DANGEROUS GOODS PANEL (DGP)
WORKING GROUP MEETING (DGP-WG/23)

Rio de Janeiro, Brazil, 15 to 19 May 2023

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

INTRODUCTION OF ALL-SOLID-STATE LITHIUM-ION BATTERIES PROPAGATION TEST RESULTS THAT CONSIDERED ACCORDING TO THE TEST PROTOCOL AT HAZARD-BASED CLASSIFICATION WORKING IN UN

(Presented by T. Tabata)

SUMMARY

In this information paper, the all-solid-state lithium-ion batteries propagation test results utilizing the hazard-based classification test protocol being considered by informal meeting of the United Nations subcommittee on Dangerous Goods (UN-IWG) is introduced.

During the propagation test (heating test at 250°C), there is no rapid temperature rise even at "the initiation cell", let alone the spread of fire.

The above test results are supported by the fact that the self-heating phenomenon does not occur in all-solid-state lithium-ion batteries that normally do in liquid-type lithium-ion batteries.

In the future, the transport requirements for these batteries should be discussed.

1. INTRODUCTION

1.1 Currently, lithium-ion batteries that do not exceed 20Wh are regulated during air transportation in spite of an exemption at UN being recommend. Meanwhile, recently, the development of all-solid-state lithium-ion batteries (all-solid-state LIBs), which has extremely high stability and reliability against heat, is progressing. This information paper introduces the high thermal stability and reliability of all-solid-state LIBs.

2. BACKGROUND

2.1 Currently, lithium-ion (secondary) batteries (LIBs) are the most widely used batteries for mobile electronic devices. They can store a large amount of electric power in a small space and can charge and discharge at high output current, so LIBs are the high performance battery for mobile electronic devices far beyond any other types. However, in today there are strong calls for higher safety LIB so that they can be used in mobile electronic devices for wider applications safely. It is because that the material components of LIB include flammable liquids, if LIBs are subjected to an external impact, short-circuits could occur causing them to overheat, and in the worst case, to ignite.

2.2 To resolve these issues, developments are being conducted around the world on all-solid-state LIBs (not semi-solid-state LIBs with a mixture of liquid and solid electrolytes) that the electrolyte[1] is changed to a non-flammable solid material for enhanced safety, which have flammable liquid in LIBs.

3. COMPARISON OF CONSTITUENT MATERIAL BETWEEN ALL-SOLID-STATE LIB AND CONVENTIONAL LIB

3.1 Table 1 shows a comparison of constituent material between all-solid-state LIBs and conventional LIBs. All-solid-state LIBs have solid positive and negative electrode just like conventional LIBs. Whereas all-solid-state LIBs use inorganic solid electrolyte instead of organic liquid electrolyte used in conventional LIBs. In addition, all-solid-state LIBs have no separator because rigid inorganic solid electrolyte separates both electrodes and avoids short-circuit (Fig.1).

3.2 All-solid-state LIBs charge and discharge by intercalation and deintercalation of lithium ion in the positive and negative electrodes same as LIBs do (Fig.2).

Table 1 Comparison of constituent material between all-solid-state LIB and conventional LIB

Constituent material	All-solid-state LIB	Conventional LIB
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, Sulfide-based solid electrolyte, etc. (Non-flammable Solid, Non-dangerous goods)	Organic liquid electrolyte (Flammable liquid, Dangerous goods)

[1] An electrolyte is a substance that serves as the path for charges and interchanging media (lithium ions in the case of LIBs) to move between the positive and negative electrodes inside secondary batteries which can charge and discharge electric power.

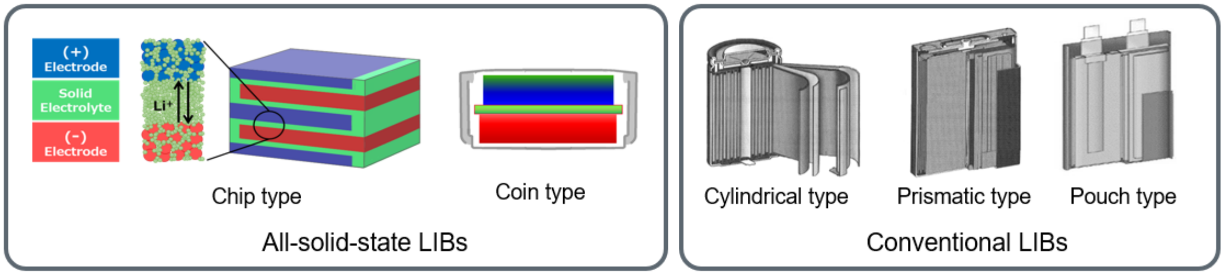


Fig.1 Schematic diagrams of all-solid-state LIBs and Conventional LIBs

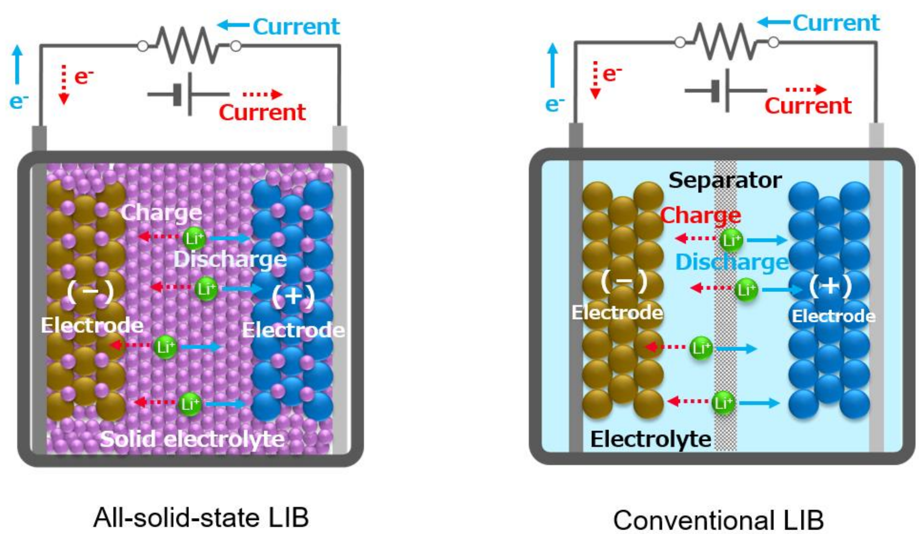


Fig.2 Operating mechanism of all-solid-state LIB

3.3 Due to these material configurations, thermal runaway (rapid temperature rise) is induced with a rising of environmental temperature in a conventional LIBs, but not in an all-solid-state LIBs (Fig. 3).

