Effect of Cathode Material and State of Charge on The Emissions of Several LIB

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• The earth is getting warmer!!

• CO₂ is main culprit

• In 2015, the Paris Agreement set out a global framework to limit global warming to well below 2°C and pursuing efforts to limit it to 1.5°C.

• In Canada, transportation is responsible for 27% of greenhouse gas emissions.¹

¹ https://www.nrcan.gc.ca/energy/efficiency/communities-infrastructure/transportation/idling/4419
• Electric vehicles are considered as an alternative greener solution
• In 2020, 2.5% of the newly registered cars in Canada were battery EV.
• LIBs are popular energy storage systems
• New technology ……. New hazard potential!

- Short circuit
- Overcharging
- Over discharging
- Crash, bend, penetration
- Heating or fire
1. Measuring the heat release and emissions resulting from the burning of LIBs with different cathode materials and states of charge (SOC).
2. This data is important for first responders during a fire event.
3. This data can be used in the early detection of LIB fires.
4. Investigating the impact of suppression on emission from LIB fires.
The burning of the LIB was conducted in Cone Calorimeter attached to FTIR.

- The heat flux was set to 50 kW/m² in all tests.
- The LIB was placed on a 10x10 cm² sample holder, rolled into fibrefrax and placed in a hollow steel tube.
- The positive side of the battery was placed up towards the cone.
- Each test was repeated once
- HRR and emissions data were collected
Six 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.

<table>
<thead>
<tr>
<th>Battery</th>
<th>Cathode</th>
<th>Nominal capacity</th>
<th>Nominal voltage (v)</th>
<th>SOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP</td>
<td>Lithium iron phosphate, LiFePO₄</td>
<td>1550 mAh</td>
<td>3.2</td>
<td>50%</td>
</tr>
<tr>
<td>LCO</td>
<td>Lithium cobalt oxide, LiCoO₂</td>
<td>2600 mAh</td>
<td>3.7</td>
<td>50%</td>
</tr>
<tr>
<td>NCA,NMC</td>
<td>LiNiMnCoO₂, LiNiCoAlO₂</td>
<td>3350 mAh</td>
<td>3.6</td>
<td>50%</td>
</tr>
<tr>
<td>NCA,NMC</td>
<td>LiNiMnCoO₂, LiNiCoAlO₂</td>
<td>3350 mAh</td>
<td>3.6</td>
<td>30%</td>
</tr>
<tr>
<td>NCA,NMC</td>
<td>LiNiMnCoO₂, LiNiCoAlO₂</td>
<td>3350 mAh</td>
<td>3.6</td>
<td>0%</td>
</tr>
<tr>
<td>NCA,NMC</td>
<td>LiNiMnCoO₂, LiNiCoAlO₂</td>
<td>3350 mAh</td>
<td>3.6</td>
<td>100%</td>
</tr>
</tbody>
</table>
All batteries displayed two separate fire events in the cone calorimeter and emissions data. The first corresponded to the activation of the integrated safety vent. The second varied greatly depending on the type of battery and the state of charge (SOC) and took place when the battery had reached thermal runaway.
• The first peak for LCO and NCA,NMC batteries showed lower HRRPUA peak (2 MW/m$^2$) followed by a higher one (6.4 and 7.7 MW/m$^2$)
• LFP showed the higher peak (8 MW/m$^2$) first followed by another peak (1.5 MW/m$^2$) at 1500s.
• Based on ignition time, the reactivity of the batteries LCO>NCA,NMC>LFP$^1$

LFP has low capacity while LCO batteries have high specific energy. It is the most commonly used LIBs.

When normalizing THR by the capacity of each battery, NCA, NMC < LCO < LFP.

The earlier release of gases from the battery (i.e., at lower temperature) associated with the low reactivity results in incomplete combustion and lower heat release. This was also confirmed by the huge amount of CO.
Fluorine compounds are formed from the electrolyte and the binder through the reaction of the Li-ions with the electrolyte and the decomposition of the Li salts. LiPF$_6$ is the most commonly used Li-salt which has a limited thermal stability.

