Hazard based classification of lithium cells and batteries

Evolution a classification scheme in complement to document UN/SCETDG/53/INF.37 and UN/SCETDG/54/INF.42

Transmitted by the expert from France and RECHARGE

Introduction

1. A two days Intersessional Informal Working group was held last December (December 5 and 6 2018) in Geneva on this issue. The reports can be found in document UN/SCETDG/55/INF.5. A Lunch Time working group took place during 55th session of the subcommittee in June 2019, dealing mostly with the organization of the test campaign for defining a reproducible test for propagation evaluation.

2. In preparation of this new meeting of the working group, ideas to address the classification of batteries are submitted in this document. An actualized flowchart is proposed. This document has been prepared only to help the discussions in the working group.

3. Some hypotheses and principles considered in the present document are similar to the one already presented in informal document INF.37 (53rd session) and 42 (54th session). Other have been modified or added following the discussions reported in informal document INF.5 (55th session). They may be modified after further discussions, data presented by other attendees during IWG and possible additional experimental testing. However, they are based on current knowledge and experience gained from testing.

4. Some points have been clarified or modified to take into account comments of last meeting while other are unchanged for the moment and are waiting the results of the test campaign to be modified.

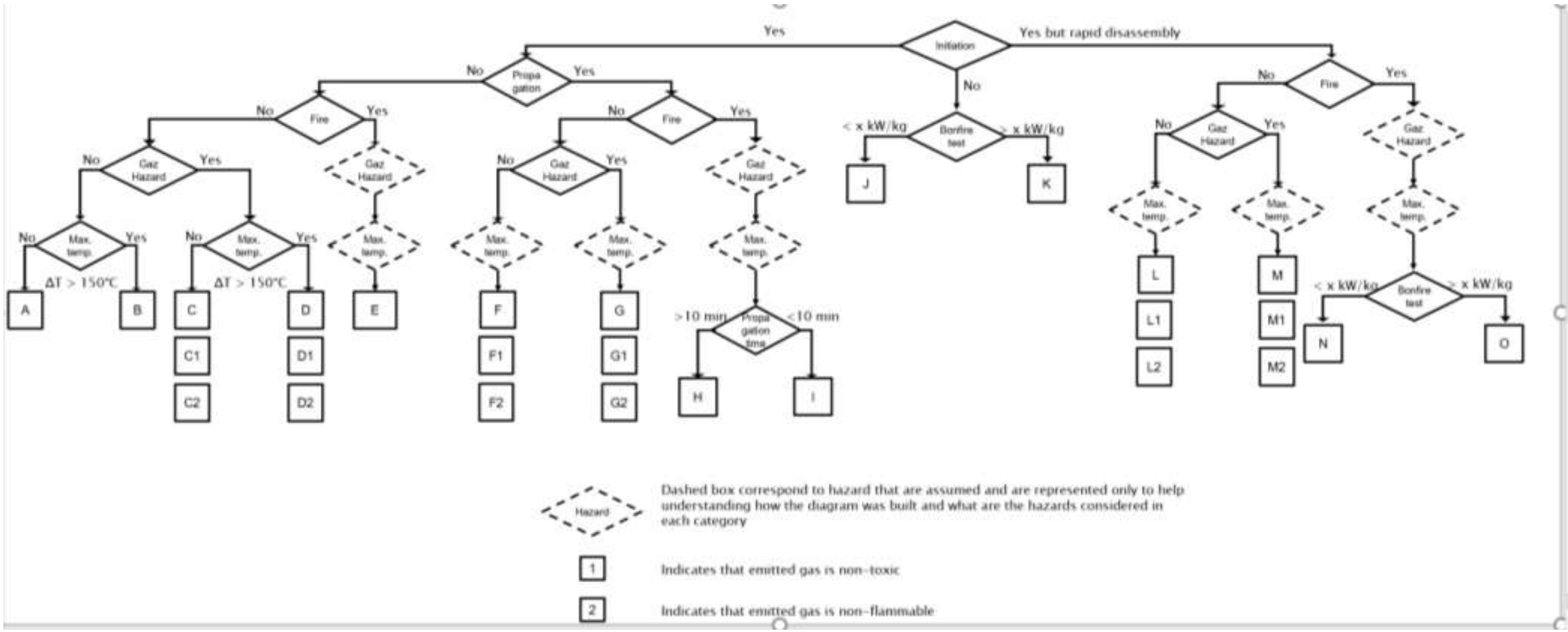
5. The definition of propagation was modified (excluding minor leakage or venting)

6. The granularity of the diagram was increase to:

- difference toxic and flammable gas,
- better define initiation sequence by integrating a bonfire test
- Integrate violent disassembly and the projection hazard

a.