3.4 Details are shown below. As shown in Fig. 3, in a normal LIB, when the ambient temperature rises to exceed 90°C, the organic liquid electrolyte and the negative electrode start the reaction, and the battery temperature rises above the ambient temperature (initiation of the self-heating phenomenon). If the ambient temperature continues to rise in that state, a meltdown of the resin separator will occur, and it will lead to a plane short circuit of the positive and negative electrodes, and will generate heat. When the temperature rises further, the cathode material thermally decomposes and releases oxygen, causing a violent combustion reaction with the vaporized electrolyte, lead to thermal runaway. On the other hand, even if the similar test is experimented by all-solid-state LIB, the battery temperature remains the same as the ambient temperature since it does not contain an organic liquid electrolyte and a separator, and it shows high thermal stability.

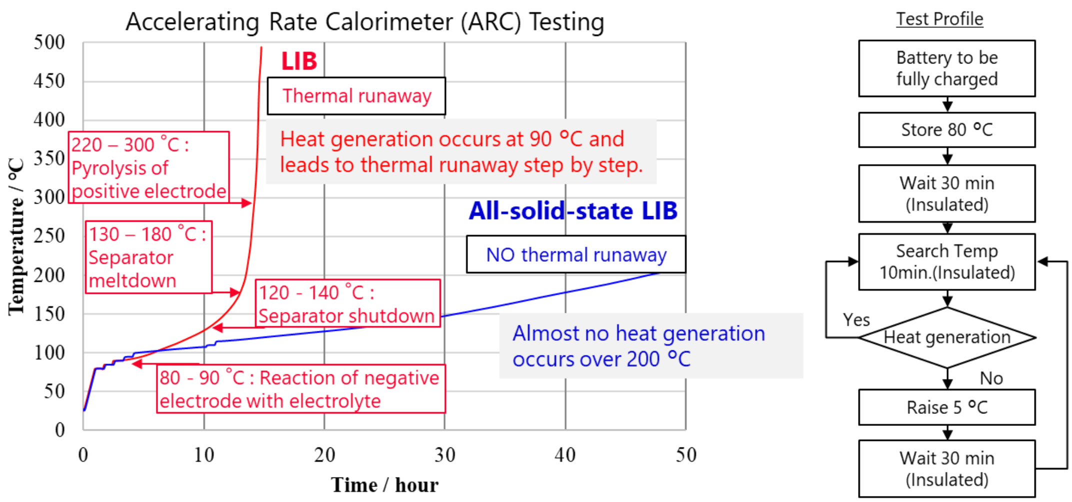


Fig.3 Thermal runaway mechanism of LIB

4. FEATURES OF ALL-SOLID-STATE LIBS

4.1 The typical features of the all-solid-state LIBs are described below.

— All-solid-state LIBs' temperature doesn't rise up rapidly at the high ambient temperature, because there is no reaction with organic liquid electrolyte and negative electrode that occur the triggered reaction or no short-circuit due to meltdown of resin separator (Fig.3).

— All-solid-state LIBs don't catch fire (also don't propagates fire) because inorganic solid electrolyte is being used instead of flammable organic liquid electrolyte.

— All-solid-state LIBs don't leak because liquid material isn't included at all.

— All-solid-state LIBs have a high heat resistance, so they can be used under high temperature conditions which would not be possible with conventional LIBs.

5. APPLICATIONS OF ALL-SOLID-STATE LIBS

5.1 The all-solid-state LIBs (especially for ultra-small size) shown in Fig. 4 are expected to be used as compact power supplies for devices requiring reliability, safety, long product life, and heat-resistance, as listed below.

— IoT (Internet of Things) equipment power supply

— RTC (Real Time Clock) backup power supply

— Sensor equipment power supply

— Wearable equipment power supply

— Medical equipment power supply (e.g. living body implantation)

— Industrial equipment power supply

— In-vehicle equipment power supply

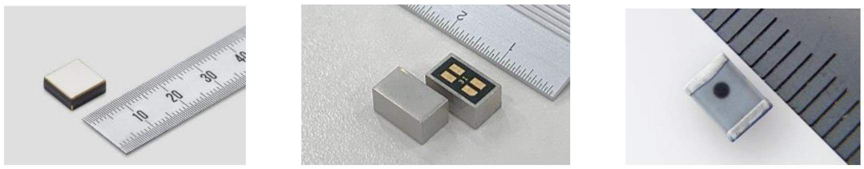
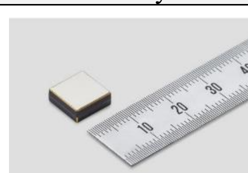
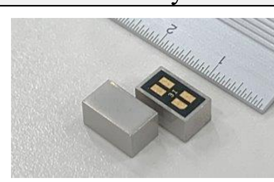
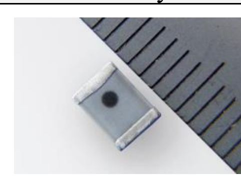


Fig. 4 Examples of all-solid-state LIBs

6. OVERVIEW AND RESULTS OF PROPAGATION TESTS ACCORDING TO HAZARD-BASED CLASSIFICATION INFORMAL WORKING GROUP.

6.1 Propagation tests were evaluated with three types of all-solid-state LIBs listed in Table 2.

Table 2 List of features by each type of all-solid-state LIB.

	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 solid electrolyte	Sulphide-based solid electrolyte	Oxide-based solid electrolyte	Oxide-based solid electrolyte
Appearance			

6.2 Propagation tests (heating to 250°C) that is according to the hazard-based classification test protocol considered UN-IWG were experimented. Type A test methods and results are shown in Fig. 8 and 9, Type B test methods and results in Fig. 10 and 11, and Type C test methods and results in Fig. 12 and 13. No propagation occurred in any of all-solid-state LIBs, and “the initiation cell” did not reach over the temperature of the hot plate.

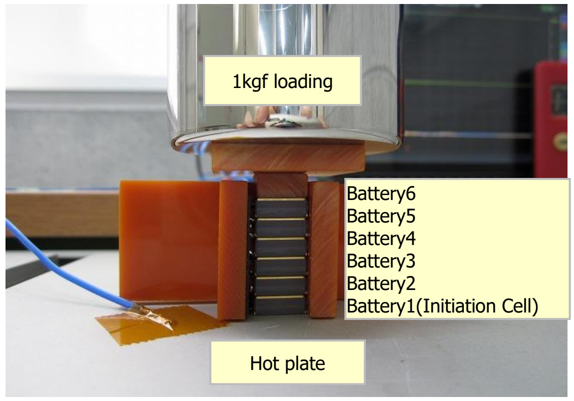


Fig. 8 Type A: Outlook of propagation test according to the hazard-based classification testing protocol.

