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Gas Emissions from Lithium-Ion Battery Cells Undergoing Abuse from External Fire

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ABSTRACT

Heat release rate, total heat released and toxic gas emissions were measured during exposure of commercial lithium-ion (Li-ion) battery cells to an external propane burner fire. Hydrogen fluoride (HF) was found in all tests and the released HF emissions measured via online FTIR range between 12-81 mg/Wh. Gas-washing bottles were used as a secondary measurement technique in one of the tests. The gas washing bottle and the FTIR measurements were in the same order of magnitude proving the usefulness of the FTIR technique even if there is an accumulation of HF in the filters used in the beginning of the test. The HF release for a large battery pack exposed to fire could thus in a worst case scenario result in a very large volume of toxic gases.

KEYWORDS: lithium-ion battery, gas emission, toxic gases, safety, fire, HRR

INTRODUCTION

Currently Li-ion has taken the position as the dominant choice for batteries used in portable battery powered consumer products. Li-ion batteries have also been introduced in electrified vehicles, in the electrical power grid and in ships. The Li-ion battery has attractive properties in form of power and energy densities, long life time, fast chargeability and no memory-effect, but has some potential drawbacks when it comes to safety.

The high energy densities of Li-ion batteries give potential for a rapid de-energizing. Additionally, the electrolyte used in Li-ion batteries is flammable. Compared to many other battery technologies, the Li-ion battery requires substantial efforts in order to manage its intrinsic safety shortcomings. The voltage and temperature ranges must be monitored and controlled. The Li-ion cell must be protected against physical damage (e.g. penetration and deformation) and from short circuit. In case of a severe failure, the Li-ion cell can undergo a thermal runaway which is a rapid exothermic reaction resulting in a fast temperature increase, gassing, fire and potentially an explosion. Furthermore, the gases released from the cell are toxic; of special interest is the production of hydrogen fluoride (HF) [1-3]. This work presents fire tests that have been performed on commercial Li-ion cells where HF is measured.

EXPERIMENTAL SET-UP

The Single Burning Item apparatus (SBI) was used to measure typical fire characteristics, e.g. Heat Release Rate (HRR), CO and CO_2 production in addition was HF measured. Multiple commercial Li-ion cells were exposed to external fire by a 16 kW propane burner. Table 1 shows the details of the cylindrical and pouch cells, including state-of-charge (SOC), used in the four tests, A-D, performed. The cells were not electrically connected to each other and not under electrical load during the tests. The cylindrical cells were placed in boxes to protect from flying projectiles and the LTO cells were both fastened to each other and fastened to the wire grating with steel wire, as seen in Figure 1. For test D the center temperature between the two cells and both cell voltages (CV) were measured every second. Gases were measured online by FTIR, particular interest was given to the emission of hydrogen fluoride (HF). The FTIR gave one spectrum every 12 seconds based on 10 scans. Detailed descriptions on the experimental set-up can be found in Larsson et. al. [1].

Table 1 Test overview.

Test	Cell type	No. of cells	Nom voltage (V)	Total nom capacity (Ah)	Electrode chemistry Anode – cathode	Cell packaging	SOC (%)
A	K2 LFP26650EV	9	3.2	28.8	Carbon – LFP	Cylindrical	100
B	K2 LFP26650EV	9	3.2	28.8	Carbon – LFP	Cylindrical	50
C	Lifetech X-1P	5	3.3	40	Carbon – LFP	Cylindrical	100
D	Leclanché LTO	2	2.3	60	LTO – NCO	Pouch	100

Figure 1 Experimental setup before burner start for test B (left), test C (mid) and test D (right).

In addition to the FTIR measurements, gas-washing bottles were used in test D in order have a second measurement technique to sample the total amount of released fluorides. The assumption here was that the absolute majority of water soluble fluorides would be HF. Two gas-washing bottles, each containing 40 mL of a carbonate/bicarbonate buffer solution, were connected in series. The flow through the bottles was 1.0 nL/min and a calibrated gas volume meter was used to measure the total sampled volume. High Performance Ion Chromatography (HPIC) was used for the analysis of the absorption solutions. The sample gas was continuously extracted from the centre of the exhaust duct during the full test time. After the test the sampling tube was rinsed to collect any HF deposited inside the tube in order to minimize any losses of HF for the analysis.

