RECHARGE

The Advanced Rechargeable & Lithium Batteries Association

Li-batteries hazards classification

UN IWG, Dec 6, 2017 Geneva

Claude Chanson- Philippe Bermis

Content

1. Li-ion batteries hazards background
2. Li-ion batteries hazards quantification
    1. Tests data base
    2. Tests results
3. Summary tables

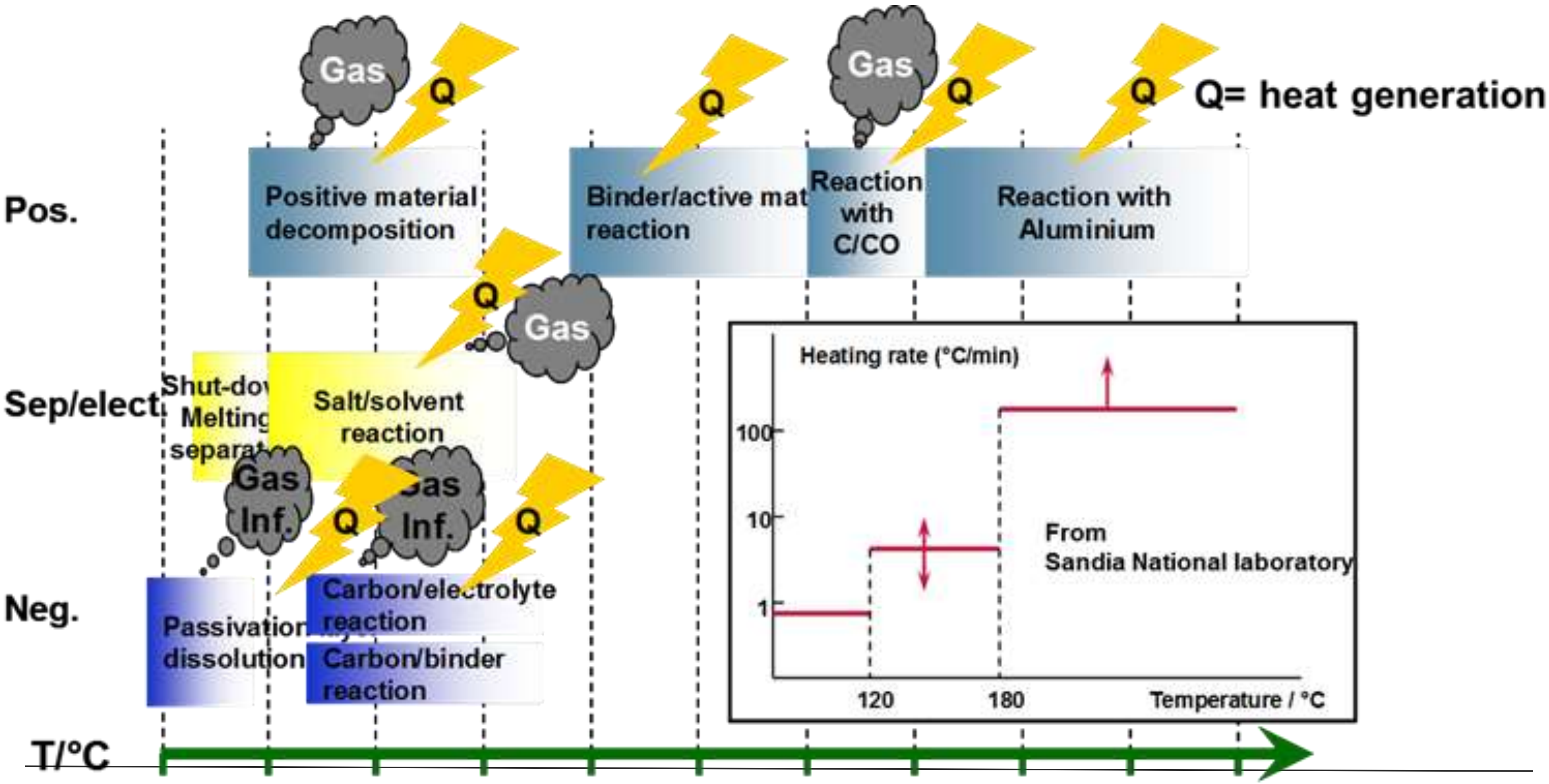
1. Identification of the Li batteries hazards

Potential hazards of Lithium batteries

- ✓ **The potential hazards of batteries**
  - The Chemical hazard
  - The Electrical hazard (and the case of high voltage)
  - Cumulative Electrical and Chemical hazards can lead to thermal run-away: heat , flame, mechanical hazards , and chemical hazards (gaz properties, smoke)
- ✓ **The three major possible consequences in case of thermal runaway:**
  - Flammable/toxic gas emission (possibly bursting: mechanical hazards)
  - Flame ignition, and possible flame propagation in the cells or batteries casing and packaging.
  - Heat emission and Thermal Runaway Propagation from cell to cell or battery to battery, in absence of flames.

2. Source of the Li batteries hazards

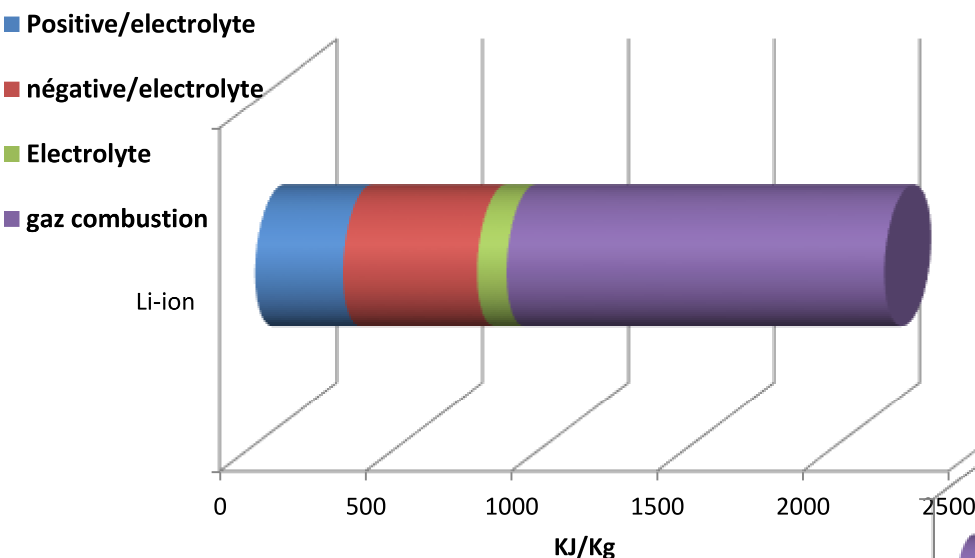
Thermal run-away: a chain of chemical reactions



3. Quantification of the Li batteries hazards

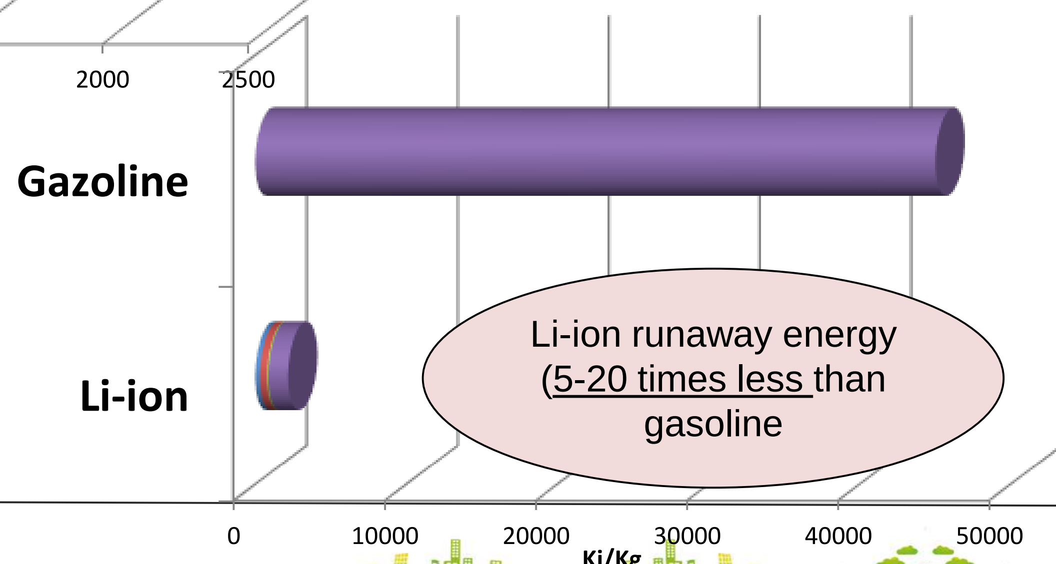
Thermal run-away: reaction energy of Li-ion cells

Total reaction energy per Kg



The gas combustion represents >50% of the total

Gazoline versus Li-ion: Total combustion energy per kg



Li-ion runaway energy (5-20 times less than gasoline

4. Tests database

Published and non-published data have been analyzed to fill an homogenous table of test results :

Product description												
Primary/secondary	Chemistry	Format/ shape	State of Charge	Voltage	Capacity	Energy	weight	surface	volume	Energy density	Specific energy	Cell Specific heat
P/R	Chemistry name	format descriptio	% SOC	Volts	Ah	Wh	grams	m2	liters	Wh/l	Wh/g	J/g.K

AbuseTest type		
		Number of cells in test
Test type	test spec	Number

Heat							Flame								Total reacti
Solid Max Temperature	Reaction initial temperature	Energy of reaction (solids)	Max Heat release rate	heat of reaction/Wh	heat of reaction/kg	total reaction duration		duration	Temperature	flame combustion energy	Flame HRR	flame energy/Wh	batt flame energy/kg battery	Flame HRR/kg battery	Solid+flame energy of reaction/kg
°C cell surfa	°C Cells surface	kJ	kW/m2	kJ/Wh	kJ/kg	s	Total reaction measured	s	°C flame	MJ	kW	MJ/kWh	MJ/kg	kW/Kg	MJ/kg

gaz					
Max Temperature	Volume at T	gaz quantity	volume/Wh	Max gaz rate	Max gaz rate/
°C gaz	m3	moles	m3/Wh	l/s max	l/s.Wh

4. Tests database

Published and non-published data have been analyzed to fill an homogenous table of test results : 199 tests results collected