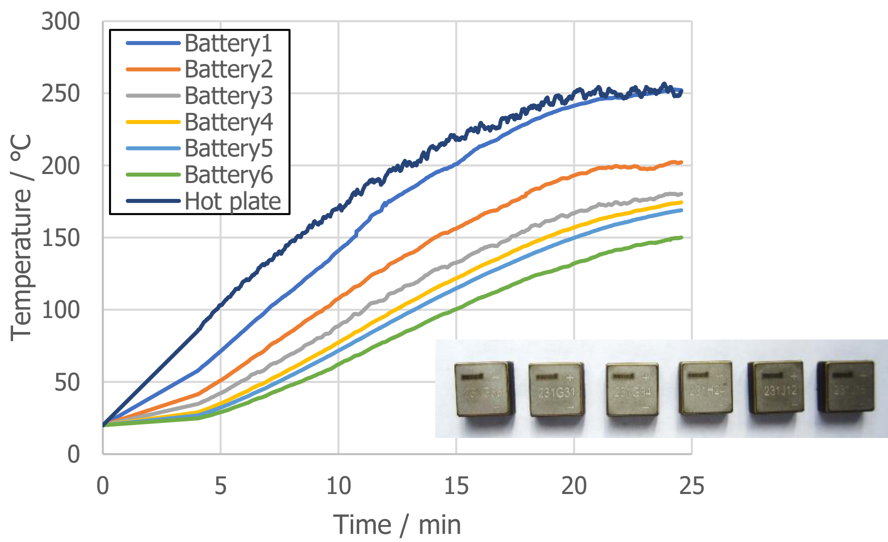
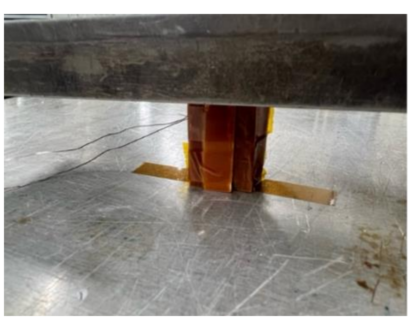


Fig. 9 Type A: Propagation test results according to hazard-based classification test protocols.
(no rapid temperature rise, including in initiation cells)



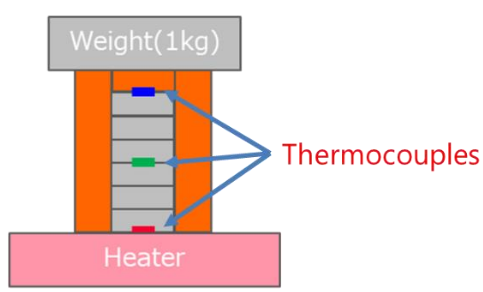


Fig. 10 Type B: Outlook of propagation test according to the hazard-based classification testing protocol.

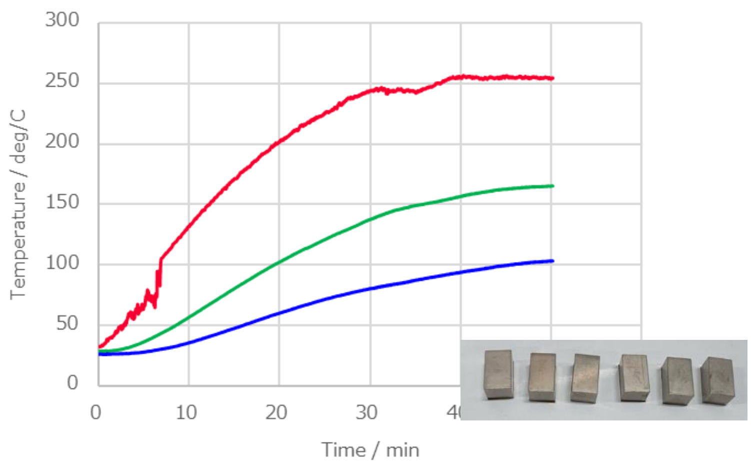


Fig. 11 Type B: Propagation test results according to hazard-based classification test protocols.
(no rapid temperature rise, including in initiation cells)

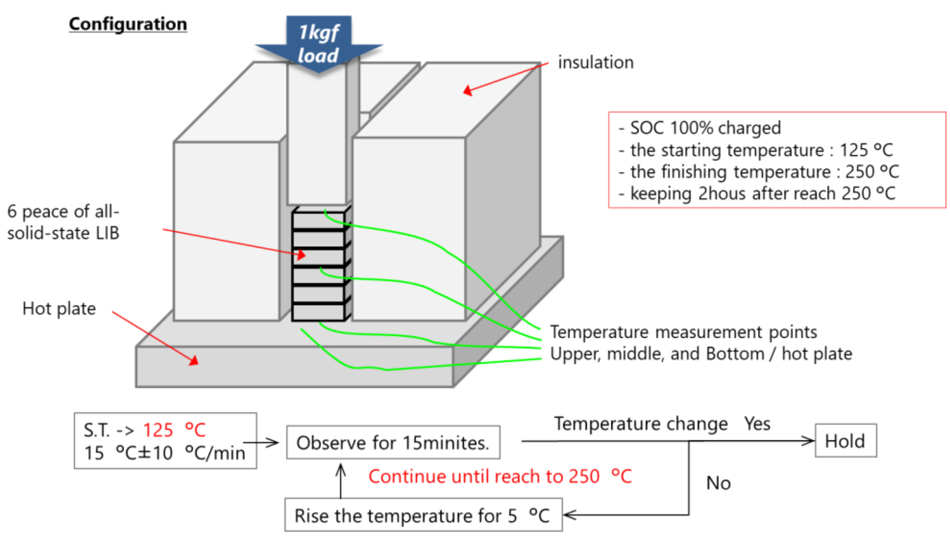


Fig. 12 Type C: Outlook of propagation testing according to the hazard-based classification testing protocol.

