DANGEROUS GOODS PANEL (DGP)
WORKING GROUP MEETING (DGP-WG/24)

Montreal, 21 to 25 October 2024

Agenda Item 4: Managing safety risks posed by the carriage of lithium batteries by air (Ref: Job Card DGP.003.04)

PROGRESS ON EFFORTS TO RELAX TRANSPORT REGULATIONS FOR ALL-SOLID-STATE BATTERIES AT THE UN SUB-COMMITTEE

(Presented by T. Tabata)

SUMMARY

The 2023 DGP Working Group Meeting (15 to 19 May 2023, Rio de Janeiro) was provided with a report on non-thermal runaway lithium-ion cells currently being developed (see paragraph 4.4.1.10 of the DGP-WG/23 Report). Based on the advice of ICAO, an informal document was presented to the sixty-third session of the UN Sub-Committee of Experts on the Transport of Dangerous Goods (UN/SCETDG/63/INF.24), and a working document was presented to the sixty-fourth session (ST/SG/AC.10/C.3/2024/42). UN/SCETDG/63/INF.24 discussed the risks associated with battery transport, highlighting the importance of preventing thermal runaway and ensuring that the contents do not leak externally. ST/SG/AC.10/C.3/2024/42 proposed updates to the UN Model Regulations based on the UN-IWG's T9 test conditions, which are designed to induce thermal runaway at 64UNSCETDG.

This document aims to share the current progress and future plans regarding these developments. During the Subcommittee meeting, some comments were given from experts. While some opinions indicated that the proposals were still insufficient, they were generally accepted. However, it was determined that the T9 test conditions required for confirming thermal runaway by the UN Informal Working Group on Lithium Batteries (UN-IWG) will not be established during this period. Japan's experts made the decision to abandon the establishment of its proposal for this period. Therefore, it has been decided to prepare new proposals for the next two years, considering future discussions and developments from the UN-IWG.

Within the UN-IWG, Battery Association of Japan (BAJ) has proposed new test conditions as a screening test, with plans to submit a formal proposal after 2025. While the proposal was not accepted, there was an understanding within the

UN-IWG regarding the necessity of a screening test to determine the presence or absence of thermal runaway.

Japan will continue to collaborate with the UN-IWG on proposals to relax transportation regulations for non-thermal runaway lithium-ion cells. We welcome any comments on Japan's approach and look forward to your feedback.

1. BACKGROUND

1.1 The 2023 DGP Working Group Meeting (15 to 19 May 2023, Rio de Janeiro) was provided with information and propagation test data of all solid-state lithium-ion cells based on the hazard-based classification test protocol that an informal working group (UN-IWG) of the UN Sub-Committee of Experts on the Transport of Dangerous Goods (UNSCETDG) was developing[1]. Propagation and thermal runaway did not occur in any of all-solid-state lithium-ion cells tested, and the temperature of the initiation cell did not exceed the temperature of the heating plate. The test results suggested that these batteries did not pose the same level of risk to transport as conventional lithium-ion batteries. Therefore, it was suggested that they should not be subject to the same stringent transport requirements.

1.2 Based on the advice at DGP-WG/23, an informal document was presented to the sixty-third session of the UN Sub-Committee of Experts on the Transport of Dangerous Goods (UN/SCETDG/63/INF.24)[2], and a working document was presented to the sixty-fourth session (ST/SG/AC.10/C.3/2024/42)[3]. UN/SCETDG/63/INF.24 highlights the importance of preventing thermal runaway and ensuring that the contents of the cells do not leak externally. The propagation test was done in which the temperature of each all-solid-state lithium-ion cells were raised to 350°C. And also, Accelerating Rate Calorimetry (ARC) analysis was done in which the temperature of each all-solid-state lithium-ion cells was raised to 400°C or 500°C.

1.3 In ST/SG/AC.10/C.3/2024/42, proposals for the UN Model Regulations were made, based on the propagation test condition that was designed to induce thermal runaway by UN-IWG. And the provided data was heating test that raised to 350 °C with high capacity (200mAh) all-solid-state lithium-ion cell.

1.4 The purpose of this information paper is to share information with ICAO stakeholders regarding the progress of activities aimed at relaxing transportation regulations for all-solid-state lithium-ion cells and component cells, and upcoming plans.

2. CURRENT STATUS

2.1 During discussions at UN/SCETDG/63, six main comments were expressed by experts regarding UN/SCETDG/63/INF.24:

a) With regard to the comment that a verification test should include not only heat but also heat with vibration, the vibration is a trigger that causes an internal short circuit,

[1] DGP-WG/23-IP/11
[2] UN/SCETDG/63/INF.24
[3] ST/SG/AC.10/C.3/2024/42

but even if an internal short circuit occurs in a particular cell, the cell will only become hotter, so it would be enough if it could be verified that it is stable at high temperatures.

b) With regard to the comment that lithium-ion phosphate (LFP) cells should also be tested under the same conditions, tests on LFP cells have been conducted by the informal working group under almost the same conditions as provided in informal document INF.24 and the occurrence of thermal runaway has been confirmed.