Product description													AbuseTest type			Heat							Flame								Total reaction	gaz					
Primary/sec ondary	Chemistry	Format/ shape	State of Charge	Voltage	Capacity	Energy	weight	surface	volume	Energy density	Specific energy	Cell Specific heat			Number of cells in test	Solid Max Temperature	Reaction initial temperature	Energy of reaction (solids)	Max Heat release rate	heat of reaction/Wh	heat of reaction/kg	total reaction duration		duration	Temperature	flame combustion energy	Flame HRR	flame energy/Wh	batt flame energy/kg battery	Flame HRR/kg battery	Solid+flame energy of reaction/kg	Max Temperature	Volume at T	gaz quantity	volume/Wh	Max gaz rate	Max gaz rate/
P/R	Chemistry name	format description	% SOC	Volts	Ah	Wh	grams	m2	liters	Wh/l	Wh/g	J/g.K	Test type	test spec	Number	°C cell surfa	°C Cells surface	kJ	kW/m2	kJ/Wh	kJ/kg	s	Total reaction measured	s	°C flame	MJ	kW	MJ/kWh	MJ/kg	kW/Kg	MJ/kg	°C gaz	m3	moles	m3/Wh	l/s max	l/s.Wh
R	Li-ion LFP	Pouch	100	3.3	7	23.1	154	0.0362	0.084	275	0.15	1.2	fire		1			6.5		0.28138528	42.2077922		Yes	>1			50	N.M	N.M	324.675325							
R	Li-ion LFP	Pouch	75	3.3	7	23.1	154	0.0362	0.084	275	0.15	1.2	fire		1			6.5		0.28138528	42.2077922		Yes	>1			20	N.M	N.M	129.87013							
R	Li-ion LFP	Pouch	50	3.3	7	23.1	154	0.0362	0.084	275	0.15	1.2	fire		1			6.5		0.28138528	42.2077922		Yes	>1			18	N.M	N.M	116.883117							
R	Li-ion LFP	Pouch	25	3.3	7	23.1	154	0.0362	0.084	275	0.15	1.2	fire		1			6.5		0.28138528	42.2077922		Yes	>1			14	N.M	N.M	90.9090909							
R	Li-ion LFP	Pouch	0	3.3	7	23.1	154	0.0362	0.084	275	0.15	1.2	fire		1			6.5		0.28138528	42.2077922		Yes	>1			12	N.M	N.M	77.9220779							
R	Li-ion LTO-NC	Pouch	100	2.8	30	84	700	0.1552	0.374	224.59893	0.12	1.2	fire		1			N.M					Yes	>1			50	N.M	N.M	71.4285714		525	0.57619692	8.8	0.00685949	110	
R	Li-ion LCO	cyclindrical	100	3.6	2.7	9.72	51.1578947	0.00571142	0.01654049	587.649021	0.19	1.2	Heating	heater cartrid	1	650		38.67536842		3.97894737	756		No	>1				N.M	N.M	N.M							
R	Li-ion LMO	Pouch	100	3.6	2.9	10.44	87	0.0217	0.049	213.061224	0.12	1.2	IR heating	IR	1			N.M					Yes	>1		0.313	24	29.9808429	3.59770115	275.862069	3.59770115						
R	Li-ion LMO	Pouch	50	3.6	2.9	10.44	87	0.0217	0.049	213.061224	0.12	1.2	IR heating	IR	1			N.M					Yes	>1		0.383	15	36.6858238	4.40229885	172.413793	4.40229885						
R	Li-ion LMO	Pouch	0	3.6	2.9	10.44	87	0.0217	0.049	213.061224	0.12	1.2	IR heating	IR	1			N.M					Yes	>1		0.36	4	34.4827586	4.13793103	45.9770115	4.13793103						
R	Li-ion LCO	cyclindrical	100	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.008	0.90909091	0.00088889		
R	Li-ion LCO	cyclindrical	90	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.006	0.68181818	0.00066667		
R	Li-ion LCO	cyclindrical	80	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.0058	0.65909091	0.00064444		
R	Li-ion LCO	cyclindrical	70	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.0045	0.51136364	0.0005		
R	Li-ion LCO	cyclindrical	60	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.003	0.34090909	0.00033333		
R	Li-ion LCO	cyclindrical	50	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.0026	0.29545455	0.00028889		
R	Li-ion LCO	cyclindrical	40	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.0024	0.27272727	0.00026667		
R	Li-ion LCO	cyclindrical	30	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.0016	0.18181818	0.00017778		
R	Li-ion LCO	cyclindrical	20	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.0014	0.15909091	0.00015556		
R	Li-ion LCO	cyclindrical	10	3.6	2.5	9	50	0.00571142	0.01654049	544.119464	0.18	1.2	Heating	heater cartrid	1			N.M					No	0				N.M	N.M	N.M		25	0.0012	0.13636364	0.00013333		
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	nail		1			N.M					No	0				N.M	N.M	N.M		350	0.22798605	4.46	0.00143931	35	0.2209596
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	nail		1			N.M					No	0				N.M	N.M	N.M		400	0.25567097	4.63	0.00161408	32	0.2020202
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	nail		1			N.M					No	0				N.M	N.M	N.M		421	0.26080164	4.58	0.00164648		
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	overcharge		1			N.M					No	0				N.M	N.M	N.M		460	0.42100513	7	0.00265786		
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	overcharge		1			N.M					No	0				N.M	N.M	N.M		440	0.76053333	13	0.00480135	45	0.28409091
R	Li-ion NCA	prismatic	100	3.6	35	126	763.636364	0.039603	0.356902	353.038089	0.17	1.2	nail		1			N.M					No	0				N.M	N.M	N.M		340	0.08550564	1.7	0.00067862		
R	Li-ion NCA	prismatic	100	3.6	21	75.6	680						nail		1			N.M					No	0				N.M	N.M	N.M		375	0.13824	2.6	0.00182857		
R	Li-ion NCA	cyclindrical	100	3.6	12	43.2	254.117647	0.04001447	0.30708518	140.677578	0.17	1.2	nail		1	210		57.93882353		1.34117647	228		No	0				N.M	N.M	N.M		298	0.07496205	1.6	0.00173523		
R	Li-ion NCA	cyclindrical	100	3.6	30	108	1100	0.05554172	0.50246392	214.940805	0.10	1.2	overcharge		1	520		660		6.11111111	600		No	0				N.M	N.M	N.M		525	0.57619692	8.8	0.00533516	110	
R	Li-ion NCA	cyclindrical	100	3.6	30	108	1100	0.05554172	0.50246392	214.940805	0.10	1.2	nail		1	274		335.28		3.10444444	304.8		No	0				N.M	N.M	N.M		437	0.23885128	4.1	0.00221159	40	
R	Li-ion NCA	cyclindrical	100	3.6	30	108	1100	0.05554172	0.50246392	214.940805	0.10	1.2	internal short		1	365		455.4		4.21666667	414		No	0				N.M	N.M	N.M		511	0.31018532	4.8	0.00287209	55	
R	Li-ion NMC	prismatic	100	3.6	40	144	847.058824	0.039603	0.356902	403.472102	0.17	1.2	nail		1	410		396.4235294		2.75294118	468		No	0				N.M	N.M	N.M							
R	Li-ion NMC	prismatic	100	3.6	40	144	847.058824	0.039603	0.356902	403.472102	0.17	1.2	nail		1	405		391.3411765		2.71764706	462		No	0				N.M	N.M	N.M							
R	Li-ion NMC	prismatic	100	3.6	40	144	847.058824	0.039603	0.356902	403.472102	0.17	1.2	nail		1	380		365.9294118		2.54117647	432		No	0				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	heater	IR 25kW/m2	1	347		412.02		2.60113636	392.4		No	10			19	N.M	N.M	19							
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	heater	IR 25kW/m2	1	367		437.22		2.76022727	416.4		No	15			58	N.M	N.M	56							
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	nail		1			N.M					No	0				N.M	N.M	N.M		450	0.16610462	2.8	0.00104864	240	1.51515152
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	overcharge		1			N.M					No	0				N.M	N.M	N.M		625	0.21736205	2.95	0.00137224	240	1.51515152
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	overcharge		1			N.M					No	0				N.M	N.M	N.M		700	0.21555692	2.7	0.00136084	210	1.32575758
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	nail		1	510		617.4	3	3.89772727	588		No	0				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	nail		1			N.M					No	0				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	44	158.4	1050	0.05554172	0.50246392	315.246514	0.15	1.2	nail		1			N.M					No	0				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	6	21.6	216	0.039603	0.356902	60.5208152	0.10	1.2	nail		1	250		59.616		2.76	276		No	>1				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	6	21.6	216	0.039603	0.356902	60.5208152	0.10	1.2	nail		1	300		72.576		3.36	336		No	>1				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	41	147.6	1050	0.05554172	0.50246392	293.752434	0.14	1.2	nail		1	400		478.8		3.24390244	456		No	>1				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	30	108	1100	0.05554172	0.50246392	214.940805	0.10	1.2	internal short		1	360		448.8		4.15555556	408		No	0				N.M	N.M	N.M							
R	Li-ion LFP	cyclindrical	100	3.3	35	115.5	1050	0.05554172	0.50246392	229.86725	0.11	1.2	nail		1	80		75.6		0.65454545	72		No	0				N.M	N.M	N.M							
R	Li-ion LFP	cyclindrical	100	3.3	35	115.5	1050	0.05554172	0.50246392	229.86725	0.11	1.2	nail		1	210		239.4		2.07272727	228		No	0				N.M	N.M	N.M							
R	Li-ion LMO	cyclindrical	100	3.6	38	136.8	1050	0.05554172	0.50246392	272.258353	0.13	1.2	nail		1	260		302.4		2.21052632	288		No	0				N.M	N.M	N.M							
R	Li-ion LMO	cyclindrical	100	3.6	38	136.8	1050	0.05554172	0.50246392	272.258353	0.13	1.2	nail		1	324		383.04		2.8	364.8		No	0				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	41	147.6	1050	0.05554172	0.50246392	293.752434	0.14	1.2	nail		1	600		730.8		4.95121951	696		No	>1				N.M	N.M	N.M							
R	Li-ion NMC	cyclindrical	100	3.6	40	144	1050	0.05554172	0.50246392	286.58774	0.14	1.2	nail		1	301		354.06		2.45875	337.2		No	>1				N.M	N.M	N.M							
R	Li-ion NMC	cyclindrical	100	3.6	40	144	1050	0.05554172	0.50246392	286.58774	0.14	1.2	nail		1	303		356.58		2.47625	339.6		No	>1				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	45	162	1030	0.05554172	0.50246392	322.411208	0.16	1.2	external short	0.4 mohm	1	590		704.52		4.34888889	684		No			1.1		6.79012346	1.06796117	N.M	1.75196117	400	0.15562145	2.81818182	0.00136084		
R	Li-ion LFP	cyclindrical	100	3.3	41.7	137.61	946	0.05554172	0.50246392	273.870409	0.15	1.2	external short	0.4 mohm	1	105		96.492		0.70119904	102		No					N.M	N.M	N.M							
R	Li-ion LFP	cyclindrical	100	3.3	41.7	137.61	946	0.05554172	0.50246392	273.870409	0.15	1.2	overcharge		1	400		431.376		3.13477218	456		No			2.6		18.8939757	2.74841438	N.M	3.20441438	200	0.172	4.43181818	0.00136084		
R	Li-ion NCA	cyclindrical	100	3.6	45	162	1030	0.05554172	0.50246392	322.411208	0.16	1.2	external short	0.3 mohm	1	576		687.216		4.24207407	667.2		No					N.M	N.M	N.M							
R	Li-ion NMC	cyclindrical	100	3.6	40	144	1050	0.05554172	0.50246392	286.58774	0.14	1.2	nail		1	447		538.02		3.73625	512.4		No	>1				N.M	N.M	N.M							
R	Li-ion NMC	cyclindrical	100	3.6	40	144	1050	0.05554172	0.50246392	286.58774	0.14	1.2	nail		1	387		462.42		3.21125	440.4		No					N.M	N.M	N.M							
R	Li-ion NMC	prismatic	100	3.6	22	79.2	609.230769	0.039603	0.356902	221.909656	0.13	1.2	nail		1	250		168.1476923		2.12307692	276		No					N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	41	147.6	1030	0.05554172	0.50246392	293.752434	0.14	1.2	external short	0.3mohm	1	550		655.08		4.43821138	636		No	>1				N.M	N.M	N.M							
R	Li-ion NCA	cyclindrical	100	3.6	41	147.6	1030	0.05554172	0.50246392	293.752434	0.14	1.2	overcharge		1	610		729.24		4.94065041	708		No	>1				N.M	N.M	N.M							
R	Li-ion LFP	cyclindrical	100	3.3	2.6	8.58	61.2857143	0.00571142	0.01654049	518.727222	0.14	1.2	Heating		1	289		19.78302857		2.30571429	322.8		No	0				N.M	N.M	N.M		25	0.00546	0.24375	0.00063636		

4. Hazards quantification: tests categories

Two different categories of quantification test must be separated:

1- measurement of the total combustion reaction: these tests are based on a non-limited heat source (like permanent Infra Read heaters, or fire sources in a Tewarson calorimeter). The aim is to achieve the complete reaction of the battery materials. The results indicates that most Li-ion batteries have rather similar results and behave like combustible materials.

