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Item 4 (b) of the provisional agenda
Electric storage systems:
hazard-based system for classification of lithium batteries

Report of the informal working group on hazard-based system for classification of lithium batteries

Transmitted by the expert from France and the European Association for Advanced Rechargeable Batteries (RECHARGE) on behalf of the informal working group*

Introduction

1. The informal working group on lithium batteries met from 6 to 8 December 2017 in Geneva. It was hosted by RECHARGE chaired by Mr. Claude Pfauvadel.

2. Mr. Claude Pfauvadel (France) and Mr. Claude Chanson (RECHARGE) welcomed participants to the second session of the 2017-2018 Informal Working Group on Lithium Batteries and presented the tentative agenda for the meeting. The Chairman explained the purpose of the meeting was to discuss the inherent hazards associated with lithium batteries. Based on lessons learned and experience gained, the Sub-Committee issued a mandate to the working group to consider a hazard-based system to classify lithium batteries and cells for transport. Such a system might include determining the inherent hazards represented by lithium batteries and the types of reaction that may result from accidents or abuse. Destructive testing should be considered. Overall concepts to guide the discussions include:

(a) Review of all available data that can already be useful to analyze the effects produced by lithium batteries when they react;

(b) Identify the additional data needed;

* In accordance with the programme of work of the Sub-Committee for 2017–2018 approved by the Committee at its eighth session (see ST/SG/AC.10/C.3/100, para. 98, and ST/SG/AC.10/44, para. 14).

(c) Prepare a plan for getting all the necessary data and the way to use them.

3. For the second session and given data that has been collected, the group was requested to:

(a) Review data collected;

(b) Consider categories for identifying level of hazards presented by lithium batteries;

(c) Identify tests to measure the level of hazards.

4. Presentations were distributed to the group prior to the meeting and are available from the Rechargeable Battery Association (PRBA) website: http://www.prba.org/lithium-battery-transport-information/un-lithium-battery-working-group-on-classification/

5. Day 1 consisted of a review of data collected earlier in 2017 and organized during a meeting in November 2017. The Chairman summarized the report of the November meeting and noted that 200 sets of data (test results from 1 test on 1 cell or battery) had been analyzed including a wide variety of methods and results. The data was tabulated for review and analysis. The table includes data regarding the type of cells/batteries that were tested, state of charge (SOC), and other parameters that describe the item tested. Test result were also tabulated including reaction temperature, energy of reaction, heat release rate (HRR), heat of reaction, duration of reaction, flame combustion energy, volume of gas generated, etc. Limited data was provided regarding the gas composition, and not all data points listed were available from all test results. A complete statistical analysis would not be appropriate given the limited data received to date. But the group felt some conclusions could be identified based on the available test data and the expertise of the attendees to the meeting. The data collected and initial conclusions were shared with the working group for further review, and support discussion of the following steps:

(a) Identify additional data needed;

(b) Development of a theoretical view on how to move forward;

(c) Propose how additional data is to be collected;

(i) Including budget issues/resource requirements;

(ii) Timeframe for test completion.

(d) The Chairman explained the results of this meeting would be submitted as an official document to the fifty-third session of the Sub-Committee so that costs associated with the data collection/testing and budget for 2019 and beyond could be considered.

6. Data providers are generally not identified and thus the data collected and presented remains anonymous. This is a benefit and encouraged participants in the working group to continue to submit data that may fill in the gaps. The group discussed whether the range of acceptable parameters had already been identified by the data collected and whether additional data was needed. For example, additional data may be needed regarding ways of initiating heat or reaction. If one initiation method is chosen over another, then the effects may be limited to consequences that result from only that initiation method while overlooking consequences from other initiation methods. It was noted that the G-27 group working on development of packaging standards for lithium batteries by air has collected some of this data and it should be included in the review.

RECHARGE presentation

7. RECHARGE gave a presentation on the existing data collected and identified conclusions drawn from the data. The presentation showed the types of information collected and parameters that were tabulated. The working group used the presentation as a basis for discussion on different points, and arrived at conclusions based on the data provided.

