>SOC</th>
<th>Time to ignition (s)</th>
<th>Time to explosion (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP</td>
<td>50%</td>
<td>350</td>
<td>355</td>
</tr>
<tr>
<td>LCO</td>
<td>50%</td>
<td>225</td>
<td>455</td>
</tr>
<tr>
<td>NCA/NMC</td>
<td>50%</td>
<td>305</td>
<td>460</td>
</tr>
<tr>
<td>NCA/NMC</td>
<td>30%</td>
<td>275</td>
<td>530</td>
</tr>
<tr>
<td>NCA/NMC</td>
<td>0%</td>
<td>110</td>
<td>-</td>
</tr>
<tr>
<td>NCA/NMC</td>
<td>100%</td>
<td>115</td>
<td>265</td>
</tr>
</tbody>
</table>

The time to ignition presented in Table 2 shows that the reactivity of the batteries based on their cathode material can be ranked as LCO>NCA,NMC>LFP. This also agrees with the findings of Doughty and Roth [2] from testing the batteries in Accelerating Rate Calorimetry (ARC). The higher stability of LFP is attributed to its stable olivine structure [3] and the strong P-O bond in the phosphate ion (PO$_4^{3-}$).

Table 2 also shows the explosion time exhibited by different batteries during the tests. Despite the long time to ignition, LFP showed a very short time to explosion (5s from ignition). This highlights the importance of early fire detection and suppression of LIB fires.

The total and peak HRRPUA for the 3 batteries are presented in Table 3. Note that the capacity of the 3 batteries (presented in Table 1) are different, therefore, in order to compare their THR and peak HRRPUA, they should be normalized by the battery capacity. According to the normalized values, the batteries can be ranked as NCA/NMC<LCO<LFP.

Table 3. Total heat release (THR) and peak HRRPUA for LIB batteries with different cathode materials

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>THR (MJ/m$^2$)</th>
<th>Peak HRRPUA (MW/m$^2$)</th>
<th>THR/battery capacity (MJ/m$^2$.AH)</th>
<th>Peak HRRPUA/battery capacity (MW/m$^2$.AH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCO</td>
<td>396</td>
<td>6.4</td>
<td>305</td>
<td>5</td>
</tr>
<tr>
<td>LFP</td>
<td>573</td>
<td>8</td>
<td>739</td>
<td>10</td>
</tr>
<tr>
<td>NCA/NMC</td>
<td>287</td>
<td>7.7</td>
<td>171</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Figure 3 shows the carbon dioxide emissions from the three batteries. Generally, CO₂ and VOCs are produced from the reactions of SEI (solid-electrolyte interface) and the electrolyte. In the range of 90-120 °C, decomposition of the SEI layer occurs through the following exothermic reaction [4–7];

\[(\text{CH}_2\text{OCO}_2\text{Li})_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{C}_2\text{H}_4 + \text{CO}_2 + 0.5 \text{O}_2]\]  

This reaction raises the temperature of the LIB and leaves the anode unprotected.

The electrolyte can exhibit 3 different types of reactions with the LIB; (1) Combustion due to the released O₂ and the high temperature within the cell, (2) Reaction with Li ions and (3) Exothermic decomposition. All these reactions result in the accumulation of gaseous products in the LIB, which consequently increase the pressure leading to the opening of the safety vent. When these gases are released outside the battery, they ignite and cause fires. Both complete and incomplete combustion occur simultaneously. However, at high temperature, the extent of complete combustion increases, and the emissions are detected mainly as CO₂, while at relatively lower temperatures, more incomplete combustion happens and CO and VOCs are released with CO₂.

Figure 4 shows the profiles of HF and POF₃. Fluorine compounds are formed from primarily the electrolyte and the binder through the reaction of the Li-ions with the electrolyte and the decomposition of the Li salts. The most commonly used Li-salt is lithium hexafluorophosphate (LiPF₆) which has a limited thermal stability. When the battery is heated, the following reactions occur:

\[\text{LiPF}_6 \rightarrow \text{LiF} + \text{PF}_5\]
\[ \text{PF}_3 + \text{H}_2\text{O} \rightarrow \text{POF}_2 + 2 \text{HF} \]  
(3)

\[ \text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiF} + \text{POF}_2 + 2 \text{HF} \]  
(4)

\[ \text{POF}_3 + \text{H}_2\text{O} \rightarrow \text{POF}_2(\text{OH}) + \text{HF} \]  
(5)

Effect of different SOC

The heat release rates per unit area (HRRPUA) from NCA, NMC batteries at 0%, 30%, 50% and 100% SOC are shown in Figure 5. Moreover, the highest 1\textsuperscript{st} peak in HRRPUA was demonstrated by 0% SOC LIB which might be attributed to overdischarge, which is known to result in internal short circuit leading to thermal runaway [8]. However, the battery tested in this cone calorimeter test didn’t have enough energy to sustain explosion.

![Figure 5. HRRPUA of NCA LIB batteries with different SOC](image)

The shortest and longest times between ignition and explosion were demonstrated by the 100% (150 s) and 30% (255 s) SOC batteries, respectively. The 30% SOC combined between relatively low reactivity and long-time till explosion and can be considered as less hazardous safe SOC. The international civil aviation organization (ICAO) and International air transport association (IATA) recommend shipping LIB at 30% SOC or less.

![Figure 6. CO\textsubscript{2} and CO emissions of NCA, NMC LIB with different SOC](image)

\[ \text{CO}_2 \text{ profiles match the HRRPUA in terms of peaks timing. Except for 50% SOC, CO concentration decreases} \]
with decreasing SOC, which also agrees with the observation in the work done by Somandepalli et al. [9].

![Figure 7. HF and POF₃ emissions of NCA LIB with different SOC](image)

The HF and POF₃ profiles in Figure 7 show that LIB with 0% and 100% SOC showed lower HF and higher POF₃ compared to 30% and 50%. This might be attributed to the different water content of the batteries.

**Conclusions**

In this work, the HRRPUA and emissions resulting from burning of LIB in a cone calorimeter facility were measured to investigate the effect of different cathode materials and SOC. In all tests, 2 peaks of HRRPUA were seen, and the highest heat release was always associated with the highest CO₂. It was found that, although LIB with LFP cathode showed the least reactivity, it produced huge heat release once ignited. The NCA, NMC battery at 30% SOC showed a safe combination of low reactivity and time to explosion and thus can be relatively safe in cargo. Moreover, some of the detected emissions were very specific to LIB fires; HF and POF₃ and can be used in the early detection of their fire. The concentration of both gases varied in the different tests which might be attributed to the different water content in the tested batteries.

**References**