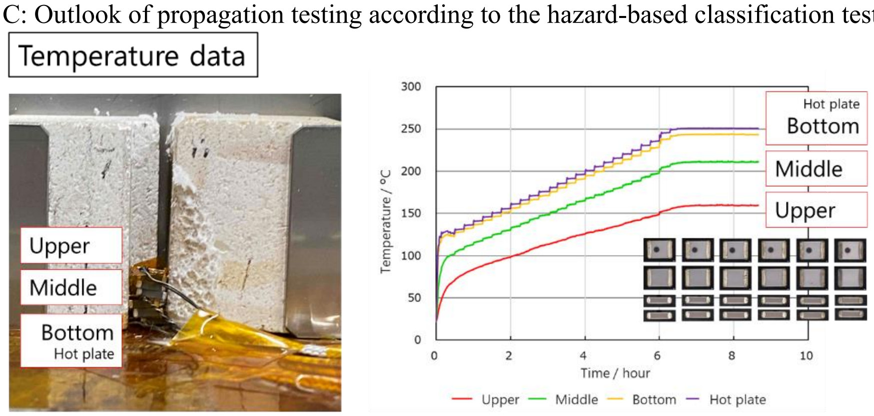


Fig. 13 Type C: Propagation test results according to hazard-based classification test protocols.
(no rapid temperature rise, including in initiation cells)

6.3 As mentioned above, there is no propagation and no rapid temperature rise even at “the initiation cell” when each companies’ all-solid-state LIBs were experimented the propagation tests (250°C heating) in accordance with the hazard-based classification test protocols discussed in UN-IWG. Therefore, it should be possible to transport them under different regulations from normal LIB.

7. **CONCLUSION:**

7.1 All-solid-state LIBs have been largely successful in eliminating the risk of thermal runaway. This is clearly demonstrated by the test results discussed above. Since this new battery technology does not represent the same level of risk during transport as conventional LIBs it seems only logical that they should not be subject to the same stringent transportation regulations.

7.2 The all-solid-state lithium-ion batteries propagation test results utilizing the hazard-based classification test protocol being considered by the informal meeting of the United Nations subcommittee on Dangerous Goods (UN-IWG) is presented in the appendix to this working paper.

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APPENDIX

INTRODUCTION OF ALL-SOLID-STATE LITHIUM-ION BATTERIES PROPAGATION TEST RESULTS THAT CONSIDERED ACCORDING TO THE TEST PROTOCOL AT HAZARD-BASED CLASSIFICATION WORKING IN UN

Introduction of all-solid-state lithium-ion batteries propagation test results that considered according to the test protocol at hazard-based classification working in UN.

15 to 19 May 2023

BATTERY ASSOCIATION OF JAPAN

Introduction

Currently,

lithium-ion batteries of 20Wh or less are exempted from dangerous goods (DG) in UN recommendations, but in air transport, they are treated as DG and regulated.

Recently,

the development of all-solid-state lithium-ion batteries (all-solid-state LIBs) with extremely high thermal stability and reliability is progressing.

In this paper,

we would like to report and share of propagation test results utilizing the hazard-based classification test protocol being considered by informal meeting of the United Nations subcommittee on Dangerous Goods (UN-IWG).

The propagation test is

designed in UN-IWG for checking the un-stable phenomenon and risks (HAZARD). So, it is assumed that the LIB should be occur the thermal runaway (rapid-temp. rise) under this test.

About UN-IWG : https://rechargebatteries.org/sustainable-batteries/unsctdg/

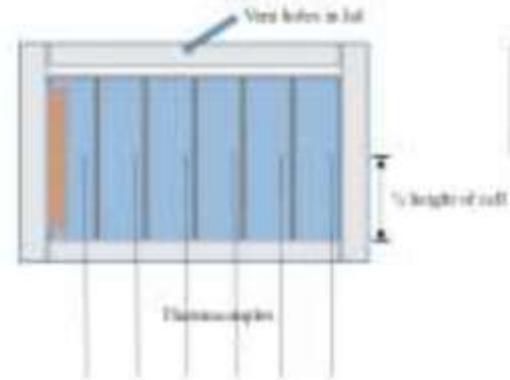
Samples

We would like to introduce the three examination results based on the propagation test with following samples.

	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 solid electrolyte	Sulphide-based solid electrolyte	Oxide-based solid electrolyte	Oxide-based solid electrolyte
Appearance			

Test condition of propagation test

		Test protocol draft 2022/2/9
Cell	State of charge	100%
Thermocouples	Type	K-type
	Accuracy	2 °C
	Response	2sec
Heating element	Rate of temperature increase	15±10 °C/min
	Size	<5cm^2 and 20% of surface area
Insulated container	Insulation point	6-sided
	Heat Conductivity	<0.3W/m*K
	Minimum Thickness	>5mm
	weight (of a load)	1kgf



Side View

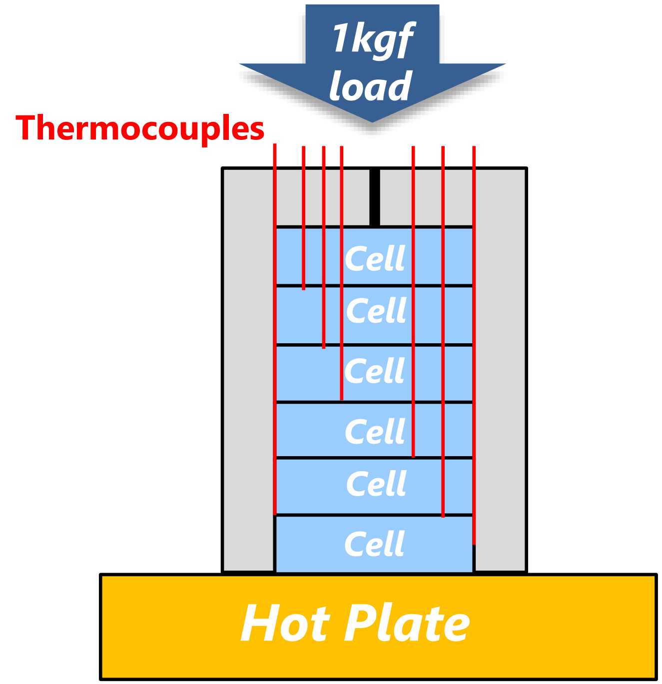
https://rechargebatteries.org/sustainable-batteries/unsctdg/

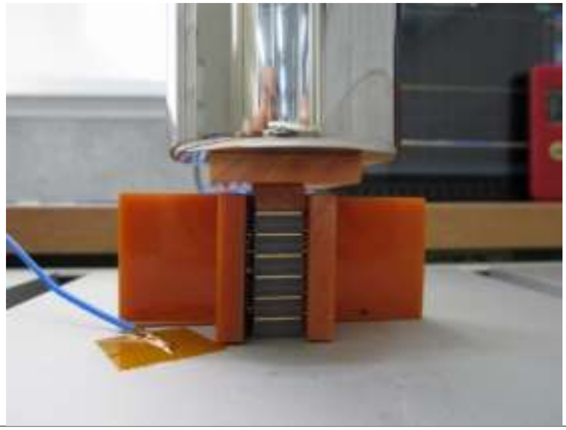
Heating test method (setup)

Type A

		Test protocol draft 2022/2/9	Test condition
Cell	State of charge	100%	<-
Thermocouples	Type	K-type	<-
	Accuracy	2 °C	<-
	Response	2sec	<-
Heating element	Rate of temperature increase	15±10 °C / min	<-
	Size	<5cm^2 and 20% of surface area	Entire bottom surface
Insulated container	Insulation point	6-sided	6-sided (1-side is Heater)
	Heat Conductivity	<0.3W/m*K	<-
	Minimum Thickness	>5mm	<-
	weight (of a load)	1kgf	<-

The outlook of testing equipment.

