Committee of Experts on the Transport of Dangerous Goods and on the Globally Harmonized System of Classification and Labelling of Chemicals

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Electric storage systems:
Miscellaneous

Proposal of 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. Currently, in the lithium ion battery industry, due to advances in material and manufacturing technologies, some companies are developing the all-solid-state lithium ion batteries that have extremely high stability and reliability against heat. The component cells of all-solid-state batteries can be mounted by a reflow process that attaches some components directly on the board by generally heating up to 260 °C, and the capacity is as small as 20 Wh or less. Such all-solid-state lithium ion cells are expected to be commercialized one after another in the near future.

2. These all-solid-state lithium ion cells differ in material and structure from the usual lithium ion cells and batteries (conventional lithium ion cells and batteries), which are currently the most widely used power sources for portable electronic devices. Table 1 below shows a comparison of the constituent materials between all-solid-state lithium ion cells and conventional lithium ion cells. The all-solid-state lithium ion cells have solid positive and negative electrodes just like conventional lithium ion cells. The all-solid-state lithium ion cells use inorganic solid electrolyte instead of a flammable organic liquid electrolyte which are used in conventional lithium ion cells. In addition, the standard conventional lithium ion cells have a separator made of resin or the like is sandwiched to prevent physical contact between the positive and negative electrodes, but all-solid-state lithium ion cells don't have the separator, because a rigid inorganic solid electrolyte separates both electrodes and avoids short-circuits (Fig.1). As for the operating principle, the all-solid-state lithium ion cells are charged/discharged by insertion/desorption of lithium ions at the positive/negative electrode in the same manner as conventional lithium ion cells (Fig. 2).

Table 1: A comparison of the constituent materials between all-solid-state lithium ion cells and conventional lithium ion cells

Constituent material	All-solid-state lithium ion cells	Conventional lithium ion cells
Positive electrode	L[NMC]O, LCO, LFP, etc. (Solid)	
Negative electrode	Graphite, Carbon material, LTO etc. (Solid)	
Separator	None	Polyolefin, Paper, etc. (Solid)
Electrolyte	Oxide-based solid electrolyte, Sulphide-based solid electrolyte, etc. (Non-flammable Solid, Non-dangerous goods)	Organic liquid electrolyte (Flammable liquid, Dangerous goods)

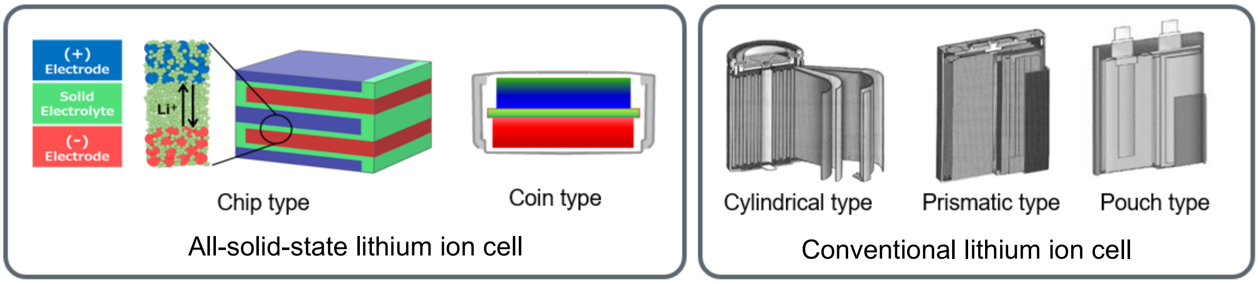


Fig.1: Schematic diagrams of all-solid-state lithium ion cells and Conventional lithium ion cells