8. The presentation provided a summary of the mechanisms that may be associated with the thermal reactions in lithium batteries and cells as drawn from scientific papers. It was noted thermal runaway reactions proceed in a measurable manner. Early in a reaction, the heat release rate is relatively low (<1 C/min). At this point, the reaction is easy to stop by cooling the cell/battery. But if the reaction is not stopped, the rate increases to 5-10 C/min. This step produces more heat and moves from a reaction of just the anode to reactions with the electrolyte. As these reactions continue, the heat release rate increases to >100 C/min. At this point, additional reactions occur between the electrolyte and the cathode. RECHARGE also explained that results of the test will differ depending on the state of charge (SOC) of the cell/battery. For example, a reaction that occurs when charging or at a high SOC would be different than if the cell/battery is being discharged or at a low state of charge. The chemical reactions are dependent on the status of the cell/battery. Thus, it is important to consider these results when developing tests to measure the safety of the cell/battery.

9. When looking at the total energy of the reaction, it was noted that the energy of the cathode/anode/electrolyte combustion is then nearly doubled when the gas produced by the reaction is combusted. To give some comparison elements, the presentation noted the total combustion energy per kg of lithium ion batteries is significantly lower than that of gasoline. The group questioned how this compared to lithium metal compositions. The data indicates the values are similar.

10. Two test categories were measured:

(a) Measurement of the total combustion reaction;

(b) Measurement of the thermal reaction after the reaction initiation is stopped.

11. For total combustion reaction, the combustion energy per kg ranged between ~2-12 MJ/kg regardless of chemistry or mass. Similarly, data suggests initial SOC also did not have an impact on total heat of combustion. When reviewing the HRR, there was a general increase in the HRR from small batteries to large batteries. But when the rate is measured per mass (kg), there is a decrease in the HRR/kg from small to large batteries, reflecting the fact that in large batteries, all the cells may not be reacting at the same time. However, SOC did have an impact on the rate of HRR. Higher SOC resulted in a faster HRR than lower SOC. *Given the review of these parameters, the total heat of combustion may not be a defining criterion for categorization, but heat of release rate may be more relevant.*

12. For the thermal runaway data, values were reviewed that were only a result of the thermal runaway effect (not total heat of combustion but only heat produced by reactions). The total heat production had a maximum of 1 MJ/kg, one (1) order of magnitude lower than total heat of combustion. It was also clear that the gas volume produced by the reaction increased with increasing cell energy. Finally, increasing SOC resulted in an increase in gas volume produced. But the gas may not always ignite.

13. The group discussed whether SOC would be a consideration of transport in the future. The Chairman explained that the working group could not answer that question at this time. Based on data reviewed so far, SOC clearly has an influence on heat release rate and gas volume production. SOC may not necessarily be a part of the classification process, but it will certainly be a parameter that would be defined in the testing procedures. Ultimately, the

working group will report to the Subcommittee a set of recommendations and the Subcommittee will determine if the arguments merit a decision.

14. RECHARGE also discussed the method for reaction initiation. They noted the overcharge test results in a larger volume of gas produced (as expected based on conclusion on gas production and SOC). Therefore, the overcharge test resulted in a high hazard condition. When heating to initiate the reaction, the rate of gas production was lower than the overcharge method. For total energy released, the heating method was slightly more effective than other methods, although the external short circuit and nail methods were less effective.

15. Participants noted the nail penetration method is difficult to reproduce and the nail itself may become an avenue for heat/energy release that then leads to a less abusive condition (less heat to propagate the reaction. Generally, it is better to apply the heat from outside the system instead of relying on initiation sources within the cell/battery. Other participants pointed out it is important to account for physical abuse conditions that could be encountered in transport, including puncture of the cell.

16. The group discussed variability of tests and that any categorization must account for a wide range of results even on the same unit tested. It was noted short circuit tests will inherently have a wide range of results because of the many factors that affect the test, including many factors that are not always known, controlled, or measurable.