7. Actualized proposition of classification for Li-ion cells:



8. As for now, the proposed classification differentiates 15 categories and up to 27 subcategories:

9. For practical reasons, the 15 categories have been assigned a letter from “A” to “O”. However, categories are currently purely descriptive and should not be seen as a hierarchy of hazard.

- A: benign hazard
- B: high temperature hazard
- C: gas hazard
- D: high temperature and gas hazard
- E: high temperature and gas hazard with the presence of flames
- F: propagation and high temperature hazard
- G: propagation, high temperature and gas hazard
- H: propagation, high temperature and gas hazard with the presence of flames
- I: propagation, violent reaction, high temperature and gas hazard with the presence of flames
- J: propagation not possible to evaluate, not susceptible to release more than X kW/kg (or kW/kW ?)
- K: propagation not possible to evaluate, susceptible to release more than X kW/kg (or kW/kW ?)
- L: propagation not possible to evaluate, subject to rapid disassembly (projection hazard), high temperature hazard
- M: propagation not possible to evaluate, subject to rapid disassembly (projection hazard), high temperature and gas hazard
- N: propagation not possible to evaluate, subject to rapid disassembly (projection hazard), fire, high temperature and gas hazard, susceptible to release more than X kW/kg (or kW/kW ?)
- O: propagation not possible to evaluate, subject to rapid disassembly (projection hazard), fire, high temperature and gas hazard, not susceptible to release more than X kW/kg (or kW/kW ?)

10. For the sake of simplicity, and to limit the complexity of the classification diagram, some hypotheses were considered:

(a) When there is propagation between cells, the temperature is generally higher than 170°C and the hazard coming from high temperature is therefore systematically considered.

(b) In the presence of fire, the high temperature hazard is systematically considered.

(c) In the presence of fire, the gas hazard is difficult to assess due to possible incomplete combustion and possible presence of toxic or suffocating gas. The hazard is systematically considered high in this case.

(d) When there is propagation between cells without fire, the reaction is propagating through thermal conduction and is usually less violent. Therefore, at this point the propagation time has not been introduced in the diagram for boxes F and G.

11. Each point where the diagram requires a decision to be made shall be based from data coming from tests. Some existing standards may provide some of those tests. However, the thermal propagation test is specific and should be developed. Once solid data will be gained by experience it could be possible to establish conservative default classification values to minimize the cost of testing.

12. At this point, cells are considered to be tested at a state of charge (SOC) of 100% because this is the most conservative test, and because shipments could be transported with incorrect states of charge which are higher than the allowed transport SOC.

Initiation and propagation criteria

13. The purpose of the initiation method is not an evaluation of a single cell but an evaluation of propagation behavior between adjacent cells. Therefore, the initiation method which create thermal runaway do not simulate internal short-circuit of the cell but is only a propagation trigger.

14. The initiation method will be further discussed after examination of the results of the ongoing test campaign. Using a thermal pad seems to be a fair option.

15. Thermal runaway of the trigger cell is demonstrated if at some point the cell temperature increases at a higher rate than the thermal pad temperature.

16. Thermal propagation is demonstrated if at least one of the following events happens:

(a) Major leakage or venting (weight loss > 50% electrolyte)

(b) The temperature of the witness cell increases abruptly

(c) The temperature of the witness cell is higher than 170°C

17. If the trigger cell does not react when exposed at the standard abuse protocol, a bonfire test should be run to determine the effective heat of combustion of the cell. A protocol for this test is proposed in annex 2. If this value is lower than one of a non-hazardous good, the cell presents a low hazard for transportation. If this value is higher than one of a non-hazardous good, the cell might present a hazard for transportation. Annex 2 address this point, and present data collected by INERIS (France).

18. If during the test, at least one of the cells is subject to violent disassembly, the test is considered invalid and should be done again. To validate the protocol, the disassembly should be reproducible (happen on three tests in a raw). The violent disassembly is determined by visual means (fragments ejected). Subsequent categories integrate projection hazard.

Fire hazard

19. The fire hazard can be determined by observation during the thermal propagation test. Fire means that flames are emitted from the cell (as defined in the UN Manual of Test and Criteria, paragraph 38.3.2.3)

20. If the observation of flame is obstructed by the apparatus used in the thermal propagation test, an alternative thermal runaway test, run on a single cell in open atmosphere, can also be used to assess fire hazard.

Gas hazard

21. The criterion for gas hazard determination relates to the total volume of gas emitted and all the gases emitted are considered potentially harmful to human and flammable. This volume threshold, in absence of fire, should be further discussed. Several options are potentially possible:

(a) A critical volume of emitted gas can be defined (example: Xl/cell)

(b) A critical volume per kWh of cell can be defined (example: Xl/kW)

(c) In analogy with the recommendations for transport of water-reactive material (Vol 1, 2.4.4.3), a gas emission rate of 20 liter per gram of battery and per hour can be proposed.