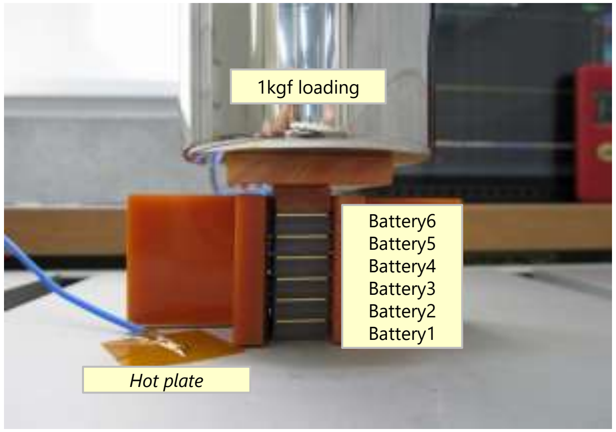




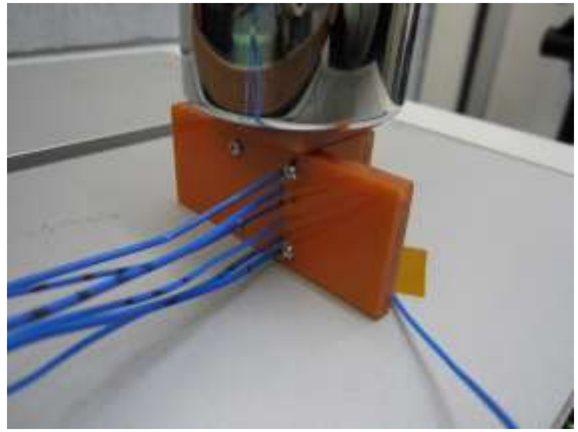
Propagation Test Results

Type A

Configuration (front)



Configuration (back)

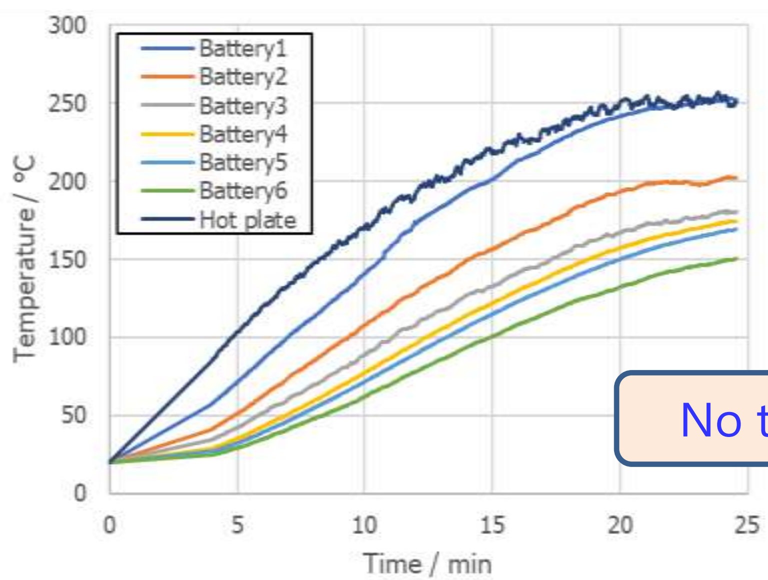


Cells after test

No rupture, No ignition.

The test in progress

Temperature profiles

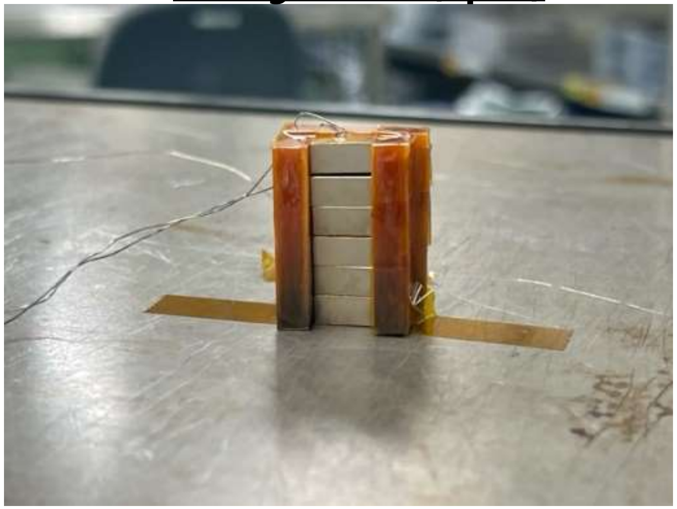


No thermal runaway

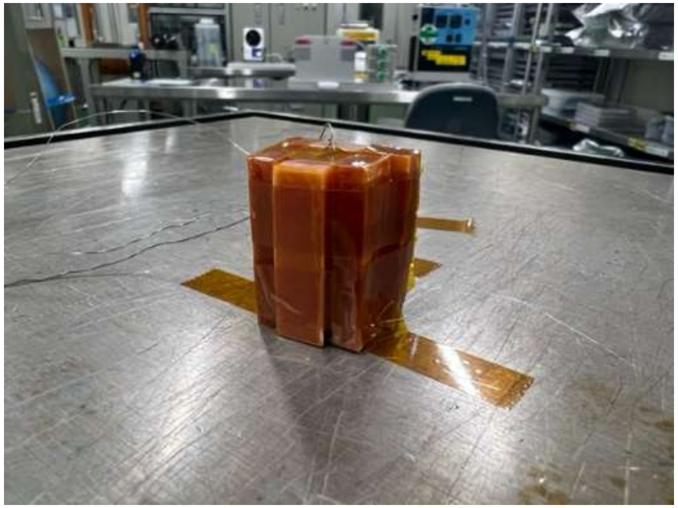
Outline of the test (setup)

