UN Informal Working Group on Lithium Batteries – 2019-2020

9-10 December 2020 – Video Conference

<u>Day 1</u>

Introduction

1. Claude Pfauvadel (France, Chairman), George Kerchner (PRBA) and Claude Chanson (RECHARGE) welcomed participants to the session. The intent of the meeting is to update the group on the testing that has been completed over the past 15 months and provide additional information as to next steps regarding propagation and test methods. Given the current restrictions on travel due to the COVID-19 pandemic, the group was not able to meet in person.
2. Agenda meeting:
   a) Day 1
      i. Review previous meeting minutes
      ii. Presentation of recent test data on propagation and initiation (presentation by Korea)
      iii. Review of test draft report by RECHARGE
   b) Day 2
      i. Presentation on propagation and initiation (presentation by MDBTC)
      ii. Clarify the learnings and remaining gaps for a relevant classification of lithium batteries hazards (i.e. question of applicability for intermediate reactivity cells, and non-reactive cells, others), and related test protocol.
      iii. Update on the discussion about the principles for the classification of lithium batteries according the hazards levels, and potential classification tree (proposals presentation).
3. Concept proposals and test data presented at the meeting are available from the RECHARGE Website https://rechargebatteries.org/sustainable-batteries/unsctdg/
4. In addition, all historical documents related to the current Informal Working Group are also posted on the RECHARGE Website.

Review of previous minutes

5. No comments were received on the previous minutes. The full text is available on the RECHARGE Website.

Presentation of recent test data on propagation and initiation (presentation by Korea)

6. A presentation from Korea was shared with the group. The tests involved included a total of 5 models(Pouch type: 2 models, Prismatic type: 2 models, Cylindrical type: 1 model) chosen according to cell type and chemistry are tested, and closed type case with venting hole, cartridge heater controlled by constant heating rate are specifically formulated to realize this test procedure.
7. The test parameters were slightly outside of the testing parameters used in other data collection activities but provide a good range of conditions:

8. Test parameters that need to be specified are SOC
    a. (20, 30, 50%)
    b. Case type (Closed type, Opened type)
    c. Heating rate (20, 100℃/ min, rapid heating)
9. It was noted by participants that the heating rate appeared to be very high, and that the measurement could have been on the heater itself instead of on the cell. If a cartridge heater was used, it may result in a non-uniform heating rate.
10. Results indicated that propagation occurred at cells at 50% SOC regardless of cell type and model. For cells at 20%, 2 of the witness cells (1 prismatic and 1 pouch) experienced thermal propagation and 2 (1 cylindrical and 1 pouch) did not.
11. When looking at case type (closed/open), cells in an open case took longer to propagate than those in a closed case, where thermal energy is trapped and contributes to heat transfer to adjacent cells. Both pouch cells experienced thermal runaway. However, Cylindrical cell at 50% in an open case did not propagate. In a closed case, the 50% cylindrical cell experienced thermal runaway.
12. Participants noted that orientation of the cells clearly matters. This might be a consideration of testing when shipping individual cells in a package vs. cells contained in a battery casing.
13. The Chairman commented the first test should be an intrinsic (worst case) test performed on cells but added that additional tests to consider propagation within a battery or package could follow.
14. Data was reviewed looking at different heating rates (20°C/min vs. 100°C/min). The data suggests that higher heating rates result in higher temperatures in the adjacent transfer cell but limit the amount of heat transferred to other cells (radiant).
15. Participants questioned whether the higher heating rates resulted in local failures and ruptures to the cells vs. the heat leading to thermal runaway of the cell. It was noted that cell design (where vents are located) can also have an impact on test results.
16. Korea made several conclusions based on their tests:
    a. SOC
        i. Cells are not classified at higher SOC in thermal propagation test because test results tend to be similar regardless of cell type, chemistry, thermal runaway is commonly created on witness cell with gas emission or flame if same experimental setup. Thermal propagation properties are varied according to SOC, and it should be conditioned by realistic simulation of transportation for practical risk levelling.
    b. Case type
        i. Thermal runaway tends to be occurred on a couple of cells at the same time in closed type case due to thermal insulation effect, the reason is because thermal energy released from multiple cells affects one cell on thermal insulation environment of closed type case continuously. It is far from realistic simulation of thermal propagation.
    c. Heating Rate
        i. The test result shows that rapid heating by cartridge heater has less influence on adjacent cells compared with slow heating rate and it affects the test result (thermal propagation time). Heating rate influence needs to be considered for more reliable test performance.