2- measurement of the thermal runaway reaction: these tests are based on a controlled abuse condition initiating the reaction. The aim is to measure the reaction consequences, including propagation ability. The results indicates that the the batteries have various results depending on their chemistry, design, state of charge, etc…

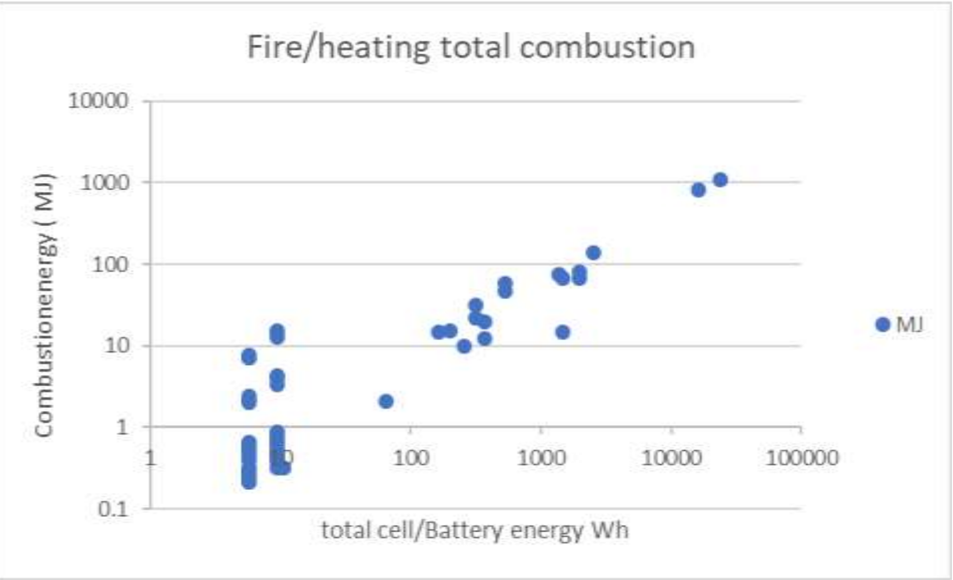
4.1 Total combustion of Li-ion batteries: total heat

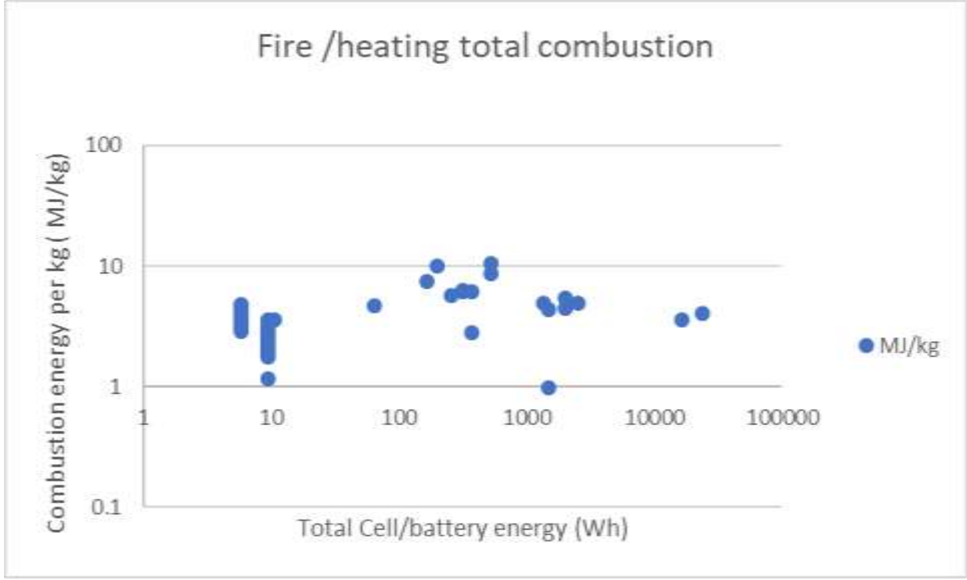
Specific case of total combustion: the total heat relase has been measured in lab tests.

Selection of complete combustion tests (fire of IR heating) and cells> 80%SOC.

-The total heat is proportional to the cell size.

-The range is 30 to 50 kJ/Wh (**4 to 10 MJ/kg maximum**) . The total heat of combustion is about 5 times less than organic materials like plastic or paper (10-40 MJ/kg

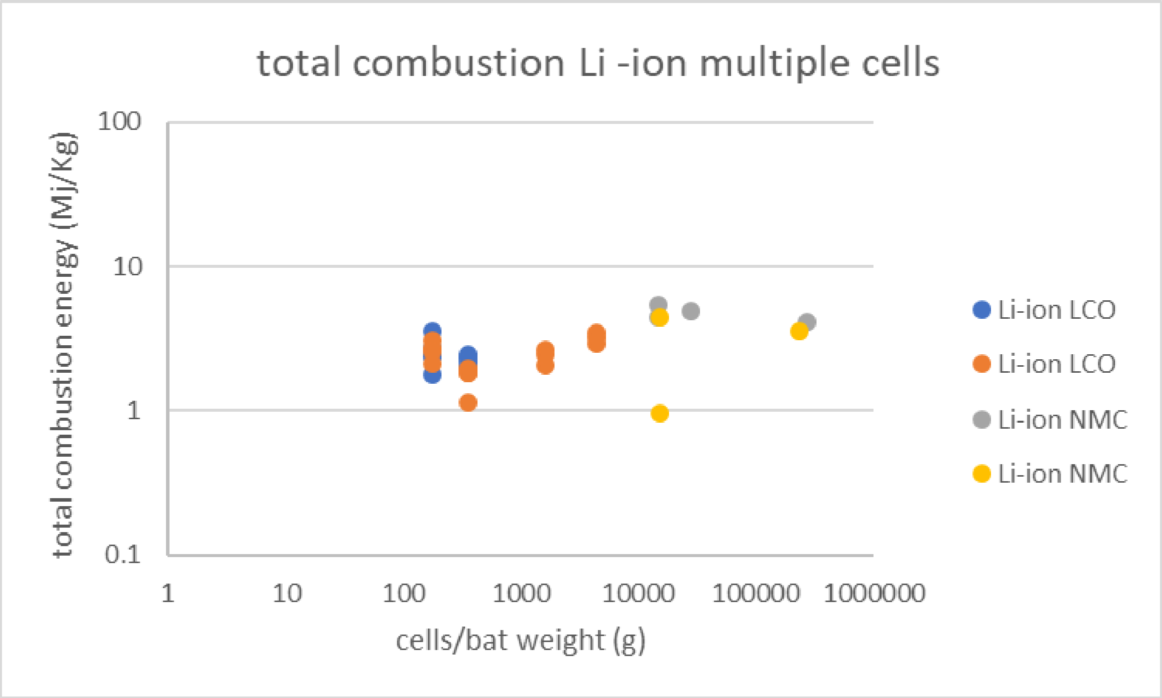




4.1 Total combustion of Li-ion batteries: total heat

Specific case of total combustion: case of Li-ion cells (>80%SOC)

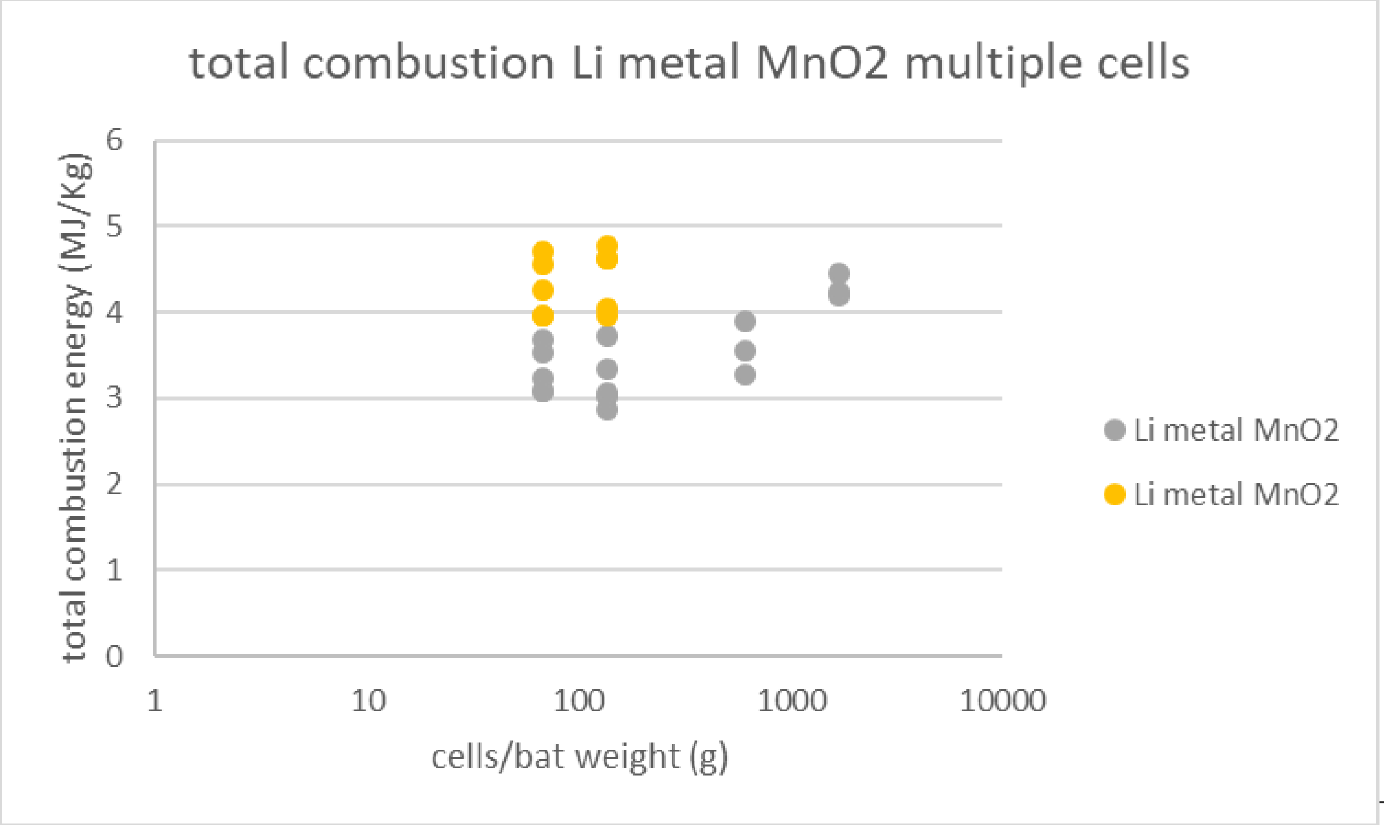
Verified for 4 tests with various number cells in a battery: **no effect of the number of cell tested or of the size of cells tested.**