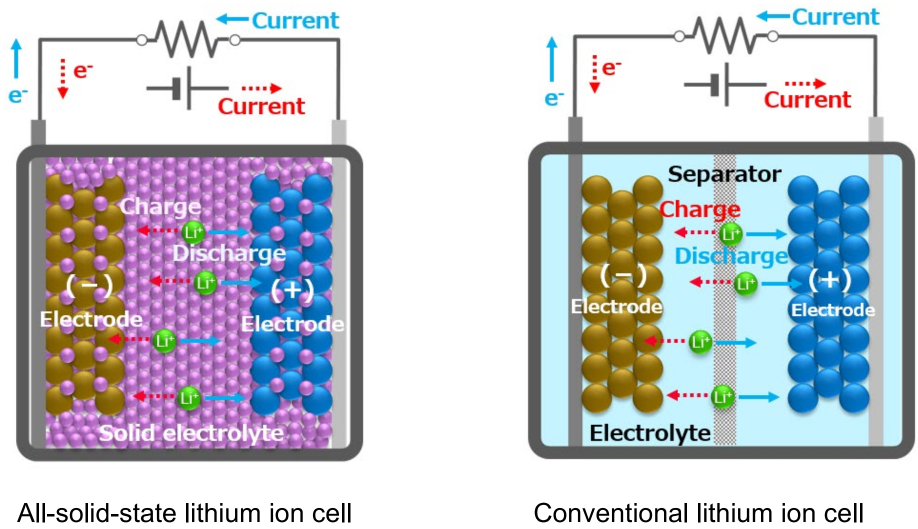


Fig.2: Operating mechanism of all-solid-state lithium ion cells and conventional lithium ion cells

3. Due to these differences in materials and structures, thermal runaway occurs with an increase in environmental temperature in conventional lithium ion cells, but not in all-solid-state lithium ion cells. The mechanism will be described later.

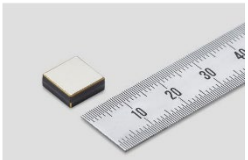
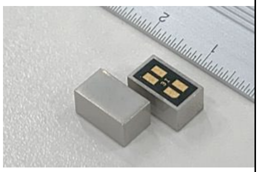
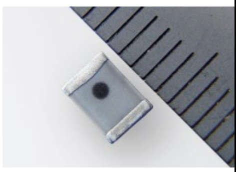
4. The cell specifications of all-solid-state lithium ion cells under development are shown in Table 2 below. Although these three types of all-solid-state lithium ion cells differ in manufacturer, material, capacity, and characteristics, they have the following common features:

(i) they use only materials whose melting point or sublimation point is not below 250 °C;

(ii) they use an inorganic solid electrolyte; and

(iii) they don’t contain the lithium metal nor combustible materials.

Table 2: Features of all-solid-state lithium ion cells.

	Type A	Type B	Type C
Nominal Capacity (mAh)	8	9	0.15
Nominal Voltage (V)	2.3	3.65	3.0
Cell size (mm)	10.5/10.5/4.0	4.55/5.7/9.7	4.5/3.2/1.25
Cell weight (g)	1.2	0.64	0.04
Type of Positive electrode	Lithium cobalt oxide	Lithium cobalt oxide	Lithium cobalt phosphate
Type of Negative electrode	Lithium titanium oxide	Graphite	Titanium oxide
Type of electrolyte	Sulphide-based solid electrolyte	Oxide-based solid electrolyte	Oxide-based solid electrolyte
Appearance			

5. Since these all-solid-state lithium ion cells can be mounted on a board by a reflow process as shown in Fig. 4, they are expected to be used as ultra-compact power sources for the following devices, which requires high reliability, high safety, long life, and heat resistance:

- Internet of Things (IoT) equipment power supply
- Real Time Clock (RTC) backup power supply
- Sensor equipment power supply
- Wearable equipment power supply
- Medical device power supply (e.g. biomedical implant)
- Industrial equipment power supply
- In-Vehicle equipment power supply

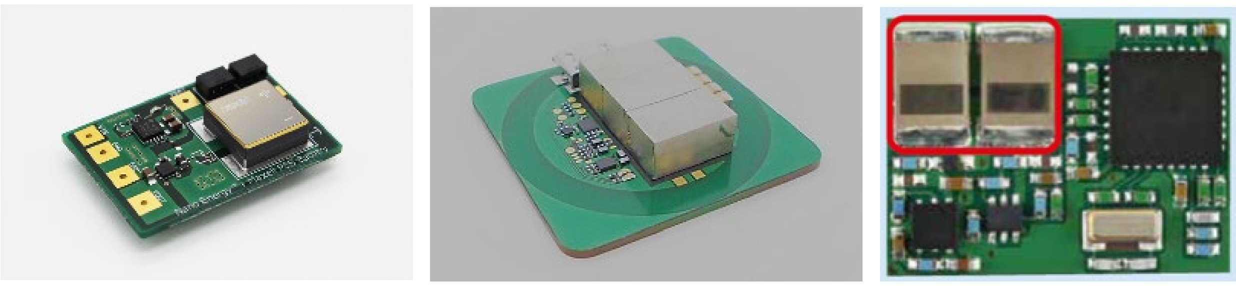


Fig. 4: The all-solid-state lithium ion cells mounted on a board.