17. Participants noted that Appendix 1 included data on when flame/sparks were observed. This is important as not all cells eventually result in flame/gas ignition.
18. The Chairman voiced caution to the SCO reference in the presentation conclusion slide. SOC was noted to be based on transport condition. However, at present there are very limited conditions that require a particular SOC (ICAO TI (Air) for batteries shipped alone). The purpose for testing cells at lower SOC in this process is to simply see what happens when a cell with less energy is tested. Test results may lead to a recommendation on SOC limit, but this is not pre-determined at this point.
19. Participants discussed whether the open case type is realistic in transport. Some felt that regardless of cells shipped alone or in a battery, the case would be effectively closed and thus the heat/gas would be trapped and could contribute to thermal propagation. The testing that has been directed by the Lithium Battery Working Group (LBWG) has been done in a closed case for this reason. However, the value of testing in an open case can simulate cells that vent to an outside location.

Lab Test Plan, Phase 1 and 2 result analysis

20. RECHARGE presented the results of Phase 1 and Phase 2
    a. Phase 1 were tests at 100% SOC, pouch and cylindrical, 6 cells in a row. 7 labs participated.
    b. Phase 2 were tests on varying SOC, determine if heating rate and SOC impacted results. 9 labs participated.
21. Phase 1 resulted in a number of conclusions. These are captured in the RECHARGE report.
    a. At 100% SOC, all cells resulted in thermal runaway.
    b. Participants noted that the total energy released from the cells during the tests was approximately 60 kJ. This matches the maximum energy contained within an 18650 cell by NASA.
    c. Propagation time was greatly reduced for pouch cells vs. cylindrical cell due to ease of heat transference.
    d. Thermal Runaway onset temperature was not identified. It was noted that some measure onset temperature as when a rapid temperature increase occurs, whereas others identify it as the temperature immediately before a spike in temperature is measured.
    e. At 100% SOC, there was no clear correlation between thermal runaway onset temperature and heating rate.
    f. Participants noted that heat flux may be more important than heating rate. The Chairman added that there may be other factors that have yet to be identified that may have a greater impact on test results. He encouraged the group to stay open to additional factors that must be considered.
    g. In pouch cells, propagation rate was not impacted by heating rate, despite pre-heating for lower heating rates.
    h. Maximum temperature also did not differ between initiation method/heating rate, etc.
    i. Using maximum temperature as a measure, differing test conditions between laboratories led to differences in the results. When test labs conducted tests under

similar conditions, the results were very similar. Thus, standardizing the test conditions will support reproducibility.

j. Using propagation rate as a measure, differing test conditions between laboratories led to differences in the results as well. But in this case, the challenge was with repeatability of the test. This may be a result of the failure mechanism being different for each cell, even using the exact same testing method.