RESULTS AND DISCUSSION

Figure 2 shows HRR and HF mass flow for the K2 cells (test A and B). The fully charged cell shows higher HRR peaks, similar to the results in Larsson et. al. [1], also the case with 50% SOC shows some peaks in contradiction to how the 50% SOC pouch cells behaved in Larsson et. al. [1]. This is probably due to that cylindrical cells can withstand more pressure before the safety valve releases the gas. The HF gas emission peaks are higher for 100% than for 50% SOC. However, the K2 50% test was the first run in the test series and it has later proved that the measurement systems, e.g. the FTIR sampling system (tubes and secondary filter etc) is catching HF before it gets saturated on HF. It is thus difficult to make a direct comparison between the 50 % and 100% SOC tests in this case, as a part of the released HF was saturated in the FTIR sampling, and lower HF values are therefore measured for K2 50%. It could also be noted that the test with K2 50% SOC was run about one year later than the one with 100% SOC. About nine “sound bangs” were heard for the test B with 50% SOC, corresponding to cell opening (e.g. safety vent) in each K2 cell while eight “sound bangs” were heard for the test A with 100% SOC, suggesting that one K2 cell did open in some other way, e.g. a softer/earlier safety vent opening, or that two cells opened at the same time.

Figure 3 shows HRR and HF gas emissions for test C. In the test, one of the five cylindrical Lifetech cells exploded and the cell interior was expelled [3]. The reason for this was that the safety vent did not open, and this happening elucidate that the safety mechanics (in this case, the safety vent) can malfunction. Figure 4 shows the results for test D. The center temperature between the two cells reaches about 600 °C. The production of HF is about 2 minutes delayed after the HRR, similar to test A-C. The cell voltage breakdown in the bottom cell occurs at the same time as HF gas emissions and cell temperature increases rapidly, suggesting the occurrence of thermal runaway starting in the bottom cell. The cell voltage of the top cell breaks down about 1 minute later. The battery cells burnt relatively fast (i.e. giving high HRR).

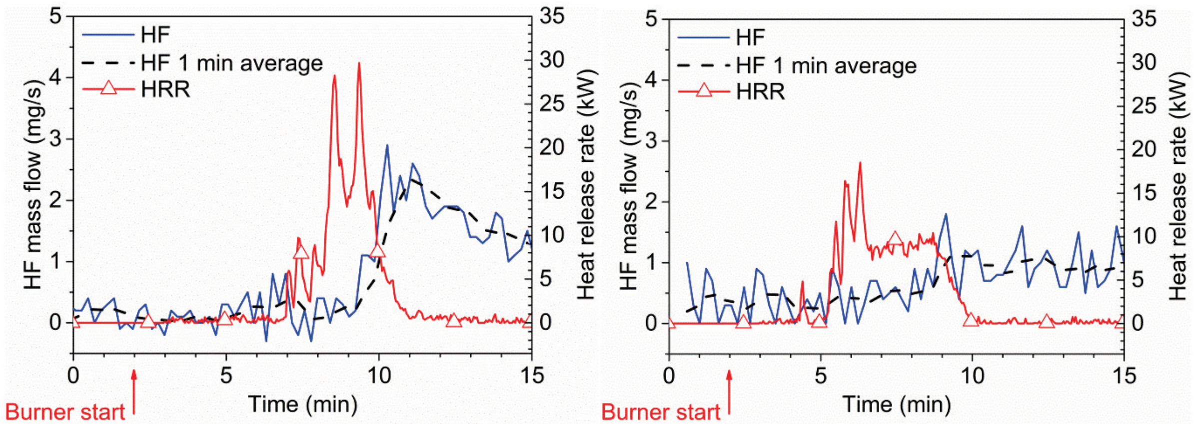

Figure 2 *Results for K2, test A 100% SOC (left) and test B 50% SOC (right). The "*1 min average" is calculated by 5 points moving average of each 12 seconds spectrum.

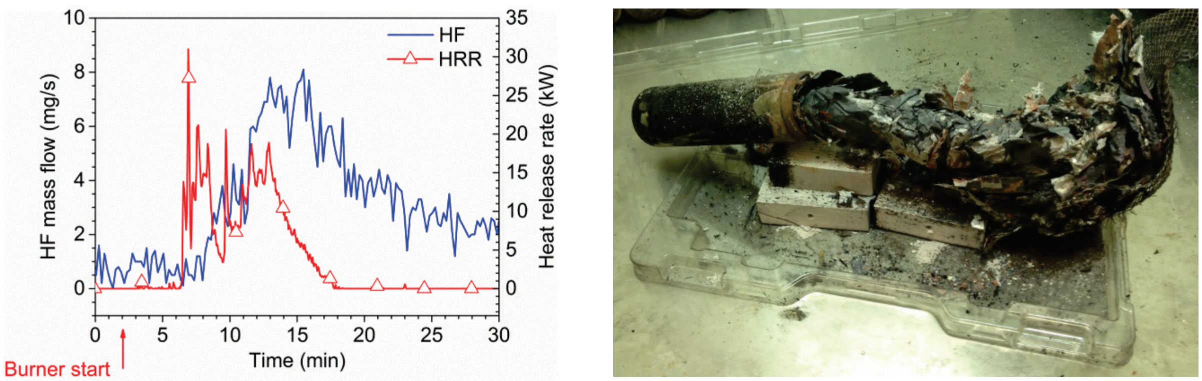

Figure 3 *Results for test C, Lifetech 100% SOC. The photo is taken during tear-down analysis and showing the cell interior expelled out. The cell was caught by the steel net in the protective test box.*