6. This document introduces the high thermal stability characteristics of the all-solid-state lithium ion cells and proposes new special provisions for the transport category.

II. Background

7. The all-solid-state lithium ion cells and batteries are considered to classify under the "lithium ion cell or lithium ion battery" described in the *Manual of Tests and Criteria, part III, sub-section 38.3.2.3* because they contain lithium ions inside. Therefore, all-solid-state lithium ion cells and batteries are assigned UN number as dangerous goods, and the same transport regulations as conventional lithium ion cells and batteries are stipulated.

8. On the other hand, in order to be classified the lithium ion cells and batteries appropriately based on differences in characteristics, the UN informal working group (IWG) is considering a new classification method based on hazards, but it is being considered on the premise that thermal runaway will occur. Therefore, it is unclear whether the regulations will define the treatment of cell and battery that are stable at high temperatures and do not cause thermal runaway.

9. Therefore, in this document, Japan would like to show some specific cells that are extremely stable in a high-temperature environment based on test data, and we would like to propose a special provision stipulating that if the cells meet specific conditions, it will be exempted from other regulations.

III. Risk assessment

10. The risk factors during transport of cells and batteries can be divided into two categories. One is the release of all internally stored energy, which eventually manifests itself in the form of heat. The other is the effect on living organisms due to the diffusion of substances used inside the cell released externally. Both of these risks do not arise in normal transport if the requirements of the *Manual of Tests and Criteria, part III, sub-section 38.3* are met, but they must be taken into account in the event of an accident, for example, if external heating occurs.

11. The most important event to be avoided during the transport of conventional lithium ion cell and battery is propagation that magnifies dangerous situations and thermal runaway that causes it. In other words, a rapid temperature rises due to chemical reactions in the internal materials, which magnifies the hazardous situation. Once thermal runaway occurs, either in the self-heating of the cell or in abnormal external heating, the amount of heat generated can cause new thermal runaway in the surrounding cells in a chain reaction, increasing the damage and placing the surrounding area in a dangerous situation.

12. On the other hand, even under extreme conditions, if the cell itself is stable and thermal runaway does not occur, the amount of heat generated via the cell will not cause further damage.

13. Therefore, to determine whether all-solid-state lithium ion cells are really stable under extreme conditions, an experiment was conducted in line with the propagation test under consideration by the IWG. This test was conducted under conditions where it is agreed that thermal runaway will almost certainly occur in conventional lithium ion cells. The results and configuration of the propagation tests for each type of cell are shown in Figures 5 to 10 below.

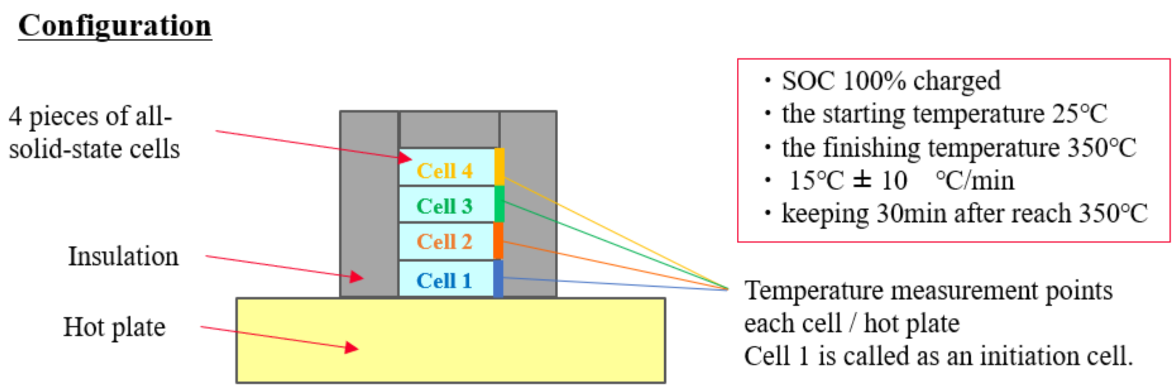


Fig. 5: Type A - Outlook of propagation test according to the hazard-based classification testing protocol.