17. The following conclusions were drawn from the presentation and the resulting discussion:

(a) Total combustion reaction can be used to determine maximum hazards for total heat produced and HRR. But the method does not discriminate between battery chemistries or safety design systems.

(b) The study of the various effects allows to identify the key parameters involved to quantify the battery hazards:

(i) The method for initiating the reaction should preferably include the application of external heat to the cell or battery. No significant difference between method of initiation/abuse, but some methods may not be reproducible.

(c) The SOC needs to be considered, but it was not decided if the parameter should be included in classification or in transport conditions.

18. RECHARGE concluded that:

(a) A number of available result allows for the assessment of the maximum reaction quantification:

(i) In case of total reaction;

(ii) In case of self-sustained thermal run-away;

(b) 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:

(i) either thanks to thermal protection, or

(ii) thanks to limited heat of reaction, below the propagation threshold.

(c) 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).

(d) Question of Li metal: more testing may be needed?

19. RECHARGE acknowledged the toxicity of the gas produced has not been completely reviewed. Two data points were received, and were discussed on Day 2.

Discussion of test results

20. To open Day 2, The Chairman summarized the discussion from Day 1:

(a) External initiation method appears to be more effective.

(b) An initiation method that stops once the reaction starts would be best.

(c) The test data reviewed suggests size and shape of the battery has little impact to the tests. Therefore, tests should be measured per mass (X/kg) and or energy of the cell or battery.

(d) SOC clearly influences how the battery reacts and must be considered.

(e) Total energy release solely would not provide for sufficient discrimination. Taking into account the heat release rate allows further granularity.

(f) The reaction releases gas and the gas may contribute to the total heat produced but current data does not completely address gas composition.

21. The group discussed if there is any clear indication as to when the reaction starts and thus the initiation method may stop. The G-27 concluded the test could be initiated by a heat method raising the cell temperature to 200 ºC (lithium metal melts at 180 ºC). However, it was also noted that if too much energy is applied to the system, a total combustion reaction would occur. Therefore, a maximum energy applied was valid. Therefore, the initial suggestion is that cell temperature should be raised to 200 ºC for 1 hour. If the cell/battery does not react, the test would be stopped. Participants noted current testing of cells have identified a number of cells/batteries that do not react at these parameters. But concern was noted that even if a battery doesn't react at these levels, the cell/battery may also need to be tested by simulating an internal short circuit which could result in a spike in temperature and accelerate the reaction. Others noted that it is nearly impossible to identify the exact point of reaction initiation. Some others indicated that measuring voltage is a way to see when the reaction begins. Others questioned if it would be beneficial to calculate volume of gas released.

22. The Chairman considered that this point was critical and should be developed further so that the final parameters were justifiable and explainable to the Sub-Committee.

23. The group noted that the definition of thermal runaway should be considered. Generally, thermal runaway is the reaction that results in cells generating heat and gas. This is different than total combustion energy. Voltage drop is an indication of reaction in the cell and may be a measurable parameter. And there are cells/batteries that may resist the 200 ºC test. In these cases, a representative test could be developed that would see what happens when the maximum release of energy in the cell is released. The accelerated rate calorimeter (ARC) machine could provide a better measurement during the reaction. Some participants noted that the cost of ARC machines may add significant costs to the test and would limit the global availability of institutions able to perform the test.

24. The group discussed whether these tests would be limited to just current lithium ion/metal technologies or whether they could be applied to new technologies, and how the tests could be revised to account for future developments, such as changing the heat of the test based on the cell/battery components. Some felt it was important to test the batteries to failure, beyond the reaction set point (RSP) or the point at which the reaction will initiate. It was noted that the total combustion energy released in a lithium ion battery is significantly less than that of gasoline. Thus, to determine what is acceptable, comparisons may be made

to existing products that are regulated but allowed for transport as dangerous goods. The Chairman noted the current procedure in sub-section 38.3 of the Manual of Tests and Criteria is identified as a classification scheme to determine eligibility for transport, but it doesn't allow categorization and it is really a qualification for lithium batteries for transport. It tests cells/batteries in foreseeable misuse conditions that may impact transport safety. It has been valuable, but it is not a true classification approach. The tests that are being considered in the working group are to measure the intrinsic hazards of the batteries, and define divisions or categories of cells/batteries based on level of hazard.