22. Phase 2 was to test effect of heating rate and SOC on propagation for 6 cells in a row.
    a. Effect of SOC on max temperature did not have a significant impact, except when propagation did not occur (20% SOC).
        i. The repeatability of results is much greater than reproducibility between laboratories, particularly at 30-50% SOC.
        ii. Dispersion increases at the point of transition for propagation (30-50% SOC). In case of propagation, the max temperature is not significantly reduced between 100-50% SOC.
    b. Effect of SOC on propagation time – contrary to max temperature, propagation time changes when measured in same laboratory.
        i. When comparing effect of SOC on propagation time and onset temperature, the lack of repeatability means the impact is not truly measurable.
    c. Gas Analysis under nitrogen atmosphere
        i. At higher SOC, the volume of gas generated is higher, and the gas composition is less oxidized (hydrogen content is higher and ration CO/CO2 is higher). As a result, it can be concluded that at higher SOC, the gas hazard due to flammability or explosion properties will increase.
    d. Gas analysis under atmosphere
        i. The same results were observed as in propagation test; no significant effect of the heating rate on the TR maximum and onset temperatures, but a significant effect on the high SOC, reducing the onset temperature and increasing the TR maximum temperature.
    e. It appeared that the quantity of gas emitted is higher at higher SOC. Nevertheless, the emitted gas volume is sensitive to the heating rate only at higher SOC with a factor almost 2 between 5 and 20^{o}C/min.
    f. Additional Data sources
        i. CATL Presentation about large cells testing (Oct 2019)
        ii. LG data about various cells testing (Dec 2020)
        iii. FAA presentation about gas production
        iv. Additional data from NASA on cell testing – Data collected includes energy released from cell in ejecta, but also what remains in the cell. Their results may be beneficial to review in depth for the efforts of this group.
    g. Participants discussed the fact that experience shows sidewall failures of cells leads to propagation nearly 100% of the time. In cell design therefore, wall failure is to be avoided if possible. There are ways to avoid cell wall failure, including modifying the test conditions, which can camouflage negative results. Thus, it would be important for the group to consider this issue in the future.

23. The FAA presented their results on gas production during cell initiation.
    a. Used a 21.7 L containment vessel.

b. CO, CO2, total Hydrocarbons (THC), and Hydrogen were identified as the critical gases to be measured.
    i. It was noted the percentages of flammable and toxic gases would be beneficial to review.
c. Increasing in heating rate resulted in combustion energy for 18650 cells and pouch cells
    i. For pouch cells, the difference in combustion energy was pronounced in lower states of charge.
d. Participants discussed how the data compared to testing results from other laboratories, noting the challenges with the different test variables from the other tests. The purpose of the FAA tests was to determine baseline gas production for lithium ion cell reactions. Additional tests could be conducted to look at more transport condition reactions (nitrogen vs. air atmosphere).
e. The FAA concluded that:
    i. Heating rate affects the combustion hazards due to thermal runaway, especially at lower states of change
    ii. It is important to test in nitrogen to measure the combustion hazard.
f. Quicker heating rate allows heat to build up in cell and not vent with gas release. The suggestion is that heating rates above 10^{o}C/min is preferred, and results are similar with gas production up to 30^{o}C/min.

<u>End of Day 1</u>

<u>Day 2</u>

Presentation on battery initiation technology – KULR

24. Common reasons for cell failures related to initiation method
    a. Non-transport related
        i. Overcharge and external short circuit
        ii. Over-discharge
        iii. Low temperature and high-rate charging
        iv. Thermal stress and high temperature use
    b. Transport related
        i. Mechanical stress
        ii. External short (for cylindrical cells CID will cutoff current
        iii. Manufacturing defects – defect occurs before transport. Unclear how defect leads to failure in transport.
        iv. External fire
25. Participants note that NASA and others observed manufacturing defects leading to failure during transport due to shocks or vibrations, or when charging/discharging leads to overcharge conditions, that then lead to unstable conditions in the battery in transport.
26. Cell characteristics significantly influence the volatility and cell failure mode, and not all cells are created equally. Heat release is a function of cell chemistry, capacity, SOC and form factor. Propagation prevention can only be achieved when you know how the cell reacts in

the thermal runaway. Therefore, they believed it was critical to study what actually happens when the cells react to determine proper safety testing methodology.