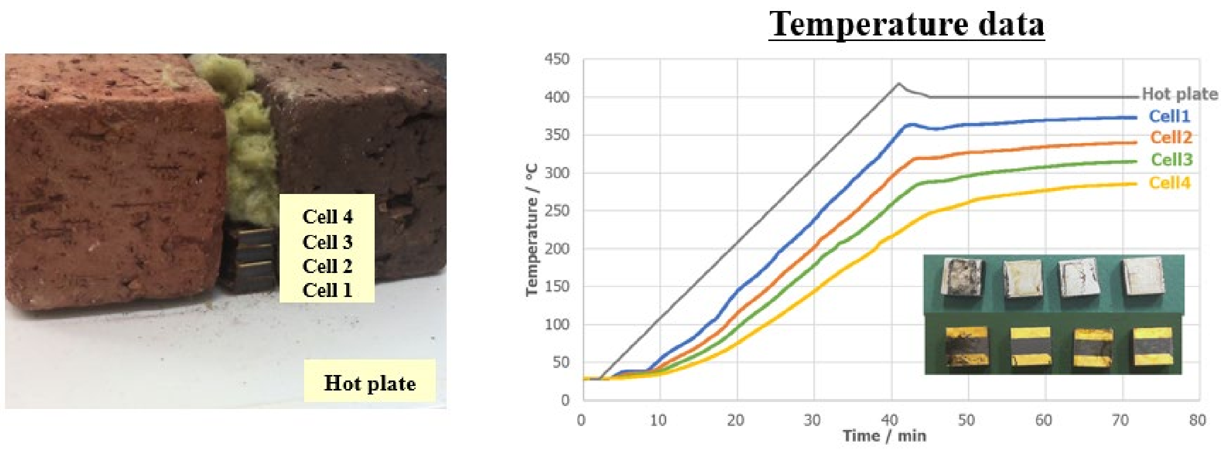


Fig. 6: Type A - Propagation test results according to hazard-based classification test protocols.
(no rapid temperature rise, including in an initiation cell)

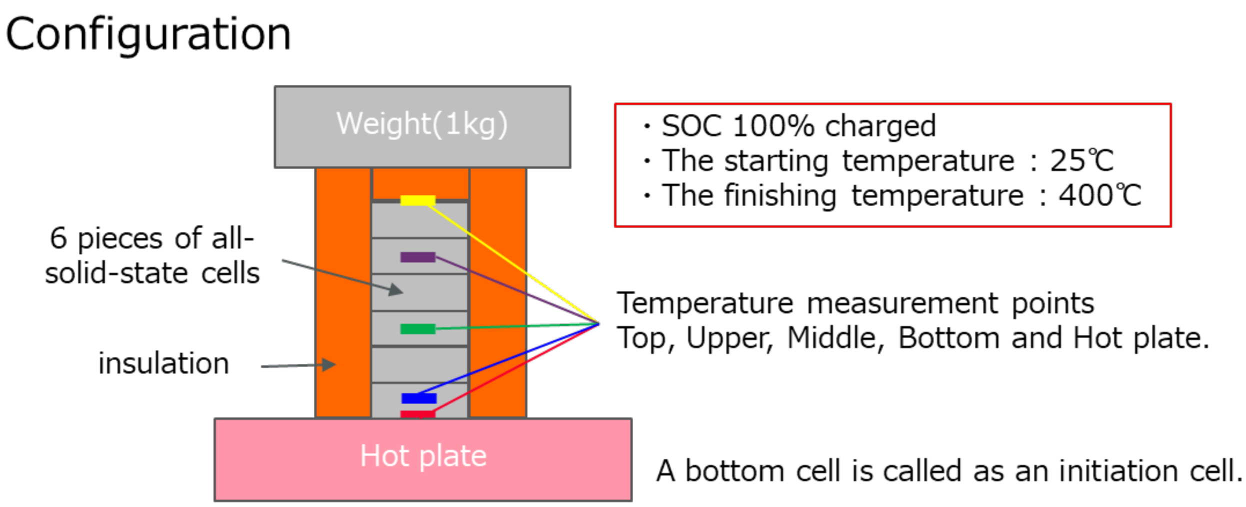


Fig. 7: Type B - Outlook of propagation test according to the hazard-based classification testing protocol.