Tests identified from the November data review meeting

25. Based on analysis of the data, the November working group summarized some elements concerning basic tests for cells and batteries (See informal document INF.59, 52nd session):

(a) Cell tests

(i) Test 1- heating test to achieve complete combustion reaction (heating or fire, fire prevents the gas volume and composition to be analyzed because it is consumed in the combustion reaction): Combustion characteristics: Results (R) 1: Energy (heat), power, gas volume / gas composition, flame, (smoke and electrical hazards have been classified as secondary hazards in the working group, however it may be important for air transport).

(ii) Test 2- heating until it starts reacting, and test the propagation to adjacent test: Propagation characteristics obtaining the result R2: propagation/no propagation/ intermediate cases? (kinetics question, is fast or slow propagation important, criteria on mechanical aspects, maximum temperature and temperature of thermal runaway ignition, flame?).

(b) Battery tests

(i) Test 3- heating a cell inside the battery until it starts reacting, and test the propagation to adjacent cells: Propagation characteristics obtaining the result R3: propagation/no propagation/ intermediate cases? (kinetics question, is fast or slow propagation, mechanical aspects?) Other criteria could be the propagation from one battery to another?

(ii) Test 4 – external heat test that may lead to a total combustion of the battery

(c) Classification (C) criteria: probably two sets of criteria may be considered

(i) C1- set of criteria for acceptable/non-acceptable hazards in normal transport condition, per mode: possibly several levels, per hazard

(ii) C2 -set of criteria for acceptable/non-acceptable hazards in fire condition

26. Classification could then be based on test results:

(a) for cells: according Test 2 result:

(i) if R2 don't propagate: results R1 and R2 compared to C1= categories 1 and 2, or more?;

(ii) if R2 propagate: results R1 and R2 compared to C1= more categories;

(iii) Intermediate cases (according propagation rate, flame no flame, etc..): more categories;

(iv) Other cases to be considered…

(b) For batteries:

(i) A stepped approach is proposed, probably based first on the classification of the components cells (?);

(ii) Then, if the cell is propagating (or intermediate), another test is necessary to possibly “improve” the classification, the non-propagation being demonstrated at the battery level. Which test?;

(c) Test 3 corresponds to a cell failure, in normal transport conditions.

(i) If the cell is non-propagating, Test3 would not be necessary;

(d) Test 4 may be useful if a demonstration of less reactive battery (when compared to the sum of cells tested to Test 1) can be achieved when exposed to external heat.

(i) Test 4 may be useful if various thresholds are applicable according the duration of the test, the HRR, or other criteria;

(ii) Test 4 corresponds to the external fire condition.

27. It was noted again that the above testing approach does not fully address gas toxicity and that concern must be further investigated.

Propagation test for cells

28. The proposed test approach would start by determining if cells propagate, or not. The group clarified that the propagation determination would be between cells adjacent to one another, not considering packaging. The cell test would include 3 cells adjacent to each other in a plane. The third cell would be required to determine if intermediate effects observed in the second cell would lead to any effects in the third cell. Some participants noted that a propagation test addresses the reaction of cells to other cells, but it does not capture the intrinsic properties of a reactive cell. It would not address two cells of different properties in the same package. While this case may be rare, it is possible. Another approach would be to measure the amount of power or energy that is required to cause a cell to propagate and then determine the maximum power or energy released during a cell reaction. Even though the propagation approach limits to consignments of identical cells, it is still a valid and important approach and should be considered early in the testing process. Experience on such an approach indicates the testing would require multiple iterations (3 out of 4 tests may result in no reaction, what would one do if the fourth test failed?). The recommendation from the G-27 is that the test must be reproducible for 3 consecutive iterations without reaction to be considered to not propagate. It may also be necessary to modify the test if the reaction generates heat in a particular direction.