c) With regard to the comment that it was difficult to define the target cells because there are also unclear cells such as semi-solid-state lithium-ion cells, the electrolyte of the target cells are defined as using inorganic solid-state material only, and the melting point or sublimation point of the cell materials are defined as not being below 250 °C, so only completely solid-state lithium-ion cells are defined.

d) With regard to the comment about dendrite risk of all-solid-state lithium-ion cells, a dendrite risk is likely to occur when a cell electrode material is lithium metal, but unlikely to occur on the all-solid-state lithium-ion cells because their electrode materials are not lithium metal, therefore, an internal short circuit due to a dendrite is also unlikely to occur. Furthermore, even if an internal short circuit occurs in a target cell, it will not cause propagation as explained in paragraphs 19 and 20 of informal document INF.24.

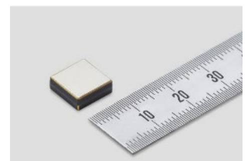
e) With regard to the question about the basis for the condition requiring the melting or sublimation point not below 250 °C, having considered the balance between high temperature stability, and selectivity and availability of materials, we concluded that such condition would be appropriate. However, since the propagation test developed by the informal working group requires the cell's temperature to reach 350 °C, the melting down of solid electrolytes which have functions of insulation and the melting down of casing which may lead the release of contents need to be prevented at that temperature. Therefore, the melting or sublimation point of inorganic solid electrolytes and casing materials among others should not be below 350 °C.

f) With regard to the question of whether these characteristics would be maintained as the capacity of cells increases, it doesn't cause the thermal runaway even when tested with a cell capacity increased by 25 times as shown in figure 2. This result is considered to be because the melting point or sublimation point of the inorganic solid electrolyte is not below 350 °C, therefore even large-scale capacity cells with an inorganic solid electrolyte with a melting point or sublimation point not below 350 °C will exhibit similar characteristics.

2.2 A test of high temperature heating with a cell of 25 times the capacity of the Type A cell referred to in informal document INF.24 was carried out. Features of the tested cell are shown in table1. Compared to the Type A cell, the cell capacity and shape of the tested cell are different, but materials of its positive electrode, negative electrode and electrolyte, and cell voltage are the same.

Table 1: Features of large capacity all-solid-state lithium-ion cell

	Type D	*Type A (reproduced)*
Nominal capacity (mAh)	200	8

	Type D	*Type A (reproduced)*
Nominal voltage (V)	2.3	Same as left
Cell size (mm)	ϕ 22.7/27.3	10.5/10.5/4.0
Cell weight (g)	22	1.2
Type of positive electrode	Lithium cobalt oxide	Same as left
Type of negative electrode	Lithium titanium oxide	Same as left
Type of electrolyte	Sulphide-based solid electrolyte	Same as left
Appearance		

2.3 The configuration of the high temperature heating test for the type D cell is shown in figure 1. This test is similar to the propagation test developed by the informal working group and the fully charged cell was heated to 400 °C. The cell temperature transition is shown in figure 2.

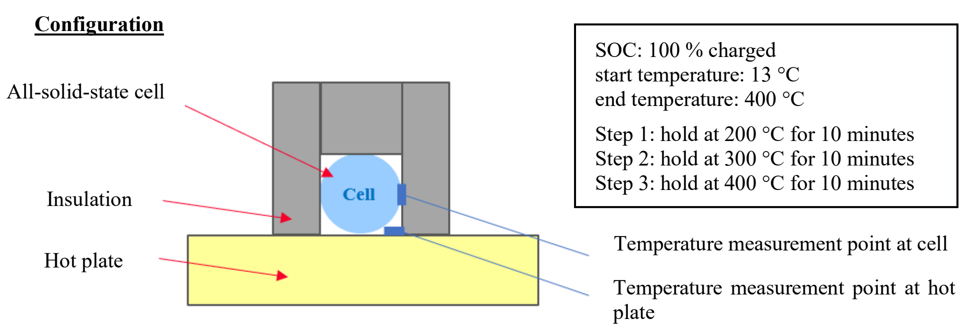
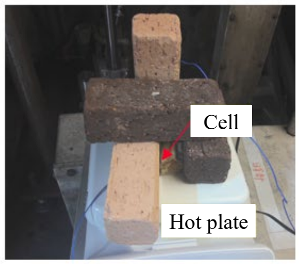


Figure 1: Type D, outlook of the high temperature heating test similar to the hazard-based classification testing protocol



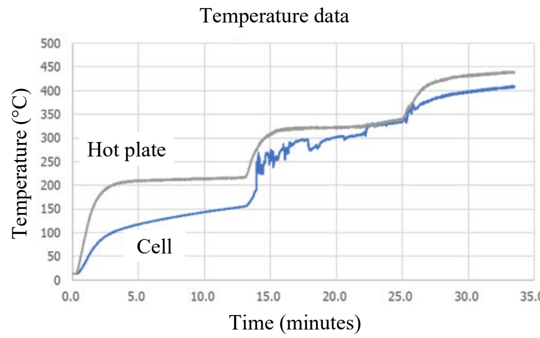


Figure 2: Type D, high temperature heating test results (no rapid temperature rise)

2.4 As shown in the temperature data in figure 2, there is no self-heating above the ambient temperature and no sign of thermal runaway. This characteristic is the same as that of the other cells introduced in informal document INF.24. There was no tendency for the cell temperature to rise rapidly even as the capacity increased.