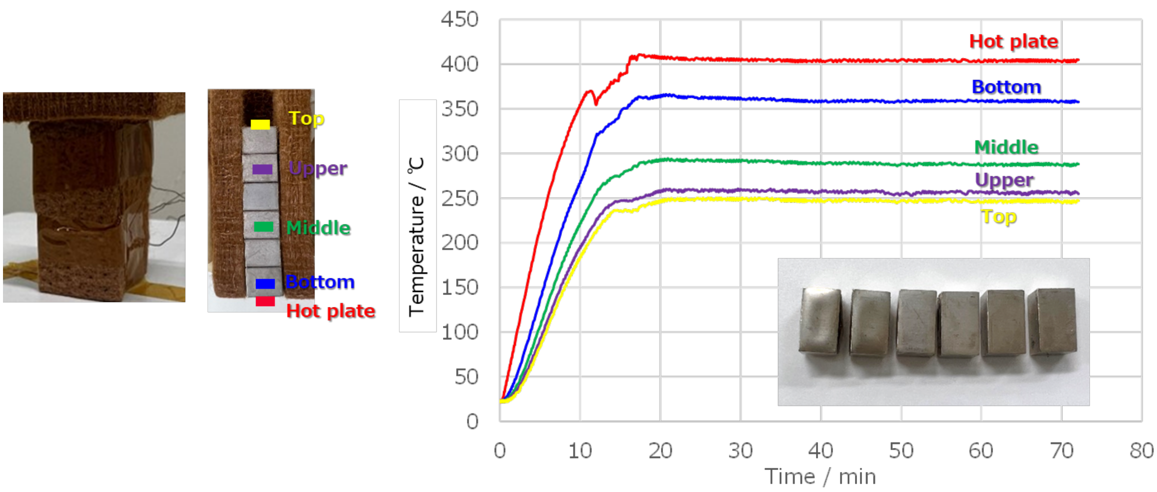


Fig. 8: Type B - Propagation test results according to hazard-based classification test protocols.
(no rapid temperature rise, including in an initiation cell)

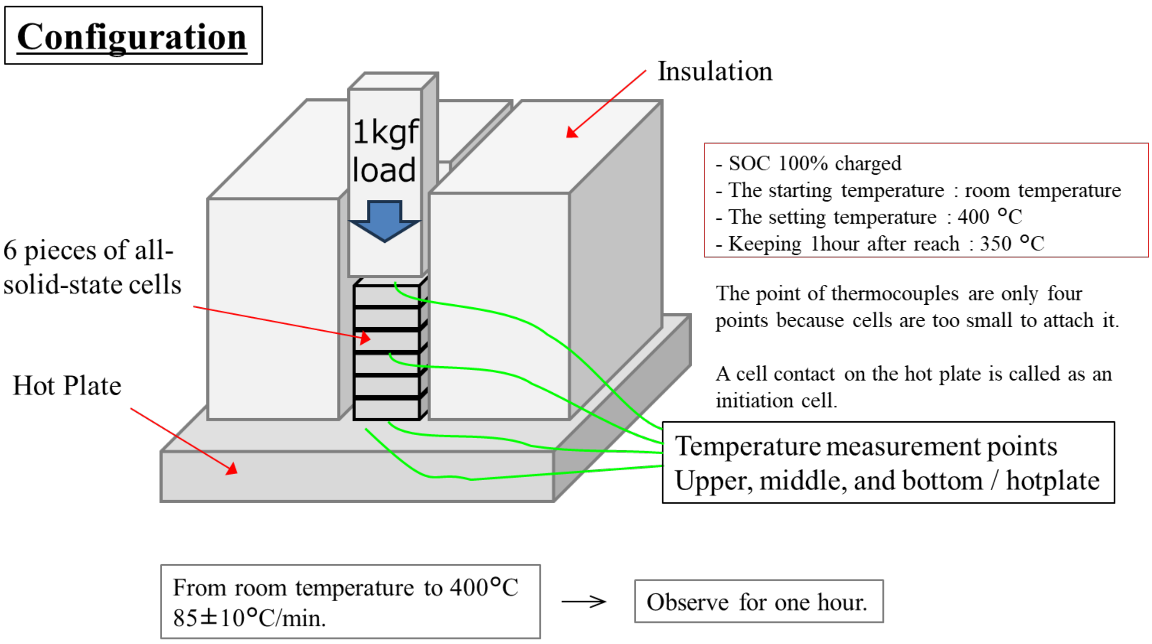


Fig. 9: Type C - Outlook of propagation testing according to the hazard-based classification testing protocol.