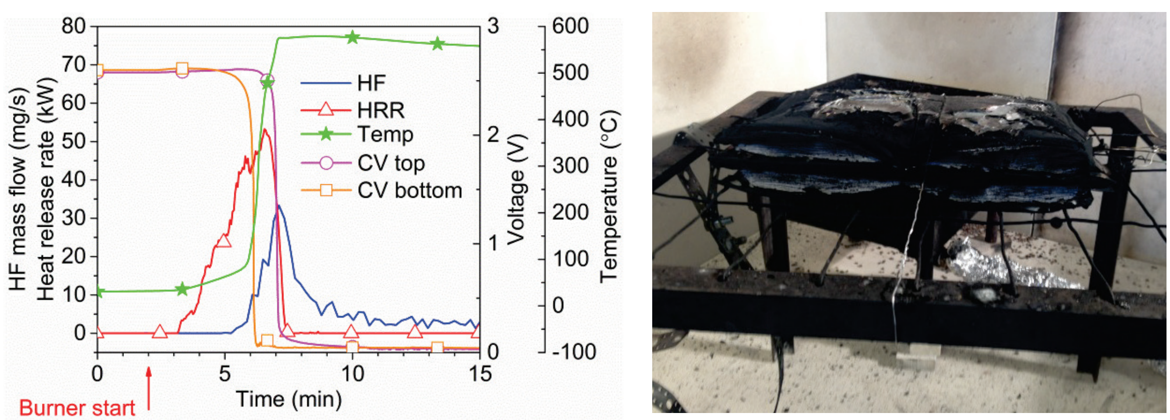

Figure 4 *Results for test D. The photo is taken from the long side, after the test is complete.*

The detection limit for HF for the equipment used in this investigation is 2 ppm [1]. The peak ppm levels for the tests in Figures 2-4 are 9 ppm (test A), 5 ppm (test B), 16 ppm (test C) and 100 ppm (test D), all well above the detection limit. Detailed results for the tests are shown in Table 2. The weight loss of the battery cells was between 19 and 25 %. The total amounts of HF gas emissions were between 12 and 81 mg/Wh and 7 and 27 mg/g (where g corresponds to the weight loss). The secondary measurement with gas-washing bottle technique in test D, gave about twice the amount of HF, however still in the same order or magnitude as the FTIR measurement.

An electrified vehicle today could have a battery pack ranging between 10-90 kWh. Battery packs in heavy-duty electrified vehicles (buses, trucks, etc), in ships and in stationary electrical grid could have significantly larger battery systems. Extrapolating for a worst case scenario of a 100 kWh battery pack (e.g. 400 VDC, 250 Ah), the amount of released HF could be 1200-8000 g. The IDLH (Immediately Dangerous to Life or Health) value for HF is 0.025 g/m^3 [4]. If the HF gas emissions would be homogenously distributed this amount of HF has to be diluted in more than 50 000 - 300 000 m^3 of air not to exceed the IDLH value. This volume corresponds e.g. to a total fire in an electric vehicle with 100 kWh battery pack parked in a 15000 – 100000 m^2 garage of 3 m in height. Another example of a larger 1 MWh battery pack in e.g. a stationary storage in an apartment-complex would result in a volume corresponding to about 1500 – 10000 apartments of 300 m^3 each (e.g. 100 m^2 with 3 m in height). These examples assume that the gases are not vented away but stay in the building. However, it is important to note that all fires produce smoke and one should also for that reason not stay within the room/building if there is a fire going on.

Table 2. Detailed results of HRR, total heat release (THR, integrated HRR) and HF gas emission release. The energy capacity in Wh is calculated by nominal voltage times nominal capacity.

Test	Weight loss (g, %)	Max HRR (kW)	THR (kJ)	Hydrogen fluoride					
				Amounts from FTIR (g)	Amounts from filter (g)	Total amounts (g)	Amounts from gas washing bottles (g)	Total yields (mg/g)	Total yields (mg/Wh)
A	145 g 19.7 %	29	2766	1.2	1.0	2.2	N/A	15	24
B	155 g 21.0 %	19	2502	0.7	0.4	1.1	N/A	7	12
C	406 g 24.6%	31	6605	6.3	1.3	7.6	N/A	19	58
D	419 g 19.1%	53	6893	4.8	1.6	6.4	11.2	15-27	46-81

CONCLUSIONS

The total amounts of HF gas emissions measured in these tests on commercial Li-ion cells were 12-81 mg/Wh for the different batteries tested. The HF release for a large battery pack exposed to fire could thus in a worst case scenario result in a very large volume of toxic gases.

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