29. Recognizing that any propagation test will generate additionally data beyond simple propagation, the group discussed the value of measuring other characteristics (HRR, heat of reaction, etc.). These additional data points are more important for classification when the cell does not propagate. For example, if a cell generates gas and vents at a given temperature, it may be possible to use the gas generation volume to determine whether the cell still represents a significant hazard.

30. The working group agreed a propagation test is beneficial. It was also agreed additional parameters would be of benefit. But it was unclear whether a total combustion test

(such as ARC) would be necessary. Subcategories for non-propagating cells may be needed, and a total combustion test (such as ARC) may be appropriate to collect data for subcategory determination. This data could also be used for segregation determination for the modes.

31. Propagation speed or rate is also important but there is no clear data available for review. It was noted that the propagation speed would be affected by design. But the speed would give an idea of how long it may take for the reaction to result in a larger fire. Even if the propagation speed is slow, that does not mean the reaction will not occur immediately. Therefore, propagation tests may need to have observations immediately as well as over time (4 to 24 hours). An example was shared that when conducing such a test, the adjacent cell did not propagate immediately after the initial cell reacted. Instead it occurred 4 hours later. The belief was that the separator experienced limited melting, led to a short circuit over time, and eventually led to the reaction. Propagation speed could be divided into several subcategories:

(a) The cell did not propagate immediately but is instead deferred until several hours later. For this reason, observation may need to continue for 24 hours.

(b) Propagation is observed immediately:

(i) Speed of reaction is constant from cell to cell;

(ii) Speed of reaction increases as reaction spreads from cell to cell.

32. It was unclear if there is a need to sub-categorize based on propagation speed at this point but the group agreed that propagation speed is relevant and worth considering.

Tests on batteries

33. Following the testing scheme noted above, batteries would contain either cells that propagate or do not propagate:

(a) For cells that do not propagate, it might be considered that the battery would not need to be tested, and the battery may be considered of the same category as the non-propagating cell. This would assume the cell propagation test is the worst-case situation. However, there may be situations where non-propagating cells could propagate if electronics of the battery do not adequately protect the cells. The working group was requested to consider such a situation and provide data in the future if such a condition is possible;

(b) For cells that propagate, the cell category could also be applied to be battery. If additional design parameters are to be added in the battery to prevent propagation, a battery test would be beneficial to “improve” the categorization. Such a battery test (Test 3 noted above) would simulate a worst-case cell failure in the battery, and determine if propagation occurs inside the battery. The challenge would be to determine what is the “worst-case” situation. Flexibility on test methodology may be needed recognizing “worst-case” for one cell or battery design may not be the worst-case or another cell or battery design. But it was questioned whether cell propagation would truly be worst-case when considering module to module or battery to battery propagation;

(c) Test 4 would be a total heat of combustion test to compare the overall reactivity of the battery to the total reactivity of the cells due to cell/battery design. If Test 3 is not possible, Test 4 could also be used to improve categorization.

34. The group considered the propagation between intermediate elements within the battery. There was some agreement to check the ability for propagation between elements, but there was not agreement that checking this issue was completely satisfactory. Some

pointed out that it would be difficult to initiate modules in a homogeneous way but there was no agreement as the most effective way to initiate the event. The group was encouraged to review the issue for future discussions.

Remaining topics

35. The remaining two items to discuss include:

(a) Gas emissions (flammable or toxic gases); and

(b) whether packaging could be considered to modify classification (similar to Class 1 classification)

36. Regarding gas emissions, it was noted that materials constructed of plastics, when burned, emit toxic gases. Therefore, some participants were not supportive of including toxic gas considerations. Others pointed out lithium batteries are reactive and may develop heat. Hydrogen fluoride and other gases may need to be considered. But calculating the potential of hydrogen fluoride production may be significant higher than what would actually be produced. The actual amount may be equivalent to the volume produced when other products are heated or burned. Some cautioned that existing text in the Model Regulations would prohibit any generation of toxic gas in a package. The concern of toxic gas production in a suppressed fire condition (in aviation for example), must also be reviewed. Further work should consider the analysis or quantification of toxic fumes. Situations where cells or batteries do not propagate may be considered as less likely to produce significant amounts of toxic fumes.