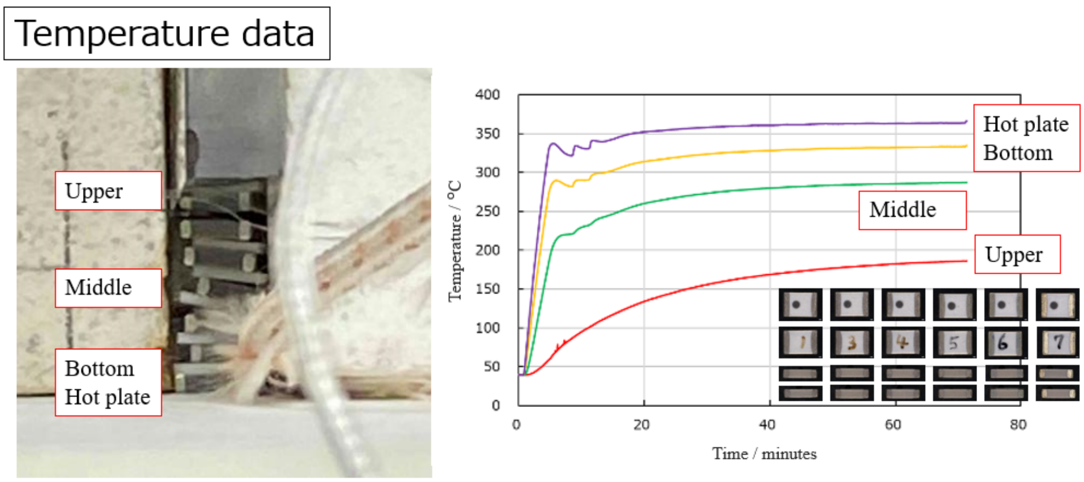


Fig. 10 Type C - Propagation test results according to hazard-based classification test protocols.
(no rapid temperature rise, including in an initiation cell)

14. As these temperature data have shown, there were no self-heating above the ambient temperature in any of the cells and no signs of thermal runaway.

15. As the results of the propagation test alone do not confirm the validity of the risk assessment, it is also verified from a reaction mechanism point of view. The temperature transition of the lithium ion cells when the environmental temperature of a cell is increased, and the generally known thermal runaway mechanism are shown in Figure 11.

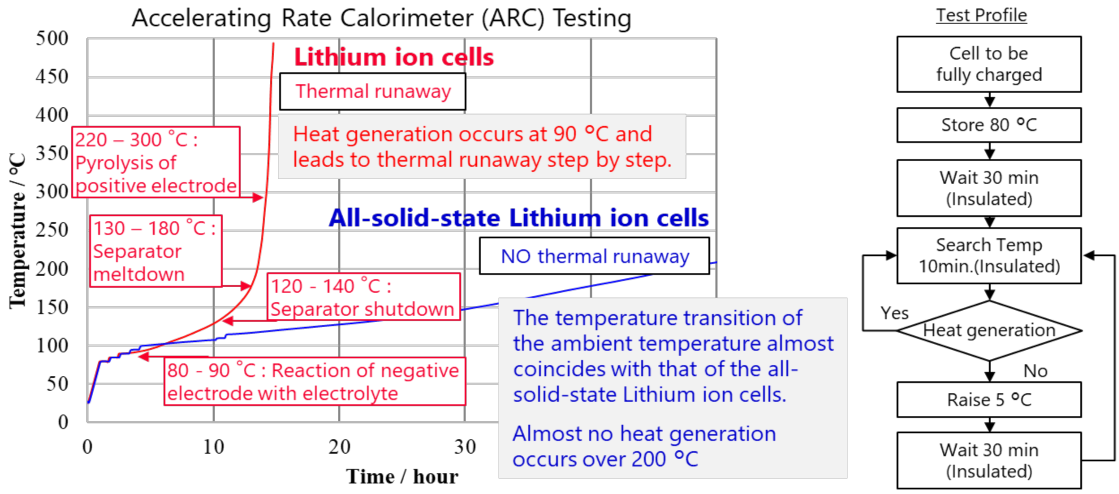


Fig.11: Thermal runaway mechanism of conventional lithium ion cells.