4.1 Total combustion of Li-metal batteries: total heat

Specific case of total combustion: case of Li-metal cells

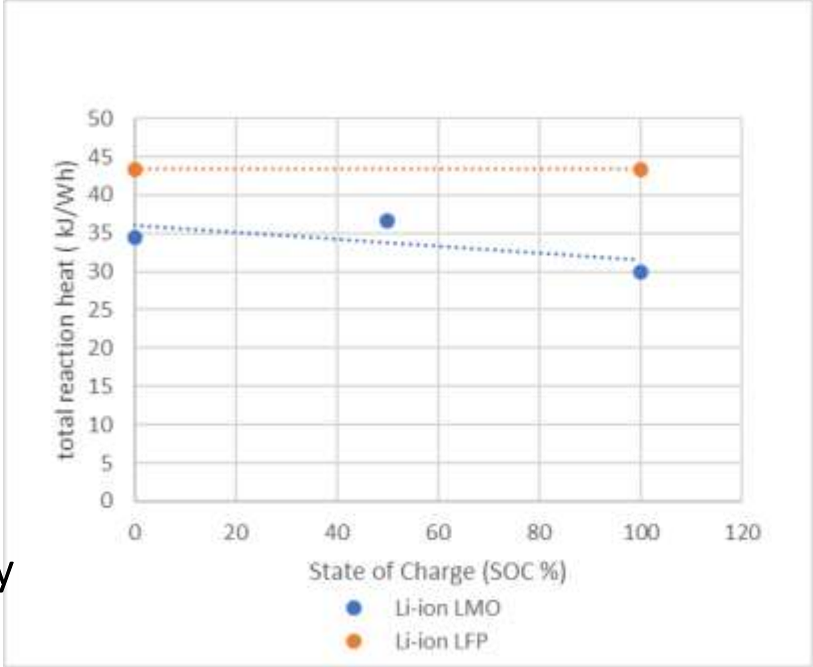
Verified for 2 tests with various number cells in a battery: **no effect of the number of cells tested.**



4.1 Total combustion of Li-ion batteries: total heat

Specific case of total combustion: effect of SOC
- Although tested with different method, the chemistry with stable cathode material (LFP) is providing more heat than LMO with reactive cathode. According some authors (Tiax*) it is due to the larger amount of electrolyte.
-Total heat independant of SOC: the less reactive cells are reacting completely due to the complet combustion method.

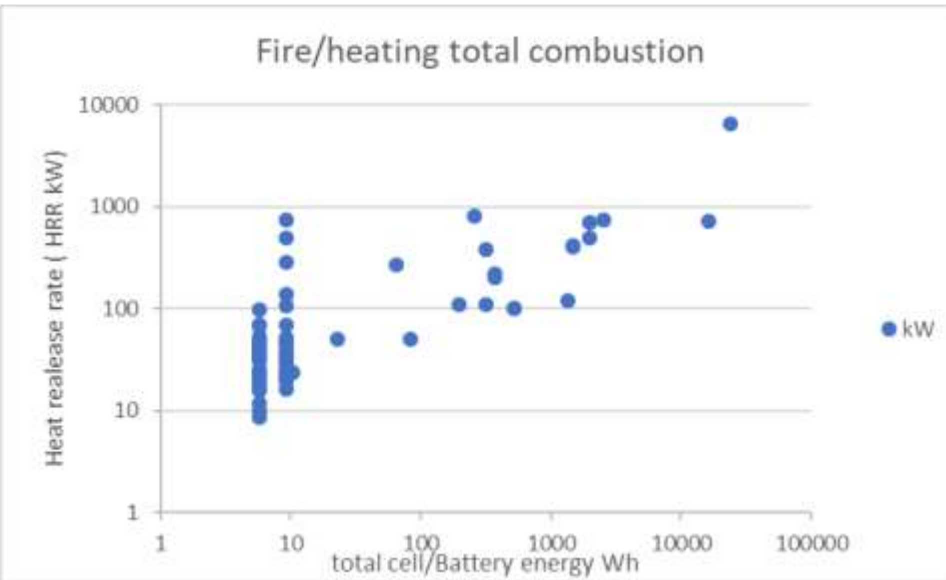
The total heat of combustion is about 5-10 times less than organic materials like plastic or paper (10-40 MJ/kg)

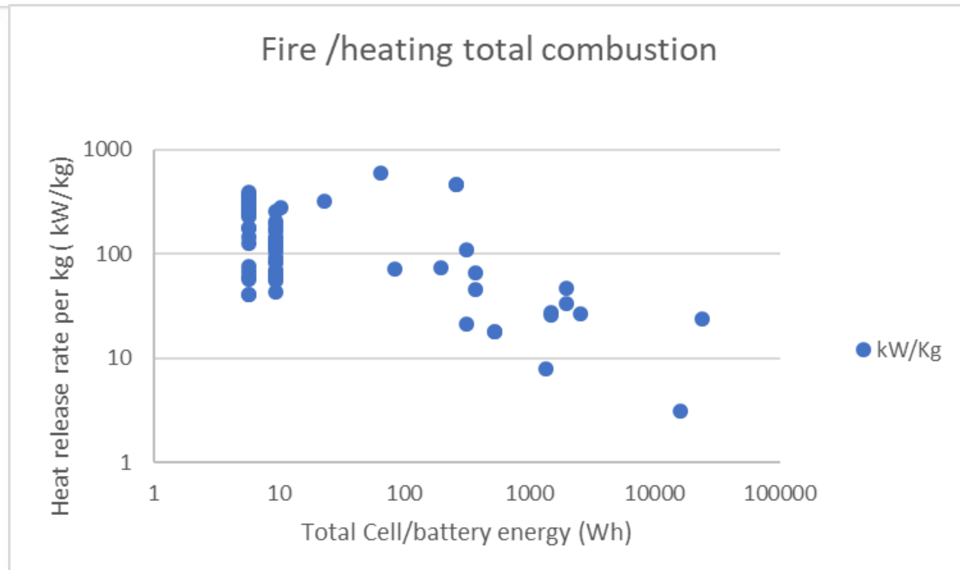


*TIAX, Fort Lauderdale, Florida 26th battery seminar, March 2009

4.1 Total combustion of Li-ion batteries: HRR

The Heat Release Rate (HRR) has been measured in calorimeter tests.
- The max HRR can reach up to 1000 kW/kg
- The max HRR is not proportional to the size of the battery in general



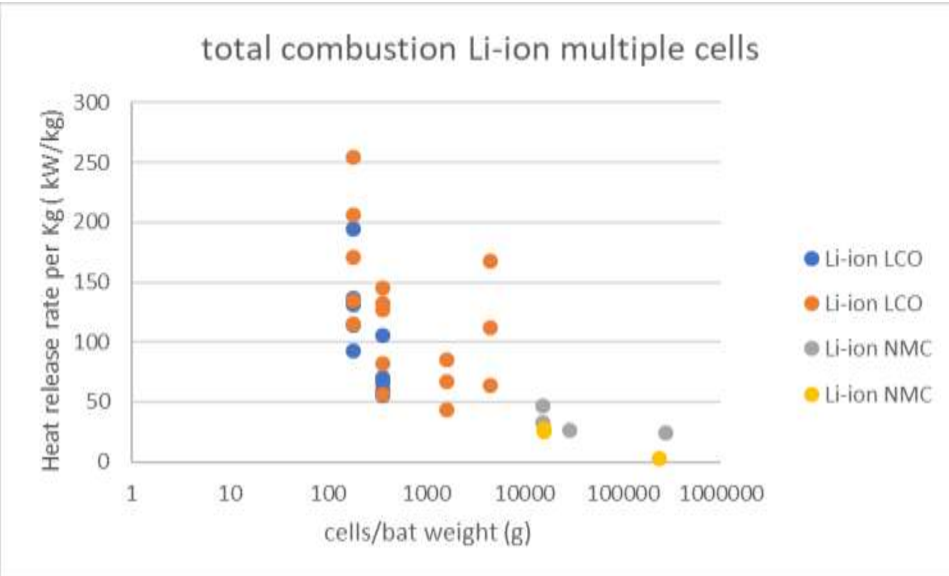


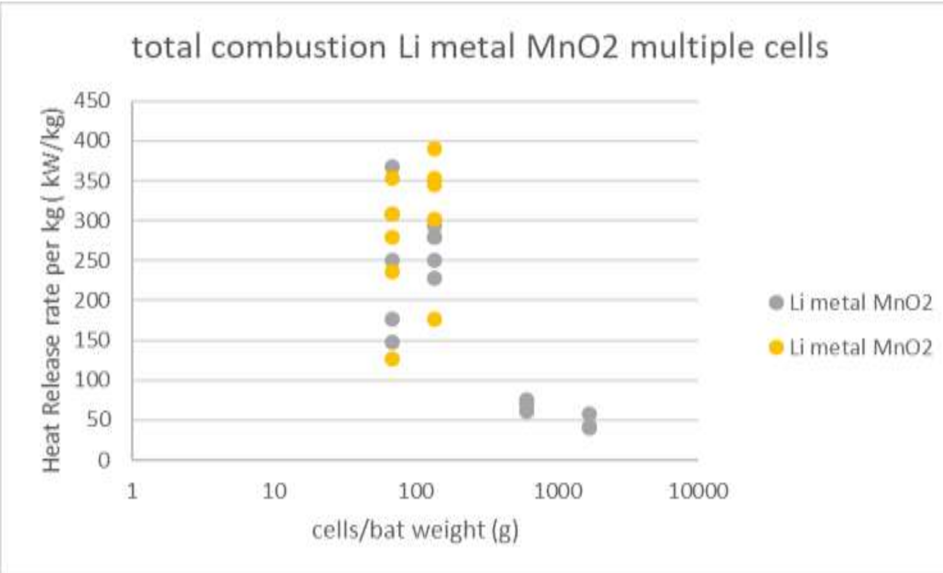
The HRR has also been measured during large test (palets of batteries or electronic equipement – see tests Exponent and for US Fire authorities): the HRR of the batteries is similar to the one from the packagings (cardboard and plastics)

4.1 Total combustion: HRR for Li-ion and Li metal

The Heat Release Rate (HRR) has been measured in tests with increased number of cells for Li-ion and Li metal.

- The max HRR per kg of batteries is decreasing with large batteries because not all the cells are reacting together. Therefore the cumulated maximum is not proportional to the size of the battery.