27. Results of testing suggest:
    a. Slow ramp rate doesn't determine failure
    b. Location of heater will influence failure mode.
    c. Type of heater determines failure. Patch and rod heater have higher chance of sidewall rupture.
    d. Uniform heating of cell has highest chance of temp vent
28. In looking at thermal Runaway Trigger Mechanisms, internal short circuit (ISC) trigger cells appear to be more effective that other methods. ISC trigger cells provide same and uniform temperature for all cells. The result is closest to an internal short circuit. The location of internal short is the same for all tests. They also remove additional materials for heating of pack which reduces heater influence on results.
29. Participants discussed the challenges of cell initiation and their impacts to test results. A single method to heat the cell may not be practical due to heat dispersion or other factors that are due to cell design or test setup. The ability to use different heating technologies is important to ensure effective test initiation. It was suggested that flexibility be retained in test setup to allow for several of the cell initiation methods.
30. It was requested that additional demonstrations on cell initiation methods be provided. Significant data has been collected by NASA and others on cell initiation and cell failure, and that data can be used as part of the Working Groups efforts.
31. In order to use the ISC trigger cell, the cell manufacturer must create the first cell (retrofitting a cell would not be possible). This introduces challenges with proper placement of ISC device in cell and requires more direct action by cell manufacturers.
32. The WG requested more comparison between ISC trigger cell and electrical heating. The group was open to allowing the ISC method as an alternate cell heating method. But it was noted the cell heating technology (ISC or otherwise) must be readily available and should not limit one specific product or technology. Instead, a number of methods that may be effective should be permitted.

Toxicity of vent gases - BAM

33. BAM shared research on the toxicity of vented gases from lithium ion battery as a result of thermal runaway. They conducted a literature search on existing documentation on the topic. They reviewed approximately 50 articles.
34. Looking at toxic gases, they reviewed:
    a. Hydrogen Fluoride
        i. Pouch cells emitted significantly more HF than cylindrical cells at 100% SOC.
        ii. HF has a AEGL value at 10 minutes of 95 ppm.
        iii. For comparison, an e-bike battery that vents using pouch cells contained in a 40 ft container could result in an atmosphere at 260 ppm.
        iv. In looking at varying SOC, HF was release between 3-170 mg/Wh at 100% SOC. But at 0% SOC, the release was between 10-200 mg/Wh.
    b. Carbon monoxide
        i. Both cyldrindrical and pouch cells release large abouts of CO
        ii. CO has AEGL value at 10 min of 420 ppm

    iii. For comparison, an e-bike battery that vents using pouch cells contained in a 40 ft container could result in an atmosphere at 1,100 ppm.
    iv. CO release was not impacted by SOC, however.

35. Participants discussed the fact that some of the gas production may be increased due to the test methodology. Lower heating ramp rate might give more time for gas release.

[GAP] – missed discussion – to be filled in by participants

36. Preliminary conclusions for discussion
    a. There is more difference between labs than within one lab
    b. Test description must be more specific and precise
    c. Identified effect of:
        i. Absence of lid on test chamber
        ii. Various efforts for cells compression during test
        iii. (Partially) heating rate range
        iv. Method for identification (max temperature, onset temperature
        v. Others to be discussed
37. Participants discussed whether the cause of the failure is relevant or whether propagation of the cell is an absolute (no regard for reason for cell failure).

Test Protocols to date

38. INERIS and RECHARGE reviewed the existing testing logic diagram and the proposed propagation test protocols. It was noted that based on the discussion from this meeting, the method of trigger cell initiation needs to be flexible to allow for use of a method appropriate for the cell design, etc. Objectives of the test is to assess:
    a. Initiation
    b. Propagation
    c. Fire
    d. Temperature
39. The trigger cell initiation is not intended to mimic any type of abuse in transport, but instead is intended only to send the cell into thermal runaway to determine of cell propagation occurs.
40. Based on testing to date, several key parameters were identified that have significant impacts on testing results:
    a. Cell positioning – cells need to be vertically oriented, touching each other, slightly compressed (especially for pouch cells) and not electrically connected.
    b. Number of cells – currently using 6 cells. Should it be reduced to less? 4?
    c. Insulation – 4 sides + lid is critical for consistency of tests. Thermal conductivity of insulation must be <0.2 W/mK. Insulation must also be rigid and maintain cell compression.
41. Participants discussed whether cells needed to be oriented vertically. Originally, the orientation of the cells was identified to limit the vent positioning to one direction. However, with the requirement for a lid, venting in any direction would be captured in the test compartment. Therefore, it may be possible to permit different cell orientation.