37. Regarding packaging conditions, some participants agreed tests in packaging could be developed to reduce the risk in transport, but they preferred these situations remain transport conditions and not a classification issue, comparing the situation with Class 1 goods and recalling the difficulty in reclassification when packaging for explosives is changed.

Continued discussion on gas emissions

38. The group discussed the production of gas during heating and combustion of lithium batteries. Based on limited data, hydrogen represents 20-40% of the gas produced from lithium ion batteries. This results in a flammable gas mixture. Some lithium metal chemistries, such as LiMn, results in a similar gas production as lithium ion batteries. But other lithium metal chemistries may generate different gases. Gas volume increases with cell/battery size, which is logical. However, the measurement of gas production is challenging if combustion is occurring during the test. Some or all of the gas would be consumed in the combustion. Recognizing the production of flammable gas is a real result of lithium battery reactions, it is important to capture some characteristics of gas production.

39. The presence of flame may also impact the test. If flame is present, then the gas would be burned and would no longer be present. At that point, total heat of reaction would be a more representative value. But if flame is not present, then flammable gas volume and rate is important. It may be appropriate to collect information on rate of gas production, as well as the total gas emission potential of a cell/battery.

40. Some participants noted concerns with these batteries in the air mode:

(a) The Federal Aviation Administration (FAA) testing has shown that fires involving lithium metal batteries are not suppressible by current halon fire suppression systems in aircraft cargo compartments.

(b) Even if halon systems can suppress the flame of a lithium ion battery fire, the flammable gas production may result in an ignitable atmosphere that could result in an explosion or a pressure pulse that can disable the fire suppression system in the cargo compartment.

41. Some participants voiced caution in pursuing the gas flammability and toxicity for reactive batteries as these gases are produced during heating or a fire which is not a normal condition of transport. There are other dangerous goods that would also produce flammable or toxic gases during a fire or in situations that are not normal in transport. Therefore, if the group includes this line of investigation in lithium batteries, it would logically lead to reviewing these properties for other dangerous goods. Others noted that some of these types of intrinsic properties (production of flammable gas) is already considered for some substances. Water-reactive substances would be one example. Thus, it is worth considering the property, but it may be more appropriate to use the information for considering transport conditions.

42. At this point, in principle it is possible to use gas production and gas flammability to support cell/battery categorization. However, not enough data is currently available to discriminate groupings. Without additional data, it may be difficult to determine thresholds or levels of hazards. A way forward may be to determine volume and rate production of flammable gas for given a battery chemistry. This could either be used as part of the classification process, or it could be used by the modes to determine stowage requirements/limitations. But others cautioned that cargo space volumes of interest will be different for different modes. It was not clear whether this would be considered for classification or for transport conditions.

43. There was agreement that the production of flammable and toxic gas was an important parameter. However, there was no agreement as to whether the property should be included in the classification process or in transport conditions. The working group was encouraged to investigate the issues raised on this point, and suggest ideas that may be considered at future sessions.

Next steps

44. In summarizing the discussions of the meeting, the working group agreed that heat production and propagation potential are key properties to consider. Next steps would include development of categories and establishment of thresholds based on these parameters. However, as that work proceeds, it may become clear that gas production may be appropriate to provide additional discrimination to the resulting categories.

45. A conceptual flow-chart should be drafted to give a visual aid to the discussion. France, RECHARGE and PRBA indicated they would prepare a draft for review for the fifty-third session of the Sub-Committee.

46. Future meetings will be considered following the discussions at the fifty-third session of the Sub-Committee.