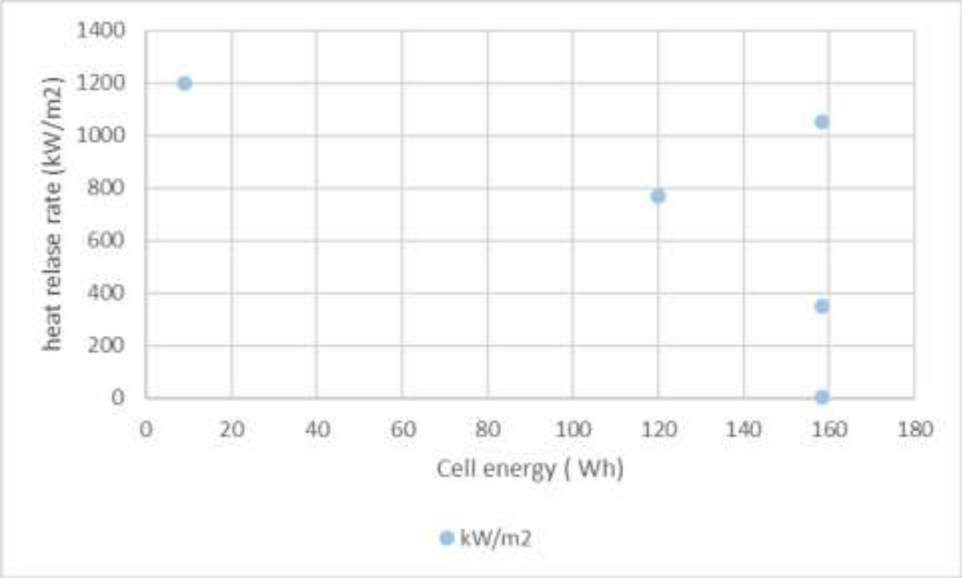




4.1 Total combustion of Li-ion batteries: HRR

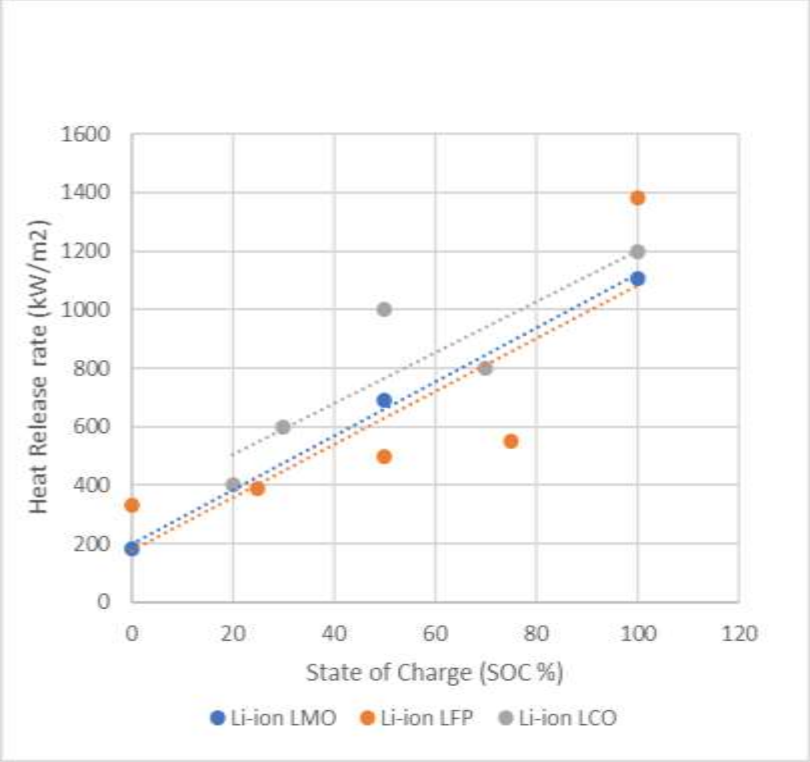
The Heat Release Rate (HRR) has been compared for large and small Li-ion cells

- The max HRR can reach up to 1200 kW/m2.
- The max HRR during combustion is the same for small and large cells in total combustion conditions



4.1 Total combustion of Li-ion batteries: HRR

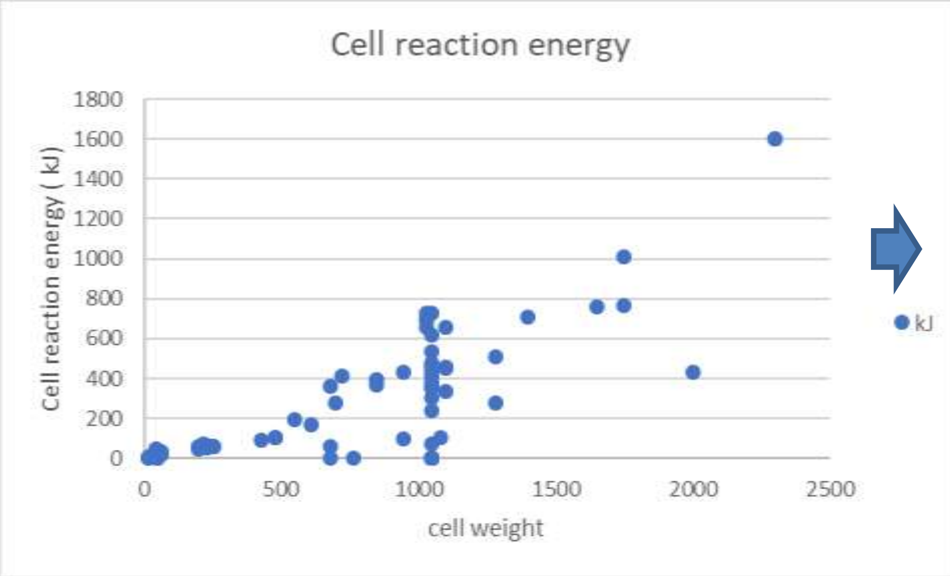
The HRR has been measured for various chemistries at different SOC:
- It confirms the total reaction is rather independant of the chemistry (tested with different methods: fire and heating).
- But the max HRR depend on the SOC: clearly the lower SOC cells are less reactive, although they end-up with a complete reaction under permanent heating conditions.

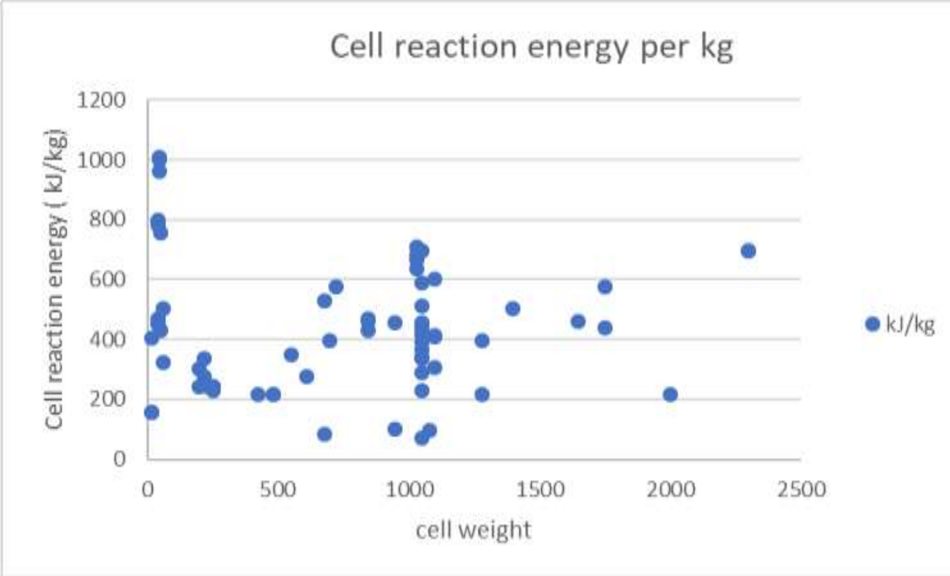


4.2 Thermal run-away quantification: Heat

Thermal runaway heat of reaction* of all Li-ion chemistries, various type of abuse:

- Maximum reaction heat of Li-ion cells is roughly proportional to the cell size.
- Maximum Reaction heat per Wh is equivalent for large and small cells.
- But the reaction is sometimes limited (particularly for low SOC cells- see specific slides)
- Always **less than 7 kJ/Wh (or 1.0 MJ/Kg):** compared to other combustibles, about 20-40 times less energy than than plastic, fuel, and other combustible materials.



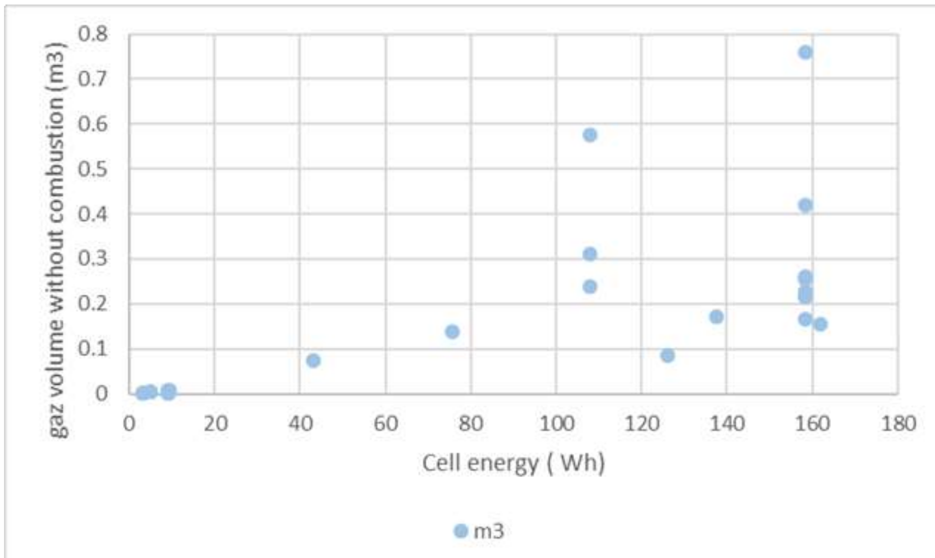


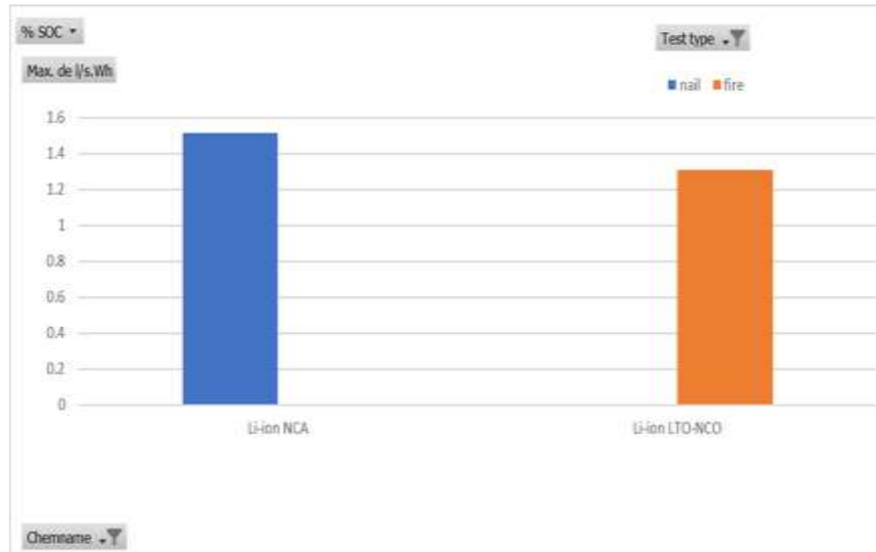
*Calculated based on the maximum temperature of cells/batteries and specific heat