42. Cell compression was also discussed. INERIS shared that cylindrical cells were minimally compressed (only enough to ensure cell to cell contact). For pouch cells, compression equal to that experienced when installed in a battery or battery pack is introduced. It was noted that in battery designs, there is typically foam or other compressible material to permit cell expansion. However, in the test, compression should only be necessary to maintain consistent cell to cell contact. A pressure should not be defined. Given that the goal is worst case conditions of cell propagation, additional protections would be considered for battery designs and eventually possibly in battery testing. But protections should not be used for cell propagation tests.
43. Regarding the number of cells, some recommended the number be reduced to 3 or 4 given the increased number of possible variables that could lead to intermediate cells failing to impact the witness cell. While that may be acceptable for cylindrical cells, some noted 6 cells were needed to be maintained for pouch cells.
44. Additional parameters that are important:
    a. Heater
        i. Small enough to not excessively heat adjacent cell (not trigger cell)
        ii. Must be less than 0.25" diameter (for cylindrical) and no longer than the cell
        iii. Must be thermally insulated
        iv. Can be cartridge, pad, micro mica, wire
    b. Heating protocol
        i. Start at 20 +/- 5°C
        ii. Heating rate proven to not be crucial
            1. A min and max rate should be fixed (5°C/min to 40°C/min)
            2. Heating temperature measured on the cell, not the pad
            3. Heating stopped when thermal runaway is achieved.
45. Participants discussed the need to designate energy input or at least heat flux to ensure proper application of the heater. Some of the heaters noted may lead to charring and ineffective cell heating. Also, the rate of heating may be too large. Goal was to be near 20°C/min. thus the maximum rate may be more appropriately 25-30 °C/min. it was agreed the rate of heating would be discussed separately by interested parties.
46. Regarding Data
    a. Data Recording
        i. 1 T/C type K per cell - important for positioning
            1. Avoid interfering with cell to cell contact
            2. Mid-height of cells at 1:30 position for cylindrical
            3. Mid-height of cell on edge for pouch cells
        ii. No voltage measurement necessary
        iii. Collection at 1 Hz (at least) or possibly 5 Hz
    b. Data reporting
        i. When a type-K thermocouple records temperature higher than 1200°K – temperatures recorded are not representative of actual conditions
        ii. Need a clear definition of thermal runaway to define
            1. Onset temperature
            2. Propagation time
    c. Test validity

    i. Reproduce test 3 times
    ii. If a cell ejects its core, rerun the test and record event
    iii. If a cell has a sidewall rupture, rerun the test and record event

47. Regarding gas evaluation
    a. Done with one cell
    b. Is it necessary to use thermal insulation?
    c. Under argon, air, or other gases?
    d. Emitted volume assessment by pressure measurement – this is easily to measure between labs
    e. Composition of gas measurements – very difficult to measure and expected to be less producible between labs.
    f. Group agreed need to analyze test results and discuss a protocol to determine how this parameter will relate to hazard characterization.
48. Group needs to determine how to evaluate cells that do not propagate or will not initiate based on protocol. Consideration of a bonfire test? Such a test would then measure all component materials. Might have to perform calculation on total amount of combustible materials to properly determine hazard represented.

Next Steps

49. The WG agreed to review the proposed the protocol as presented in the INERIS/RECHARGE presentation available from the RECHARGE website.
50. Specific parameters in question should be identified and presentations on variations prepared for the next meeting.
51. Further, the propagation concept needs to be expanded to include batteries (both cell propagation within a battery, and propagation between batteries).
52. Participants discussed the possibility of holding monthly or quarterly telephone conversations. Laboratories will plan a separate call to discuss test methodology. Additional group will consider calls to further develop details of testing/protocol.
53. INF paper for June 2021 UNSCOE session to be developed.

Schedule of next meetings

54. February/March 2021 – telephone conversation with laboratories over methodology
55. February/March 2021 – telephone conversation to discuss how to move from cell to batteries
56. April 2021 – Brussels, Belgium – meeting of full IWG depending on COVID-19 travel restrictions

<u>End of Day 2</u>