During fire:
- LiPF$_6$ → LiF + PF$_5$
- PF$_5$ + H$_2$O → POF$_3$ + 2 HF
- LiPF$_6$ + H$_2$O → LiF + POF$_3$ + 2 HF
- POF$_3$ + H$_2$O → POF$_2$(OH) + HF
• SOC 0% and 100% showed the earliest ignition, followed by 30% then 50%
• Explosion time 100%<50%<30%<0%(no explosion)
• The highest 1st peak was shown by 0%
• Overdischarge results in internal short circuit leading to thermal runaway\(^1\), however the battery doesn’t have enough energy to sustain explosion.
• The international civil aviation organization (ICAO) and International air transport association (IATA) recommend shipping LIB at 30% SOC or less

\(^1\)Guo et al., Mechanism of the entire overdischarge process and overdischarge-induced internal short circuit in lithium-ion batteries, Scientific reports (2016).
- CO\textsubscript{2} profiles match HRR profiles
- Except for 50% SOC, CO concentration decreases with decreasing SOC.}\textsuperscript{1}

\textsuperscript{1}Somandepalli et al, Quantification of Combustion Hazards of Thermal Runaway Failures in Lithium-Ion Batteries, SAE Int. J. Alt. Power. (2014)
• 0% and 100% showed lower HF and higher POF$_3$ compared to 30% and 50%.
• This might be attributed to the different water content of the batteries.
What are the best gas sensors for detecting LIB fires?! 

<table>
<thead>
<tr>
<th>Cathode</th>
<th>SOC</th>
<th>$T_{ig}$ (s)</th>
<th>$T_{ex}$ (s)</th>
<th>$CO_2$ (5000 ppm) (s)</th>
<th>CO (TWA 400 ppm) (s)</th>
<th>HF (TWA 3 ppm) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP</td>
<td>50%</td>
<td>350</td>
<td>355</td>
<td>396</td>
<td>412</td>
<td>394</td>
</tr>
<tr>
<td>LCO</td>
<td>50%</td>
<td>225</td>
<td>455</td>
<td>474</td>
<td>376</td>
<td>253</td>
</tr>
<tr>
<td>NCA</td>
<td>50%</td>
<td>305</td>
<td>460</td>
<td>506</td>
<td>500</td>
<td>361</td>
</tr>
<tr>
<td>NCA</td>
<td>30%</td>
<td>275</td>
<td>530</td>
<td>557</td>
<td>502</td>
<td>324</td>
</tr>
<tr>
<td>NCA</td>
<td>0%</td>
<td>110</td>
<td>-</td>
<td>-</td>
<td>353</td>
<td>131</td>
</tr>
<tr>
<td>NCA</td>
<td>100%</td>
<td>115</td>
<td>265</td>
<td>273</td>
<td>502</td>
<td>151</td>
</tr>
</tbody>
</table>
• Fires of LIBs are not typical due to the contribution of the reactions of its components.
• Water is considered as a good suppressant for LIB fires
• Water was used to suppress the fire of a LIB with LFP cathode and 50% SOC.
• A small ¼” water line was directly placed above the battery.
• Once a flame was seen, the water was slowly dripped. Once the fire was out, the water was turned off until a second event happened and the water was turned on again at a slow drip rate.
• Water was applied for 8 mins then 2 mins.
• The total heat release and peak HRRPUA when using the water suppression were 275 MJ/m² and 6.9 MW/m², respectively.
• 52% reduction in THR was achieved.
• Less concentrations of CO, CO₂ and HF are emitted during the suppression of LFP battery fire while higher concentration of POF₃
• Higher concentrations of methane, DEC, DMC, EMC, C₂H₄ and NO were detected when suppressing the LFP fire using water. Moreover, measurable quantities of acetone and acetaldehyde were only detected during suppression.
This might be attributed to the cooling and suppression effect of water which prevented further oxidation of the emissions.

Carbonates (EMC, DMC and DEC) and hydrocarbons are mainly produced from the decomposition of the electrolyte through reduction and nucleophilic attack, which means that they don’t need oxygen from air to be produced.¹

It should be noted that, the water was applied in the test directly at the reaction zone (i.e. the battery) which amplified its impact.

¹Gachot et al., Thermal behaviour of the lithiated-graphite/electrolyte interface through GC/MS analysis, Electrochimica Acta. (2012)
Conclusions
- SOC and cathode material affect the amounts of heat released and emissions
- The highest heat release was always associated with the highest CO₂.
- Some of the detected emissions are very specific to LIB fires; HF and POF₃.
- Although LFP LIB is relatively stable, it produced huge heat release once ignited.
- 30% SOC showed a safe combination of low reactivity and HRR.
- HF can be a good candidate for early detection of LIB fires.

Future work
- Investigate the effect of water suppression on emissions from LIB fires.
- Conduct the tests using LIB packs in ISO room.
THANK YOU

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