4.2 Thermal runaway quantification: gaz

Gaz volume emitted (without combustion) during thermal run-away of all Li-ion chemistries, various type of abuse:

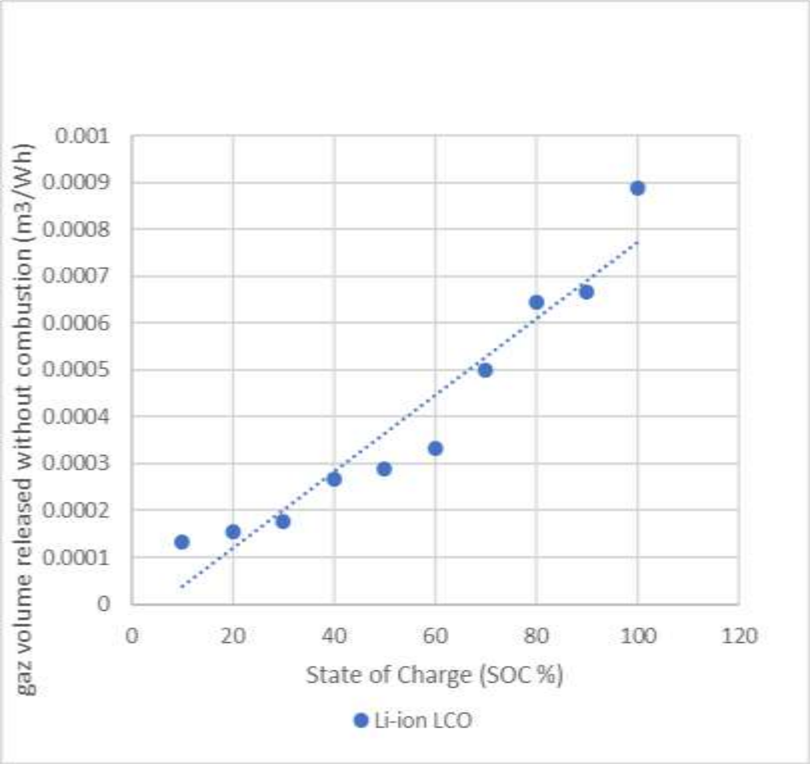
- Maximum gaz volume is roughly proportional to the cell size - But the reaction is sometimes limited, as in the case of heat produced (low SOC).
- The maximum gaz flow rate is similar for 2 chemistries with flow measured data (with 2 different ignition methods: nail and fire): **1.5 l/s.Wh**

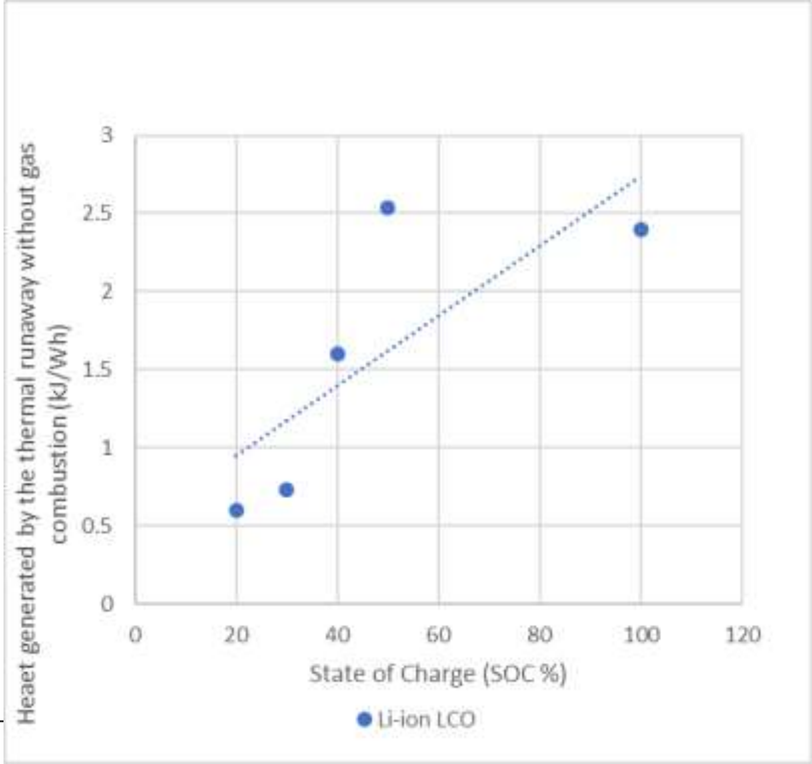




4.2 Effect of State of Charge (SOC)

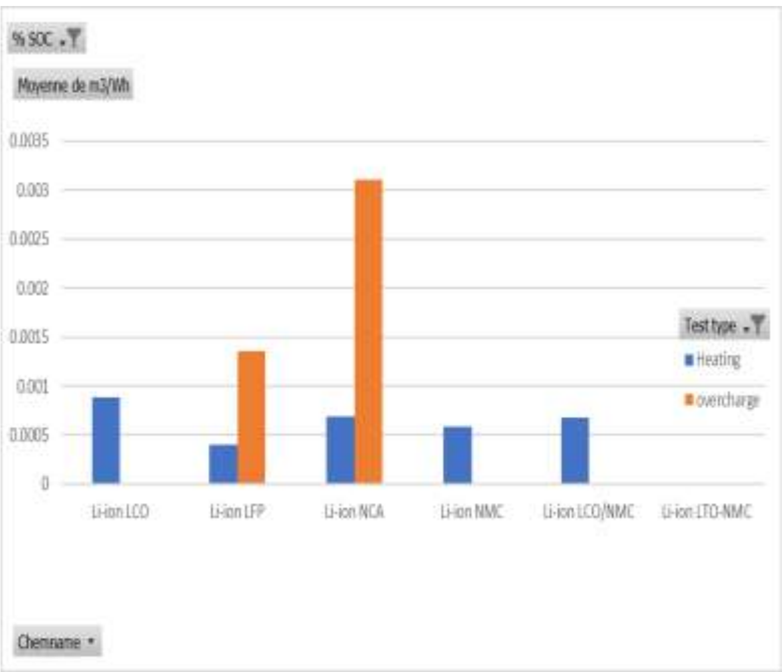
- Heat and gaz released are depending on SOC: max 1 l/Wh in this test.
- Self heat release is dependant on SOC, and significantly lower than total combustion.
- gaz volume is dependent on SOC. The calculated heat of combustion of the gaz is close to the complete combustion test for 100% SOC = 35 kJ/Wh for LCO