16. In the conventional lithium ion cell, when the ambient temperature starts to exceed 90 °C, the reaction between the organic electrolyte and the negative electrode starts and the cell temperature begins to rise above the ambient temperature (start of the self-heating phenomenon). If the ambient temperature continues to rise further in this state, the meltdown of the resin separator triggers a thermal runaway reaction. On the other hand, the all-solid-state lithium ion cells do not contain organic electrolyte that reacts with the negative electrode or a separator melting process that triggers thermal runaway, so the battery temperature remains almost the same as the ambient temperature in the same test. It is showing an all-solid-state lithium ion cells have high thermal stability.

17. In fact, the analysis results of a temperature rise to 400 or 500 °C are shown to see whether a rapid temperature rise occurs when the ambient temperature rises as show in Figures 12 to 14.

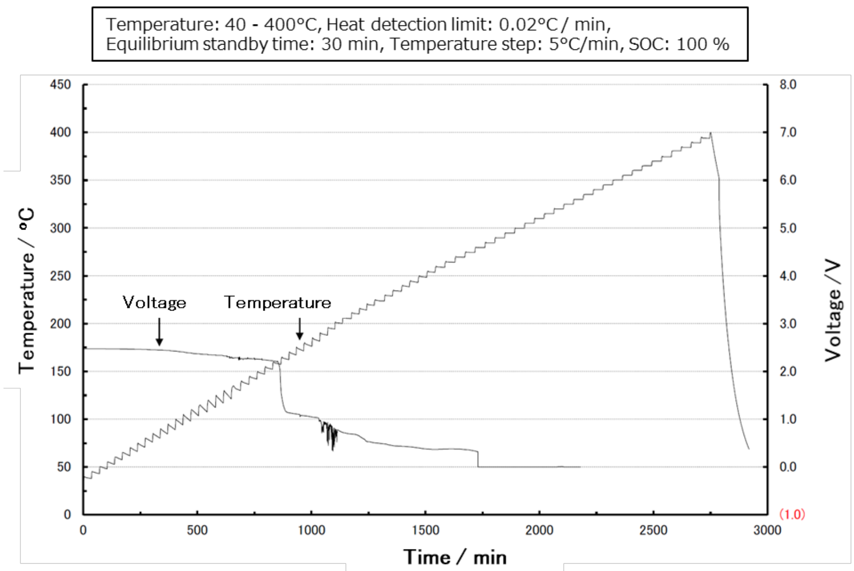


Fig. 12: Type A - Confirmation of thermal runaway reactions using Accelerating Rate Calorimetry (ARC).

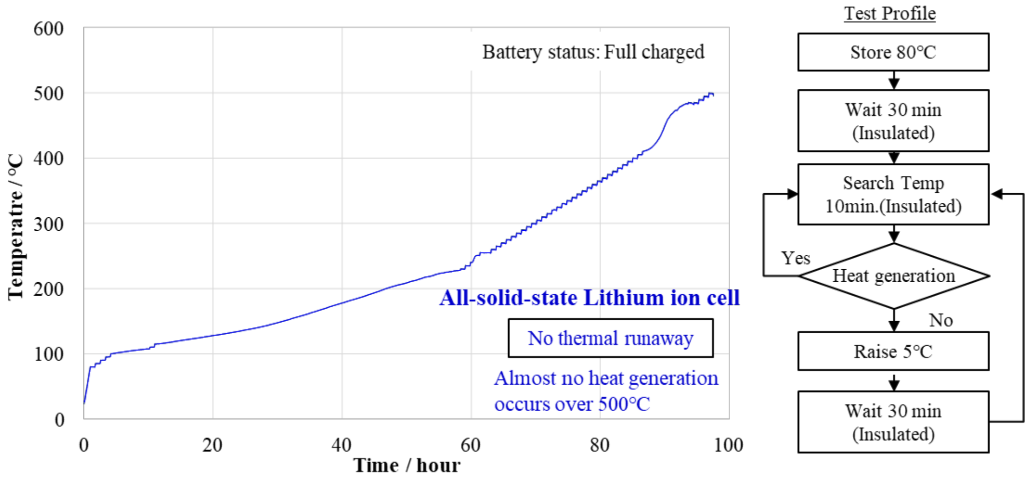


Fig. 13: Type B - Confirmation of thermal runaway reactions using ARC.