(d) An opacity criterion (which is often used in official reaction to fire testing of materials that can be used in rolling stock and air transportation). In addition and to some extends this criterion will be bounded to toxicity and total volume of gas emitted.

To make a choice between those options, data and bibliographical work are welcome.

22. The gas hazard could be assessed also during the thermal propagation test. An alternative thermal runaway test, run on a single cell, can also be used to assess the volume of gas emitted. The test must be performed in a set-up allowing the measurement of the total volume of emitted gas. For example, an airtight box equipped with temperature and pressure sensors can be used.

23. Gases emitted may include, but are not limited to:

(a) Carbon dioxide (CO_2)

(b) Carbon monoxide (CO)

(c) Carbonates

(d) Hydrogen (H_2)

(e) Hydrogen fluoride (HF)

(f) Oxygen (O_2)

They are considered *a priori* harmful to human, flammable and corrosive.

24. If the volume of emitted gases is higher than the non-hazardous criterion, the responsible organization can prove that emitted gases are not hazardous in the expected concentration by using advanced characterization method (FTIR, gas analyzer, GC-MS …). Those cells can then be considered as non-hazardous regarding to the gas hazard.

25. In most cases, gas emitted are a mix of toxic and flammable gas. In some specific cases there might be non-flammable emissions. If the IWG validate this approach, the inflammability of the gas emissions could be tested by implementing an additional device (for example using an electric arc generator).

26. Even if the gas is demonstrated nontoxic and non-flammable, limit quantities should still be imposed to avoid asphyxia.

27. Explosion hazard that might be caused by emission of fine dust or mist is not considered since (a) it is an extremely marginal phenomena during cell thermal runaway and (b) the inflammation energy is much higher for dust than gas (10-100 mJ for dust versus few mJ for gas).

High temperature hazard

28. The temperature threshold considered as hazardous is 170°C. It has been chosen to be under the melting point of metallic Li (170°C) and under auto-ignition temperature of paper (218°C). This temperature is also harmonized with criterion in the recommendation on the transport of dangerous goods UN Manual of Test and Criteria, paragraph 38.3.4 (6^{th} revised edition).

29. The high temperature hazard is considered if (Tmax-Tignition) of the trigger cell is higher than 150°C

Propagation time

30. The threshold for propagation time has been fixed at 10 min between two neighbors cells experiencing a thermal runaway. It is estimated that above this lapse of time the thermal runaway of a single cell cannot lead to a massive thermal runaway event where a large amount of cell is simultaneously involved. This time threshold must be discussed during the IWG.

Next steps

31. The following actions are already identified to elaborate a concrete categorization of Li-ion batteries:

32. For cell assembly (modules and packs) the same categorization can be applied. For some large batteries, it should be nonetheless possible to avoid testing. For example, a pack verifying some construction requirements and being composed of class A cells can be considered safe for transportation.

33. At this point, cells are considered to be tested at a state of charge (SOC) of 100%. In further work, it must be assessed how the SOC could lead to other classifications. Introducing this consideration in the test scheme would lead to the introduction of other regulation modifications to ensure that the battery is transported at the specified SOC.

34. The packaging requirements associated to the risk in transport of the different categories identified in this document should be considered in a later stage.

Annex 1 Classification criteria definitions

1. Fire: Fire means that flames are emitted from the cell (as defined in UN Manual of Test and Criteria, paragraph 38.3.2.3).

2. Gaz hazard: a volume of gas above at the threshold value, and with a composition presenting either flammability risks or toxicity risks.

3. Intermediate cell: The first cell adjacent to the trigger cell

4. Propagation: Transfer of heat energy from a cell experiencing thermal runaway that results in thermal runaway in one or more adjacent cells or batteries. The criteria for propagation is defined as: The witness cell vents, leaks (weight loss > 50% electrolyte) or goes into thermal runaway; the temperature of the witness cell increases abruptly; the temperature of the witness cell is higher than 170°C.

5. $T_{ignition}$: the temperature (°C) at which the temperature of the cell starts to increase faster than the temperature set by the thermal pad.