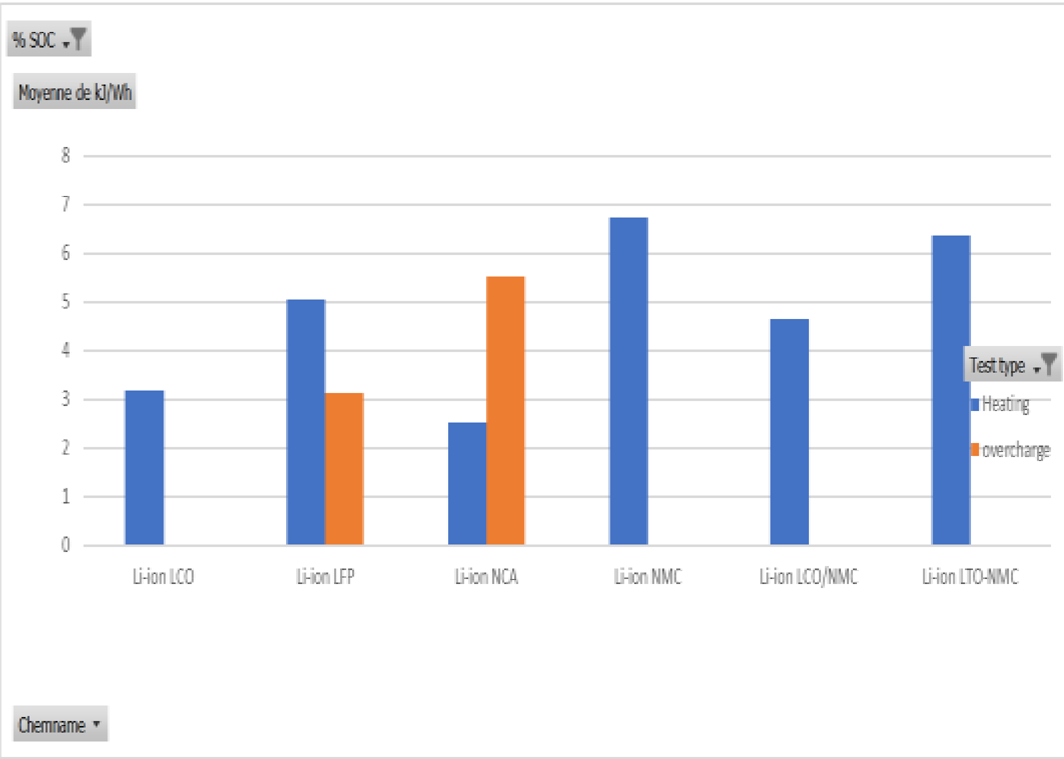




4.2 Effect of ignition method

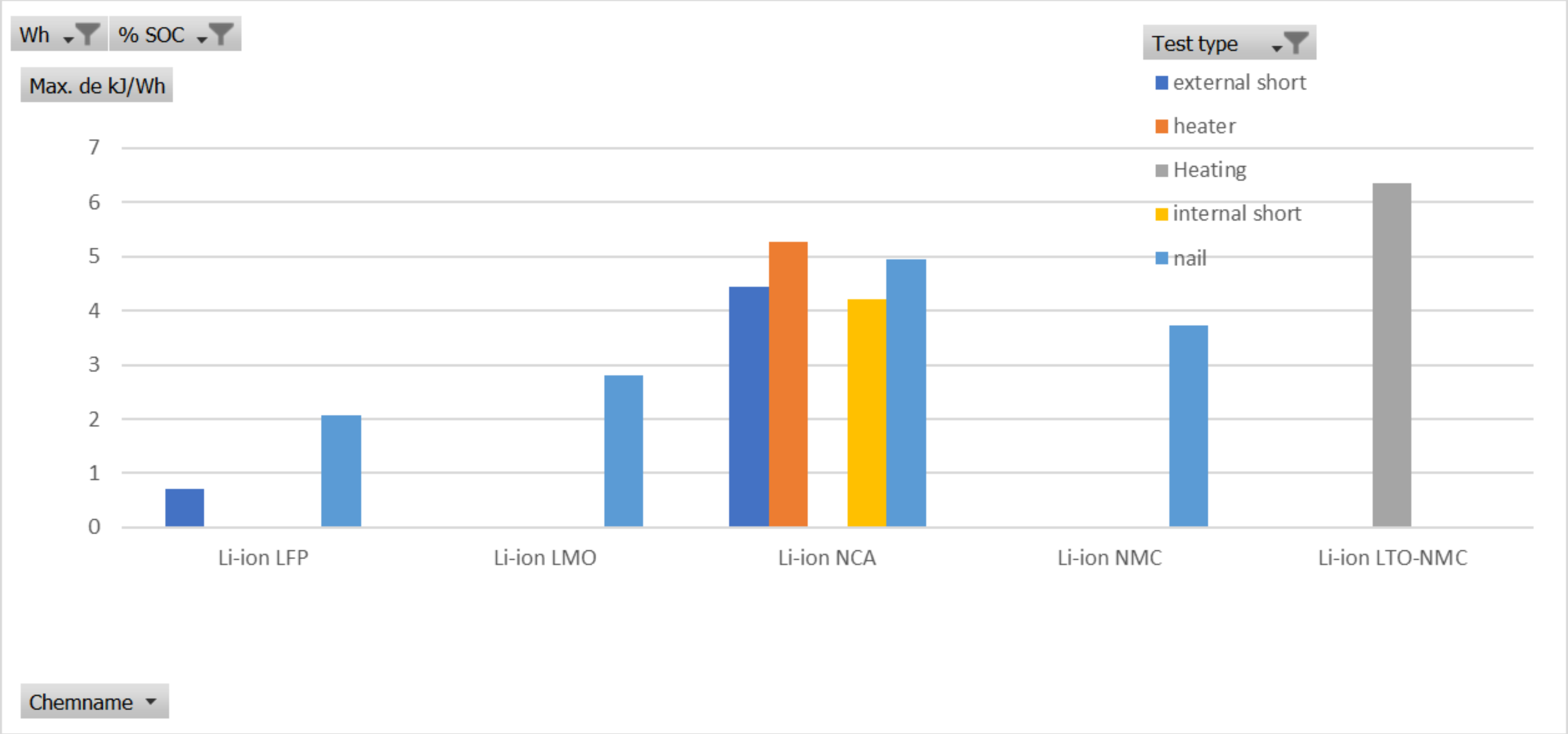
-Specific case of overcharge: Gaz released is higher (left graph).
-Average heat of reaction per chemistry and test type (right graph): overcharge producing more reaction heat for the unstable oxides types (NCA,LCO,NMC,..), but not for LFP (less reactive=no cathode decomposition reaction).
Maximum gaz production 1 l/Wh (0.1 to 0.2 m3/Kg)





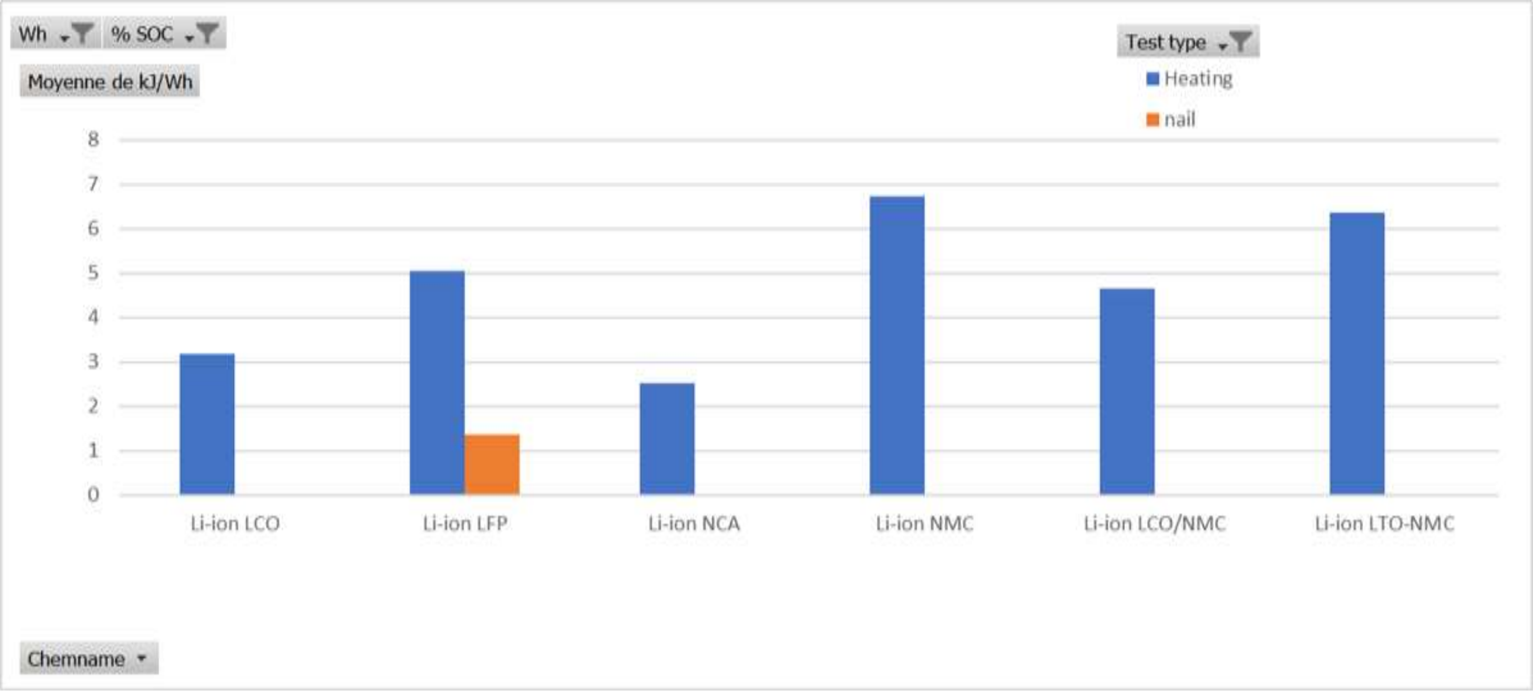
4.2 Effect of ignition method

Other test type (various abuses), case of large cells (> 20 Wh).
The test type do not change significantly the maximum energy of reaction measured: range 1-6 kJ/Wh.



4.2 Effect of ignition method

Other abuses: small cells(< 20 Wh): same range of reaction energy than large cells. Lack of data to compare reproducibility of other methods, but the example of nail test is typical: mechanical test methods are less reproducible.



5. Quantification of the thermal runaway: conclusions for testing methods

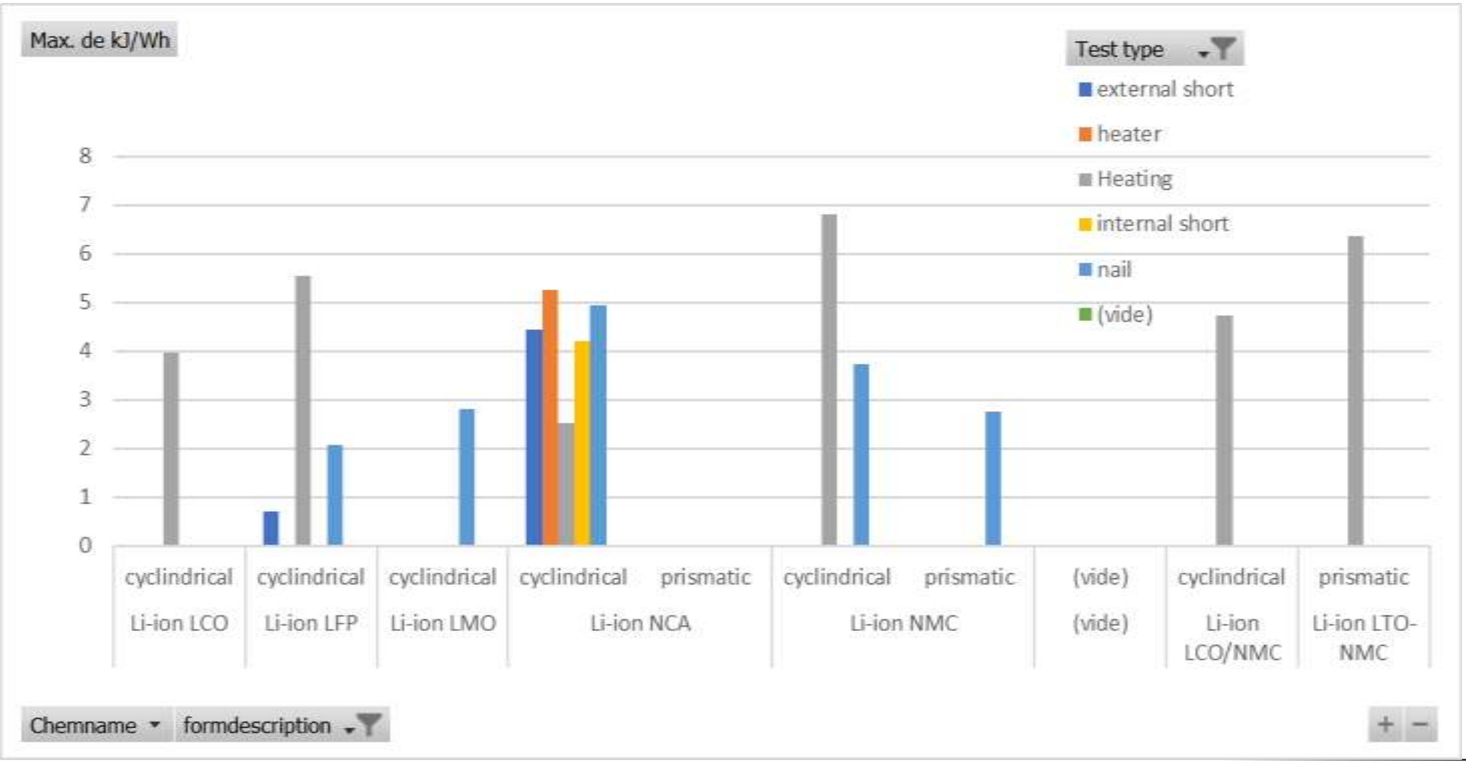
1- Total combustion reaction can be used to determine the maximum hazards: Total Heat produced, HRR. But as it is obtained under continuous external abuse (heat of fire), the hazards linked to the batteries on their own cannot be measured. Particularly the propagation to the whole battery is always induced by the continuous heating.

2- The study of the various effects allows to identify the key parameters involved to quantify the Li batteries hazards:

- type of triggering methode:
  - no interest of overcharge (too large amount of gaz, not representative of risk in transport).
  - No big difference between the other methods of abuse: because of issue of reproducibility, the more reproducible the better (probably heater for cells).
- Major effect of SOC: cells need to be tested «at SOC».