2.5 At 64UNSCETDG, it is proposed to insert in 3.3 of the Model Regulations a new special provision applicable to UN 3480 and UN 3481 to exclude lithium-ion cells and batteries that satisfy the following conditions from the application of the regulations as follows:

"XXX: Cells and batteries offered for transport are not subject to other provisions of these Regulations if they meet the following conditions:

(a) cells and batteries meet the provisions of 2.9.4 (a), (e) and (g);
(b) cells and component cells satisfy the following (i) -(ii):
   (i) the melting point or sublimation point of cells' and component cells' materials electrolyte and casing materials is not below 350 °C and of other materials is not below 250 °C; and
   (ii) only an inorganic solid is used as for their electrolyte;
(c) cells or component cells do not cause thermal runaway, rupture, fragmentation, or ignition in the propagation test provided in paragraph [38.3.6.1.2] of the Manual of Tests and Criteria,; and
(d) cells and batteries are protected from short circuits. When cells and batteries are installed in equipment, the equipment is provided with an effective means of preventing accidental activation. These requirements do not apply to devices which are intentionally active in transport and which are not capable of generating a dangerous evolution of heat."

2.6 As a result, while some opinions indicated that the proposal was still insufficient, it was generally accepted. In the Subcommittee, views expressing inadequacy were raised, but the information provided was acknowledged, and Japan's proposal was recognized. However, since the T9 test conditions, which were intended to confirm thermal runaway, were determined not to be established during this session, Japan had to abandon the establishment of its proposal at this time. At the UN, it was suggested to prepare a new proposal for the next two years, considering future discussions and developments from the IWG.

2.7 Based on the comments from the UN, new test conditions were proposed by BAJ at the UN-IWG held in Washington, starting August 27, 2024. This is positioned as a screening test, with plans for a proposal to be made after 2025.

38.3.6.1 Test T.9: Cell propagation test

[…]

38.3.6.1.4. Purpose of alternative test T.9a : heating test

The purpose of the test is to screen cells or batteries that do not undergo ignition when fully charged by a simple test.

38.3.6.1.5 Test procedure

The heating test is conducted by placing one cell inside a thermally insulated test fixture designed to tightly maintain the one cell. The cell shall be placed with the heater on the side of the cell. If the battery is small, you can use the method of applying heat to 1 of 6 sides. The quality of direct contact will be ensured by use of rigid test fixtures, or in the case of flexible material, by use of a compression force of the row of 1 kg force. The test fixture must have 6 sides to maximize heat containment. The test fixture shall have the required mechanical robustness to contain all mechanical ejections, including through the lid, but allow for gas and flame exhaustion.

[The cell shall be heated with a device enabling a heat transfer to the cell at an initial rate of [20 ± 2] Watts/cm2 [other unit in W/mm2/kg cell] [examples of devices are heating wires, copper contact shapes, …]. The size of the contact surface between the cell and the device shall not exceed 20 % of the total cell surface, with a minimum of 10 mm2]. The efficiency of the heat transfer shall be controlled by a thermocouple placed at 5± 2 mm of the side of the heating device.

As a result, the cell should be heated at a rate of [15 ±10 °C per minute, TO BE AGREED UPON - REFERENCE TO UN GTR/ISO 6469-1 TO BE CHECKED IF APPLICABLE TO LARGER CELLS], based on the measure of the control thermocouple. The power of the heater shall be controlled manually or electronically to maintain the heating rate constant during the whole test duration. The heater power shall be cut off when a thermal runaway is detected (detection of a continuous increase of the temperature of the initiation cell without increase of the heater power for more than 3 minutes, or when the cell temperature has reached 375°C for at least 1 minute. The data are recorded for 6 hours after stopping power to the heater.

The maximum temperature determination is based on the use of a thermocouple on the cell. To capture the maximum temperature during the test the thermocouple will be insulated from any test fixture contact. The thermocouples shall be thermally protected against direct ambient gas temperature measurement.

38.3.6.1.6 Testing of lithium cells

When testing rechargeable lithium cells under test T.9a the following shall be tested in the quantity indicated.

(i) one cell at first cycle, in fully charged states:

38.3.6.1.7 Test criteria

The cell does not cause fragmentation or ignition in the heating test.

2.8 Although the proposal was not accepted, the UN-IWG achieved an understanding of the necessity for a screening test to determine the presence or absence of thermal runaway. Moreover, there were no opposing opinions regarding the test conditions.

3. FUTURE ACTIVITIES

3.1 Japan will continue to collaborate with the UN-IWG on proposals to relax transportation regulations concerning non-flammable batteries. We welcome your comments on Japan's approach and any feedback you may have.

— END —