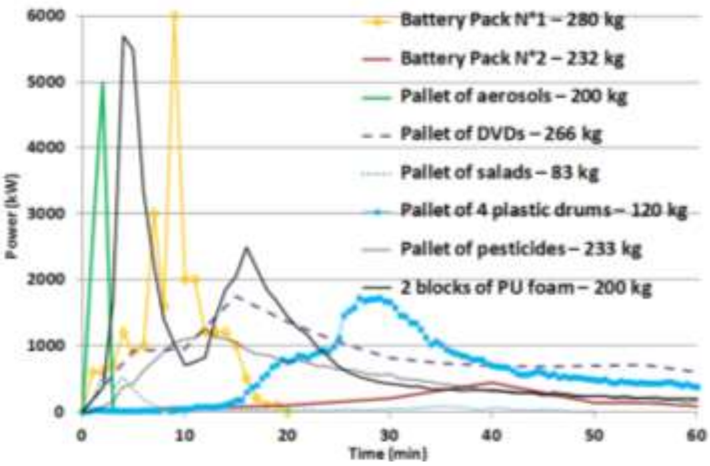
6. Thermal runaway: Uncontrolled increase in the temperature of a cell or battery driven by exothermic processes.

7. Trigger cell: The cell being abused in order to create a thermal runaway.

8. Witness cell: A cell different from the trigger cell and the intermediate cell that is used to asses propagation of the thermal runaway.

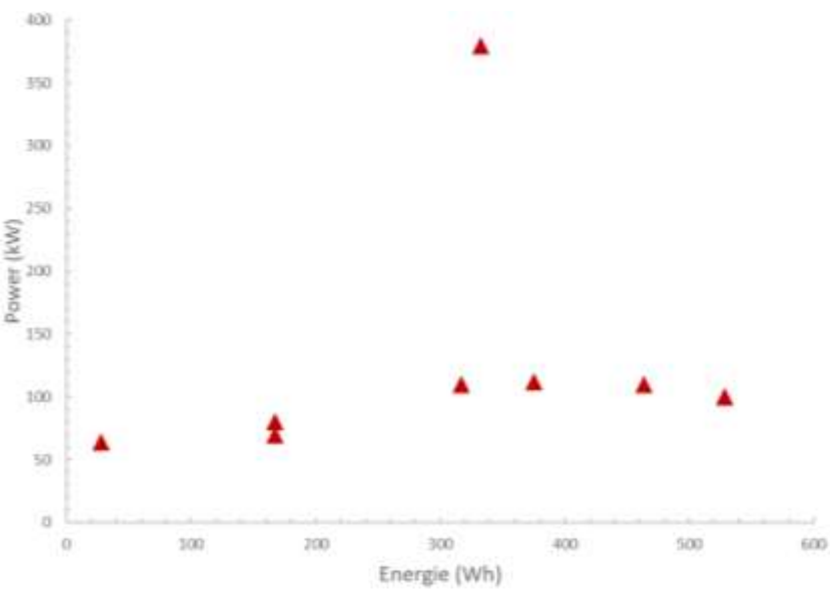
Annex 2: Bonfire test

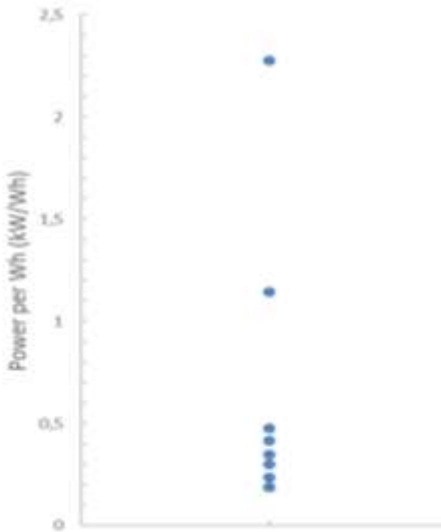
This type of test is already present in the UN model regulation. For explosives, test series 6 type (c) (16.6.1 of manual of tests and criteria), is a test used to determine whether there is a mass explosion or a hazard from dangerous projection, radiant heat and/or violent burning or any other dangerous effect when involved in a fire.
For batteries, the aim would be to quantify the power peak of the batterie combustion (or the maximal amount of thermal energy that can be released by the cell). This value can be different between batteries, and possibly lower than materials transported without special dispositions. The figure bellow, already presented in UN/SCETDG/50/INF.31/Add.2 illustrates this point



Power of the fire of single elements.

The two graphs bellow present power emitted during fire tests, for cells (or bi-cells). The power emitted per Watt hour can vary by almost an order of magnitude.





In order to fix a threshold, results of fire tests done on different type of samples can be use. The amount of power/total energy released acceptable for different mode of transport also have to be considered.

To evaluate those thermal properties, several protocols are possible:

- Wood bonfire → difficult to calibrate
- Tewarson calorimeter → limited to small samples, expensive
- Fuel (or ethanol) fire
- Gas burners

The measurement of thermal power peak and/or total thermal energy released can be done by using fluxmeters or by measuring CO and CO_2 emissions.