Type B

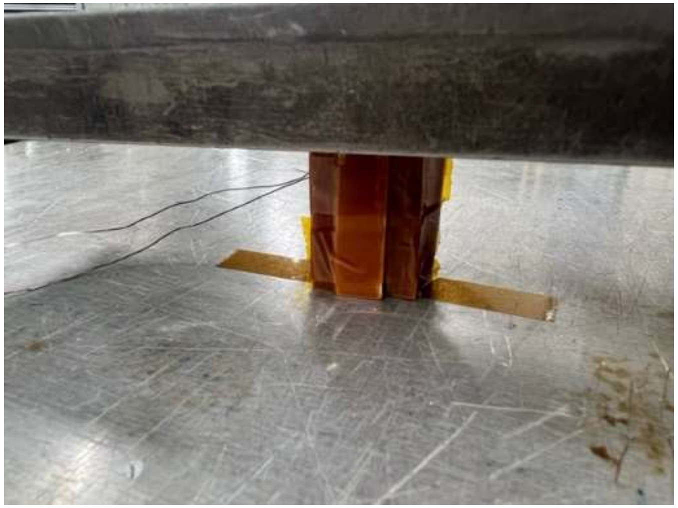
Configuration (open)

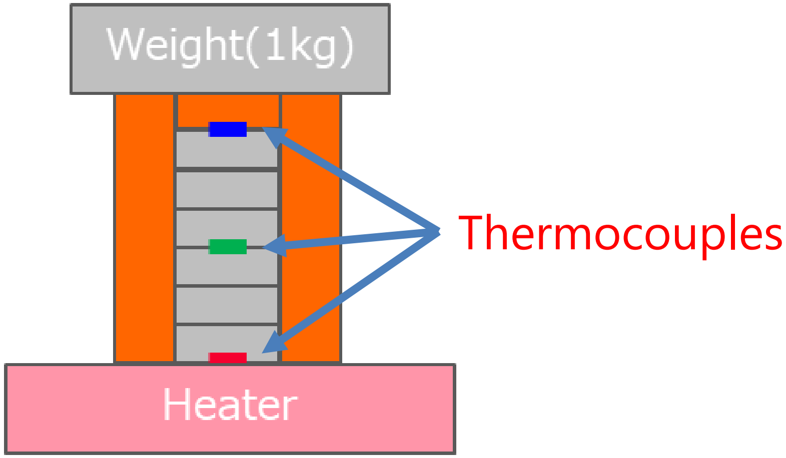


Configuration (Closed)



Configuration (with weight)

