



**Committee of Experts on the Transport of Dangerous Goods
and on the Globally Harmonized System of Classification
and Labelling of Chemicals****Sub-Committee of Experts on the Transport of Dangerous Goods****Sixty-fourth session**

Geneva, 24 June-3 July 2024

Item 4 (f) of the provisional agenda

Electric storage systems:**Miscellaneous****New special provision for all-solid-state lithium ion cells and
batteries (UN 3480 and UN 3481) that do not cause thermal
runaway****Transmitted by the expert from Japan*****I. Introduction**

1. At the sixty-third session of the Sub-Committee, Japan presented informal document INF.24 to propose a new special provision for all-solid-state lithium ion cells and batteries (UN 3480 and UN 3481) that do not cause thermal runaway. The Sub-Committee noted a number of comments on informal document INF.24 and acknowledged that further work was necessary. The informal working group was invited to resume discussion of this subject when considering a new classification method based on hazards.
2. At the subsequent informal working group, informal document INF.24 was introduced and it was concluded that the Sub-Committee would need to define how to address situations where a cell does not enter into thermal runaway.
3. Consequently, taking into account the discussions at the Sub-Committee and the informal working group, Japan proposes a new special provision for all-solid-state lithium ion cells and batteries that do not cause thermal runaway.
4. This proposal contributes to simplifying the transport procedures, it is linked to Sustainable Development Goal (SDG) 9 “Build resilient infrastructure, promote inclusive and sustainable industrialization and foster innovation” and SDG 12 “Ensure sustainable consumption and production patterns”.
5. Japan invites the Sub-Committee to revisit the information in informal document INF.24 from the sixty-third session, sections I to IV (section V containing a proposal is superseded by the updated proposal included below).

* A/78/6 (Sect. 20), table 20.5.

II. Discussion

6. During discussion at the sixty-third session of the Sub-Committee, mainly six comments were expressed by experts on informal document INF.24.

7. 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, 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.

8. 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.

9. 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.

10. With regard to the comment about a 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.

11. 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.


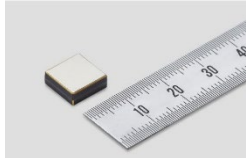
12. With regard to the question of whether these characteristics would be maintained as the capacity of cells increases, it doesn't cause the thermal runaway even when tested with a cell capacity increased by 25 times as shown in figure 16. This result is considered to be because the melting point or 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.

III. Additional test data¹

13. 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 table 3. 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.

¹ The author of the test results gave the authorization to use the materials contained in the section for the purpose of the discussion at the sixty-fourth session of the Sub-Committee of Experts on the Transport of Dangerous Goods. For reproduction permission and all other issues, please contact inose@baj.or.jp.

Table 3: Features of large capacity all-solid-state lithium ion cell.

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

14. The configuration of the high temperature heating test for the type D cell is shown in figure 15. 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 16.

Figure 15: Type D, outlook of the high temperature heating test similar to the hazard-based classification testing protocol.

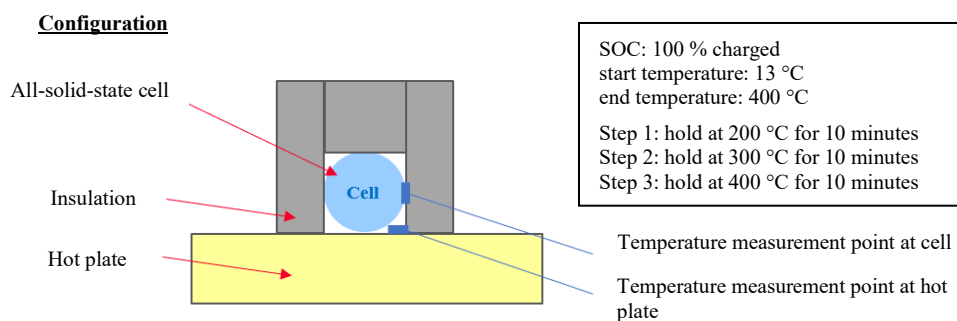
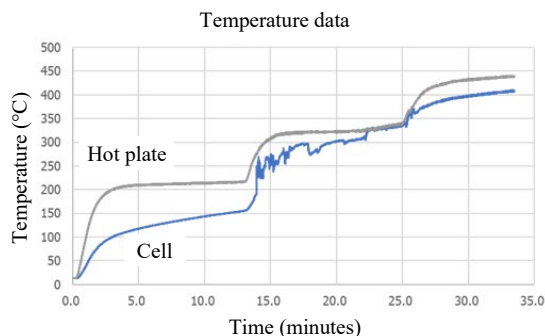
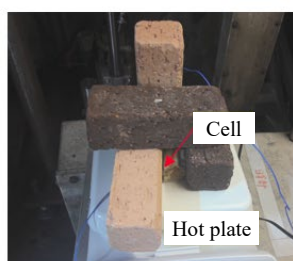


Fig. 16: Type D, high temperature heating test results (no rapid temperature rise).



15. As shown in the temperature data in figure 16, 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.

IV. Conclusion

16. Regarding the conditions, the following points are changed from the proposal in informal document INF.24. In sub-paragraph (i) of (b), only the melting point or sublimation point of the electrolyte and casing materials is changed from 250 °C to 350 °C. Additionally, since the proposed special provision applies to UN 3480 and UN 3481, the possibility of containing lithium metal is excluded. By this reason, sub-paragraph (iii) of (b) is deleted. Furthermore, even if deleted, stability at high temperatures can be ensured by the condition provided in sub-paragraph (i) of (b).

V. Proposal

17. Based on the above, 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 (Added texts to the draft special provision proposed in informal document INF.24 are underlined, deleted texts are in ~~striketrough~~):

“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)–(iii)~~:
 - (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; ~~and~~
 - ~~(iii) cells or component cells are not made of lithium metal and/or combustible materials;~~
- ~~{~~(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*, ~~xx.x.x.x~~; } ~~}~~ 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.”