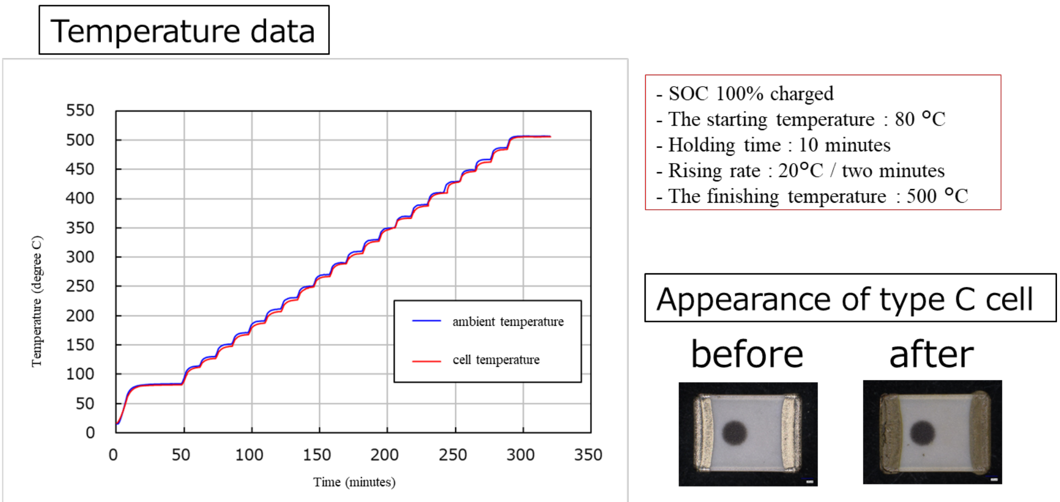


Fig. 14: Type C - Confirmation of thermal runaway reactions using ARC.

18. The validity of the results of the propagation test is supported by the results of these analyses and the absence of a melting process of the separator.

19. Besides external overheating, other factors that can cause cell and battery temperatures to rise is the release of internal electrical energy (short-circuit events). In the case of conventional lithium ion cells, without an effective means, a short-circuit event can cause the temperature of the cell to rise above 100 °C. Under some conditions, a short-circuit event can lead to thermal runaway, and propagate the damage due to thermal runaway.

20. On the other hand, in the case of all-solid-state lithium ion cells, even if the temperature rises above 100 °C by short-circuit events, thermal runaway does not occur in the first place, so the electrical insulation of the cells in the surrounding area is maintained and the temperature rise is not propagated. Therefore, all-solid-state lithium ion cells are stable in high-temperature environments and there is no risk of a sudden temperature rise.

21. Another hazard is the release of internal materials. In fact, some of the main solid electrolytes of all-solid-state lithium ion cells that are commonly studied, such as sulphide-based solid electrolytes are known to react with external moisture to produce hydrogen sulphide. However, in the case of all-solid-state lithium ion cells, only materials whose melting point or sublimation point is not below 250 °C are used, even if the ambient temperature exceeding 100 °C, the cells are kept hermetically sealed. Therefore, no moisture from the outside can enter during transport and hydrogen sulphide is not generated. In

addition, no thermal runaway and no cracking of the outer packaging in actual propagation tests confirm that the seal is maintained and that no internal material is released.

IV. Conclusion

22. All-solid-state lithium ion cells and batteries with higher stability than conventional lithium ion cells and batteries are being developed. Although these cells are “lithium ion battery”, they have the features of "using only materials whose melting point or sublimation point is not below 250 °C," "using an inorganic solid electrolyte," and "not being made of lithium metal and combustible materials". In these cells, thermal runaway (rapid temperature rise) did not occur during the propagation test and the ARC analysis that the environmental temperature was gradually increased. In addition, sufficient sealing performance was maintained even in such a high temperature environment.

V. Proposal

23. Based on these test results and mechanism, we would like to consider the possibility of formulating special provisions for UN 3480 and UN 3481 to exclude lithium ion cells and batteries that satisfy the following conditions from the application of the regulation:

“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 is not below 250 °C;

(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 the *Manual of Tests and Criteria, xx.x.x.x*. (to be developed by the IWG);] and

(d) cells and batteries are protected from short circuits. When cells and batteries 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.”