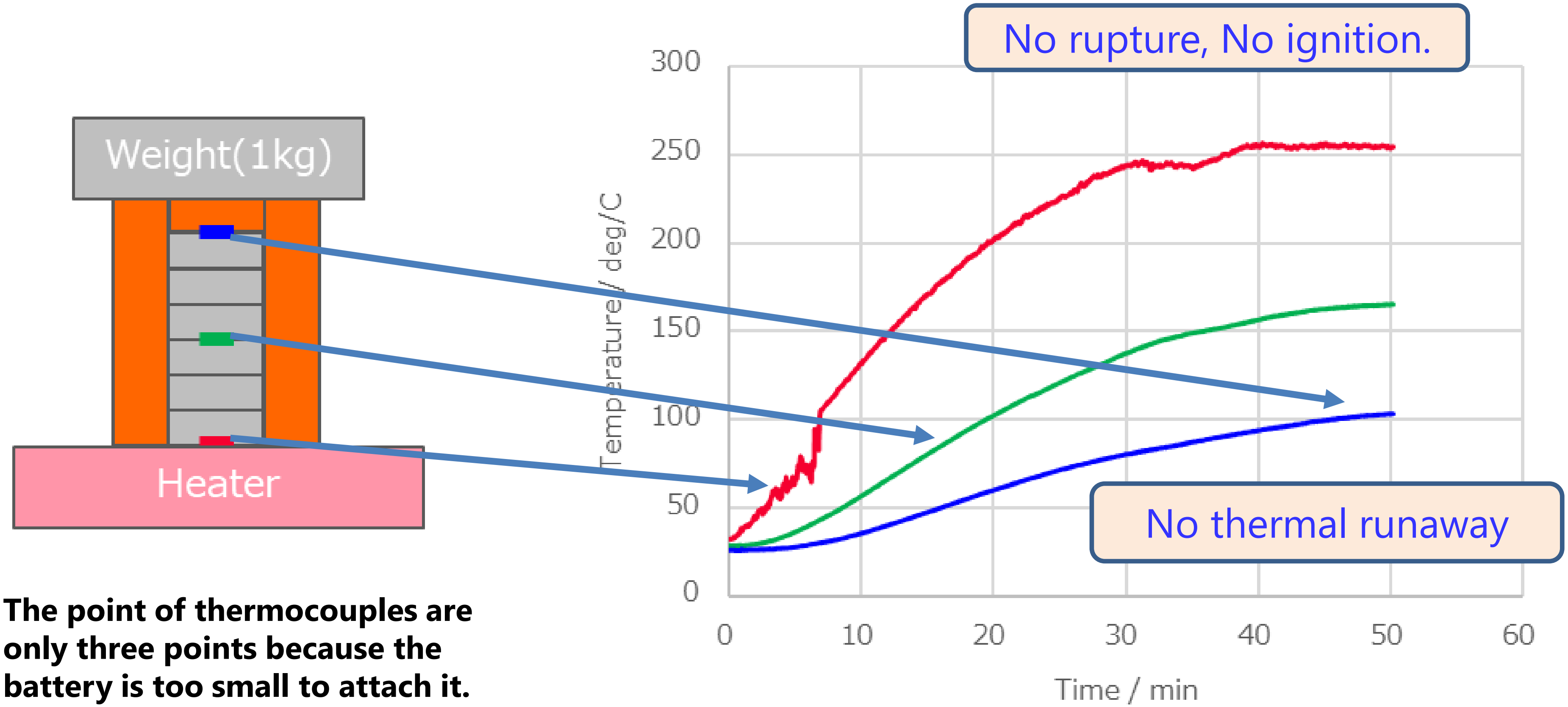




Propagation Test Results

Type B

Cells after test

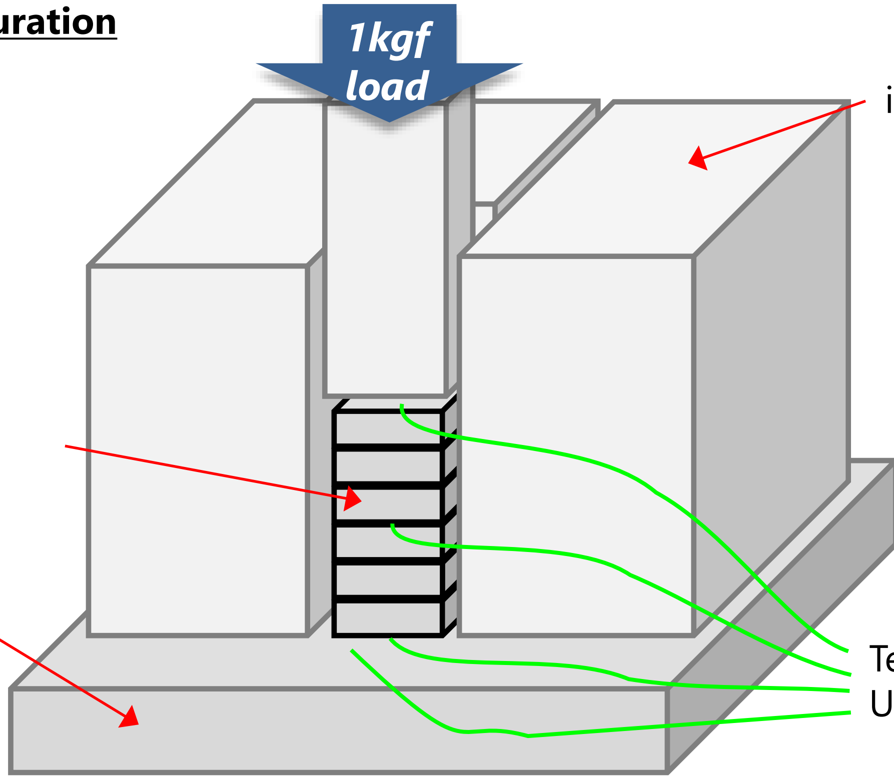


The point of thermocouples are only three points because the battery is too small to attach it.

Outline of the test (setup)

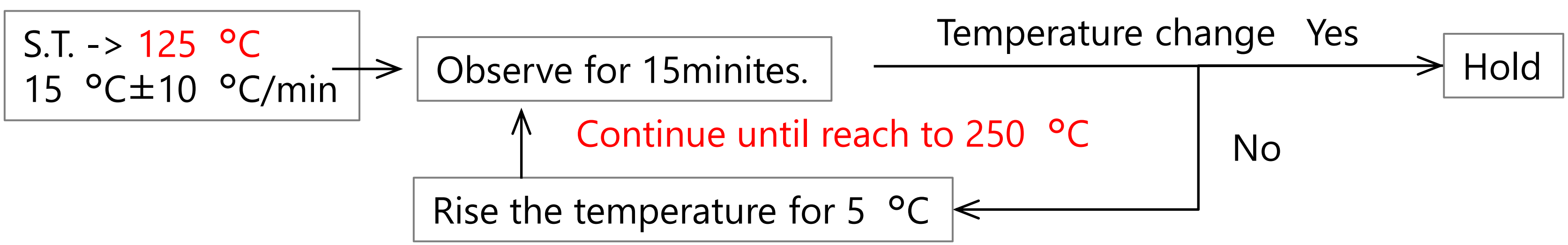
Type C

Configuration



- SOC 100% charged
- the starting temperature : 125 °C
- the finishing temperature : 250 °C
- keeping 2hous after reach 250 °C

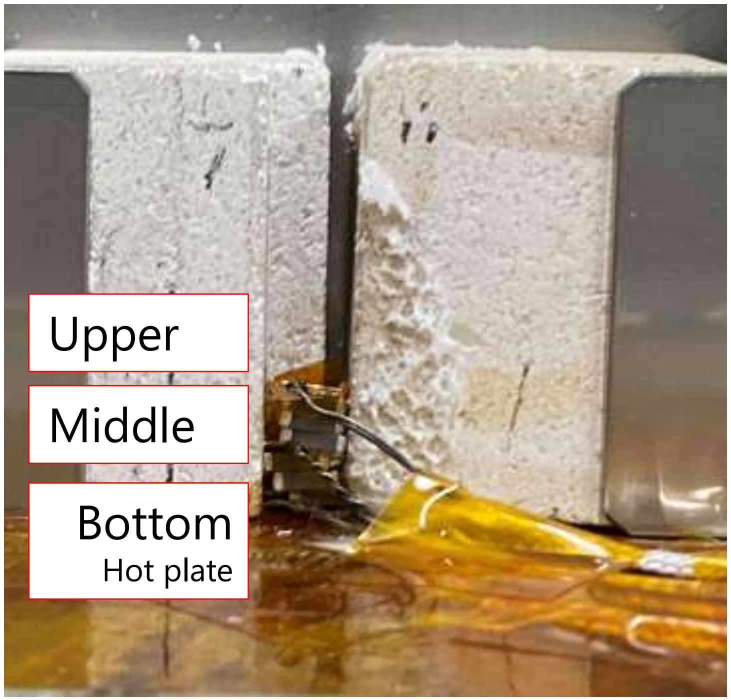
The point of thermocouples are only four points because the battery is too small to attach it.