5. Quantification of the thermal runaway: conclusions for the cells type and size

1- Effect of cell design (prismatic or cylindrical): no major differences for small or large cells, or cylindrical or prismatic at least on the max. heat at 100% SOC.
2- effect of size was shown not significant, for 100% SOC cells: max 7 kJ/Wh



RECHARGE The Advanced Rechargeable & Lithium Batteries Association

6. Quantification of the thermal runaway: reproducibility

USTC and Boeing Lithium Battery Fire Research

Brand	Config	Net Total HR Smoothed (KJ)	Net HRR Peak (kW)	Net Peak Side Heat flux (kw/m2)	Peak Temp. (° C)	Peak Pressure (psia)	Mass Loss (g)	Total HR/Initial Battery Mass (KJ/g)	Total HR/Battery Mass Loss (KJ/g)	Total HR/Cell (KJ)	Total HR/ Capacity (KJ/Ah)
Secondary #1	2X2	377.4	20.5	0.6	711	0.00329	53.4	2.1	7.1	94.4	45.4
Secondary #1	2X2	436.3	30.5	0.9	766	0.0042	58.8	2.4	7.4	109.1	52.4
Secondary #1	2X2	550.1	36.7	1.3	788	0.00359	58.7	3.1	9.4	137.5	66.1
Secondary #1	2X2	471.3	23.9	1.3	711	0.00499	63.6	2.6	7.4	117.8	56.6
Secondary #1	2X2	488.1	45.3	4.2	811	0.00362	51.8	2.8	9.4	122.0	58.7
	Mean	464.6	31.4	1.7	757.4			2.6	8.1	116.2	55.8
	Standard DEV	63.86	9.96	1.46	45.13			0.36	1.16	15.96	7.68
Secondary #1	2X4	689.4	47.3	3.0	863	0.00694	112.0	1.9	6.2	86.2	41.4
Secondary #1	2X4	694.0	51.8	1.6	893	0.00511	106.8	1.9	6.5	86.8	41.7
Secondary #1	2X4	410.5	20.2	1.3	824	0.00328	108.6	1.1	3.8	51.3	24.7
Secondary #1	2X4	649.1	29.1	1.0	756	0.00329	99.6	1.8	6.5	81.1	39.0
Secondary #1	2X4	652.5	45.2	0.6	747	0.00803	118.0	1.8	5.5	81.6	39.2
	Mean	619.1	38.7	1.5	816.8			1.7	5.7	77.4	37.2
	Standard DEV	118.41	13.43	0.92	64.52			0.33	1.14	14.80	7.12
Secondary #2	2X2	431.6	24.4	1.2	883	0.00316	47.5	2.4	9.1	107.9	51.9
Secondary #2	2X2	424.3	20.4	1.4	799	0.0045	32.0	2.3	13.3	106.1	51.0
Secondary #2	2X2	317.7	16.5	1.0	742	0.00475	57.6	1.7	5.5	79.4	38.2
Secondary #2	2X2	477.2	34.7	0.8	765	0.00462	37.3	2.6	12.8	119.3	57.4
Secondary #2	2X2	639.0	23.4	3.1	858	0.00268	51.4	3.5	12.4	159.8	76.8
	Mean	457.9	23.9	1.5	809.4			2.5	10.6	114.5	55.0
	Standard DEV	116.90	6.77	0.92	59.85			0.64	3.29	29.23	14.05
Secondary #2	2X4	725.1	21.1	0.5	809	0.0042	84.7	2.0	8.6	90.6	43.6
Secondary #2	2X4	869.0	37.6	1.9	760	0.0064	84.7	2.4	10.3	108.6	52.2
Secondary #2	2X4	823.7	23.6	1.3	795	0.00289	87.3	2.3	9.4	103.0	49.5
Secondary #2	2X4	780.7	25.1	1.5	882	0.00305	88.4	2.2	8.8	97.6	46.9
Secondary #2	2X4	842.3	19.7	0.8	779	0.00453	75.8	2.3	11.1	105.3	50.6
	Mean	808.1	25.4	1.2	805.2			2.2	9.6	101.0	48.6
	Standard DEV	56.49	7.13	0.55	46.79			0.16	1.05	7.06	3.40

Propane Burner Test Results for Secondary Batteries

6. Quantification of the thermal runaway: reproducibility

USTC and Boeing Lithium Battery Fire Research

Brand	Config	Net Total HR Smoothed (KJ)	Net HRR Peak (kW)	Net Peak Side Heat flux (kw/m2)	Peak Temp. (° C)	Peak Pressure (psia)	Box Mass (g)	Mass Loss (g)	Total HR per Initial Battery Mass (KJ/g)	Total HR per Battery Mass Loss (KJ/g)	Total HR/Cell (KJ)	Total HR per Capacity (KJ/Ah)
Primary #1	6X6	2001.6	46.4	1.3	1029	0.00475	69.7	142.6	3.6	14.0	57.2	36.9
Primary #1	6X6	2388.5	41.9	2.4	842	0.00401	69.9	134.5	4.3	17.8	68.2	44.0
Primary #1	6X6	2178.8	36.5	3.2	1034	0.00378	69.6	128.1	3.9	17.0	62.3	40.2
	Mean	2189.6	41.6	2.3	968.5				3.9	16.3	62.6	40.4
	Standard DEV	193.69	4.97	0.91	109.39				0.33	1.97	5.53	3.57
Primary #1	10X10	7566.0	98.7	2.0	999	0.00365	148.7	333.8	4.7	22.7	76.4	49.3
Primary #1	10X10	7143.4	69.4	1.4	1166	0.00343	165.5	328.1	4.5	21.8	72.2	46.6
Primary #1	10X10	7189.5	69.4	1.4	1166	0.00343	163.1	357.9	4.4	20.1	72.6	46.9
	Mean	7299.6	79.2	1.6	1110.1				4.5	21.5	73.7	47.6
	Standard DEV	231.84	16.92	0.32	96.17				0.12	1.31	2.34	1.51
Secondary #1	6X6	3339.6	69.7	11.7	881	0.00889	74.2	437.6	2.1	7.6	95.4	45.9
Secondary #1	6X6	4281.5	137.5	5.9	1116	0.02301	73.7	417.4	2.7	10.3	122.3	58.8
Secondary #1	6X6	3981.7	108.3	5.9	1153	0.01108	73.6	414.2	2.5	9.6	113.8	54.7
	Mean	3867.6	105.1	7.8	1050.2				2.5	9.2	110.5	53.1
	Standard DEV	481.16	34.02	3.33	147.73				0.31	1.37	13.75	6.61
Secondary #1	10X10	14201.8	499.4	10.9	1018	0.04512	151.5	1319.2	3.2	10.8	143.5	69.0
Secondary #1	10X10	12883.4	283.6	4.8	929	0.01801	134.7	1239.3	2.9	10.4	130.1	62.6
Secondary #1	10X10	15444.8	748.6	8.8	992	0.04512	176.1	1934.2	3.5	8.0	156.0	75.0
	Mean	14176.7	510.5	8.2	979.9				3.2	9.7	143.2	68.8
	Standard DEV	1280.87	232.72	3.10	45.57				0.30	1.51	12.94	6.22

Heater Cartridge Test Results for Primary and Secondary Batteries

7. Li primary: similar results for Li-MnO2

USTC and Boeing Lithium Battery Fire Research

Brand	Config	Net Total HR Smoothed (KJ)	Net HRR Peak (kW)	Net Peak Side Heat flux (kw/m2)	Peak Temp. (° C)	Peak Pressure (psia)	Mass Loss (g)	Total HR/Initial Battery Mass (KJ/g)	Total HR/Battery Mass Loss (KJ/g)	Total HR/Cell (KJ)	Total HR/ Capacity (KJ/Ah)
Primary #2	2X2	270.5	16.2	0.2	816	0.00239	43.7	4.2	6.2	67.6	43.6
Primary #2	2X2	314.0	19.1	0.7	1111	0.00378	37.7	4.9	8.3	78.5	50.6
Primary #2	2X2	322.9	18.6	0.7	1108	0.00199	34.1	5.0	9.5	80.7	52.1
Primary #2	2X2	288.2	24.1	4.1	969	0.00326	25.9	4.5	11.1	72.1	46.5
Primary #2	2X2	267.9	20.4	0.3	1004	0.00182	29.3	4.2	9.1	67.0	43.2
	Mean	292.7	19.7	1.2	1001.8			4.6	8.9	73.2	47.2
	Standard DEV	24.94	2.91	1.64	121.29			0.39	1.80	6.24	4.02
Primary #2	2X4	648.2	47.9	0.8	1007	0.00378	54.3	5.0	11.9	81.0	52.3
Primary #2	2X4	535.9	23.8	0.7	790	0.00341	66.1	4.2	8.1	67.0	43.2
Primary #2	2X4	626.1	47.1	1.1	776	0.00864	61.8	4.8	10.1	78.3	50.5
Primary #2	2X4	546.7	40.8	2.5	758	0.00402	63.1	4.2	8.7	68.3	44.1
Primary #2	2X4	628.6	52.7	1.5	1103	0.00232	68.5	4.9	9.2	78.6	50.7
	Mean	597.1	42.5	1.3	886.5			4.6	9.6	74.6	48.2
	Standard DEV	51.78	11.26	0.74	157.62			0.40	1.50	6.47	4.18
Primary #1	2X2	245.3	20.6	0.5	1044	0.00196	25.0	3.8	9.8	61.3	39.6
Primary #1	2X2	215.9	9.8	0.4	752	0.00171	26.8	3.6	8.1	54.0	34.8
Primary #1	2X2	205.2	11.8	0.3	945	0.00162	24.8	3.2	8.3	51.3	33.1
Primary #1	2X2	207.6	24.8	1.4	636	0.00332	35.4	3.4	5.9	51.9	33.5
Primary #1	2X2	241.7	16.7	0.2	874	0.00176	28.0	3.8	8.6	60.4	39.0
	Mean	223.1	16.7	0.5	850.2			3.5	8.1	55.8	36.0
	Standard DEV	19.04	6.20	0.48	160.14			0.27	1.44	4.76	3.07
Primary #1	2X4	455.3	31.3	0.3	1254	0.0028	47.9	3.5	9.5	56.9	36.7
Primary #1	2X4	391.7	38.0	1.1	956	0.00206	37.1	3.0	10.6	49.0	31.6
Primary #1	2X4	412.4	39.7	1.1	821	0.00255	37.4	3.2	11.0	51.6	33.3
Primary #1	2X4	416.8	34.0	0.7	1036	0.00207	39.7	3.2	10.5	52.1	33.6
Primary #1	2X4	508.6	37.9	0.6	1019	0.00219	43.2	3.9	11.8	63.6	41.0
	Mean	437.0	36.2	0.7	1017.3			3.4	10.7	54.6	35.2
	Standard DEV	46.17	3.43	0.33	157.31			0.35	0.83	5.77	3.72

Propane burner test results for Primary Batteries

8. Quantification of the thermal runaway: global assessment.

1- A number of available result allows for the assessment of the maximum reaction quantification

- In case of total reaction
- In case of self sustained thermal run-away.

2. Reduced effects are often measured with various abuse testing method. It indicates that the propagation of the cell reaction can be hindered in many cases: either thanks to thermal protection, or thanks to limited heat of reaction, below the propagation threshold.

Therefore the propagation test is needed in addition to the thermal run-away test in order to verify the propagation properties (by a test or a calculation: i.e when the calculation can show that the heat released is too small to heat a single cell above 100°C?)

3. Question of Li metal: more testing may be needed?

Thank you for your kind attention !

The Advanced Rechargeable & Lithium Batteries Association
www.rechargebatteries.org
Avenue de Tervueren, 168 - Box 3
B - 1150 Brussels, Belgium
Tel. +32 2 777 05 67
Fax +32 2 777 05 65