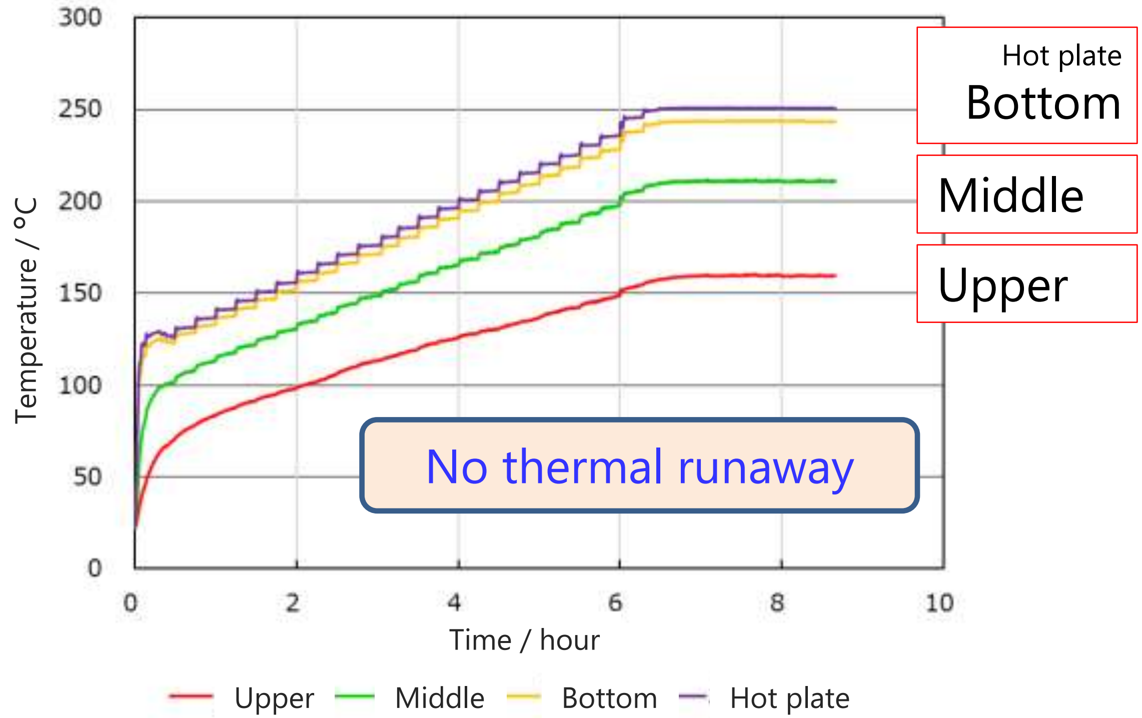


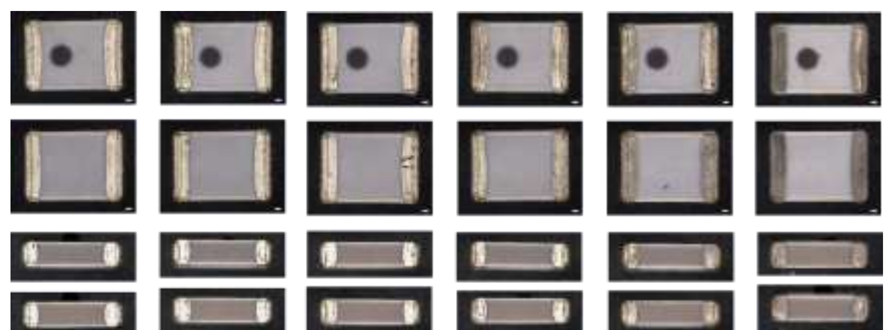
Propagation Test Results

Type C

Temperature data



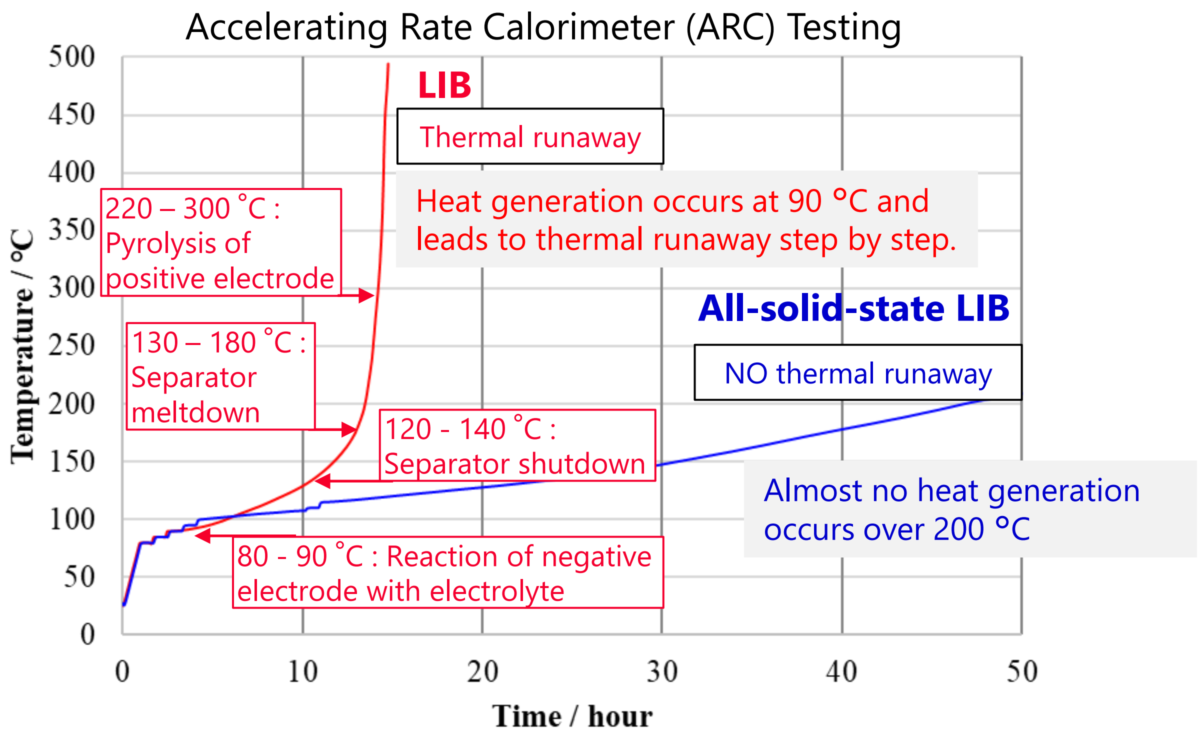


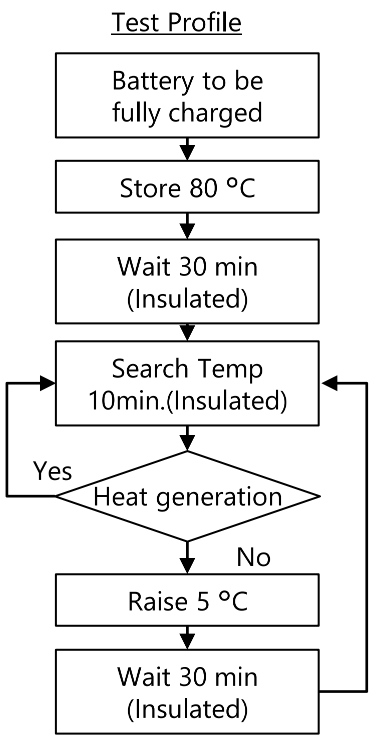


No rupture, No ignition.

Thermal runaway mechanism

This all-solid-state LIB consists of following points
- stable the solid-state at the high temperature (i.e. 200 °C)
- using inorganic solid-electrolyte
- not including the lithium metal or flammable material.





The temperature transition of the ambient temperature coincides with that of the all-solid-state battery.

https://en.wikipedia.org/wiki/Calorimeter

Conclusion

The results of the propagation test discussed in the UN-IWG were presented with all-solid-state lithium-ion batteries prepared by three companies.

In accordance with this test, no rapture and no ignition occurred at “the initiation cell” on the 250 °C heating plate. And also, it is no thermal runaway. These test results are supported by the fact of ARC test.

We hope that the transportation requirements will be discussed in the future to determine how they should be addressed for batteries that are no hazard at propagation test.