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Safety Design Features of GS Yuasa's Large Lithium-ion Cell

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Introduction

GYT has developed 50, 100 and 175Ah cells.
We fixed their chemical design at 1999 and did not change.

Dimensions	Satellite type (Long cycle life type)		
	Capacity	Mass	Specific energy*
H 263mm W 165mm T 50mm	Nominal 186Ah (Rated 175Ah)	4.65kg	146 Wh/kg
H 208mm W 130mm T 50mm	Nominal 110Ah (Rated 100Ah)	2.79kg	146 Wh/kg
H 123mm W 130mm T 50mm	Nominal 55Ah (Rated 50Ah)	1.50kg	136 Wh/kg

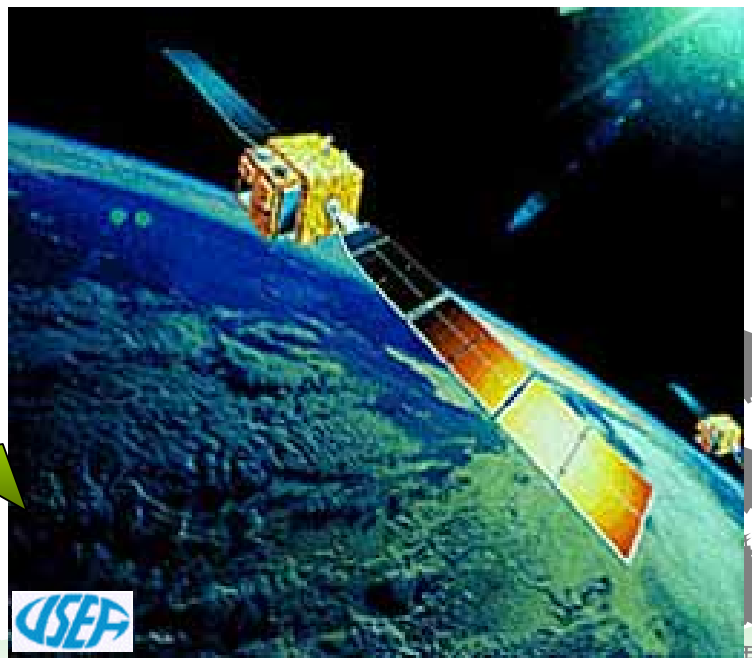
Experience in programs

Launched

SERVIS (Japanese experimental LEO satellite): Installed and launched in 2003
THAICOM4 (Very large commercial GEO satellite): Installed and launched in 2005
INSAT4 (ISRO Communication GEO satellite): Installed and launched in 2007
And three other satellites

Near future launch

Other contracts have been made on 16 GEOs, 3 LEO programs(>50 satellites), and other space vehicle programs.



Published Information

1. Published information on SONY 18650 cell in 2006

1-1. The cell and battery type

Cell: SONY 18650 type cell (G7, 2400mAh)

Shape - Cylindrical
Diameter - 18mm
Length - 65mm
Cell case – Steel, Negative terminal potential

Battery: 4 series or 3 series and 2 parallel string pack

1-2. Production number for whole consumer market

22 Billion cells/ 10 years(1995-2005) All brand included

1-3. Accidents reported from SONY

6 fire accidents
SONY published that probability of fire accident is 1 / 3,500,000.

Published Information

2. Published information on SONY cell in Oct. 2008

Editors Notes: Outline of the Voluntary Recalls by PC Manufacturers and Incidents

1) Affected battery cell type: 2.15Ah cells

2) Number of battery packs to be recalled by PC manufacturers: About 100,000 packs worldwide

3) Reported overheating incidents: 40 overheating incidents

4) Cumulative global shipment quantity of 2.15Ah cells since 2002: About 260 million cells

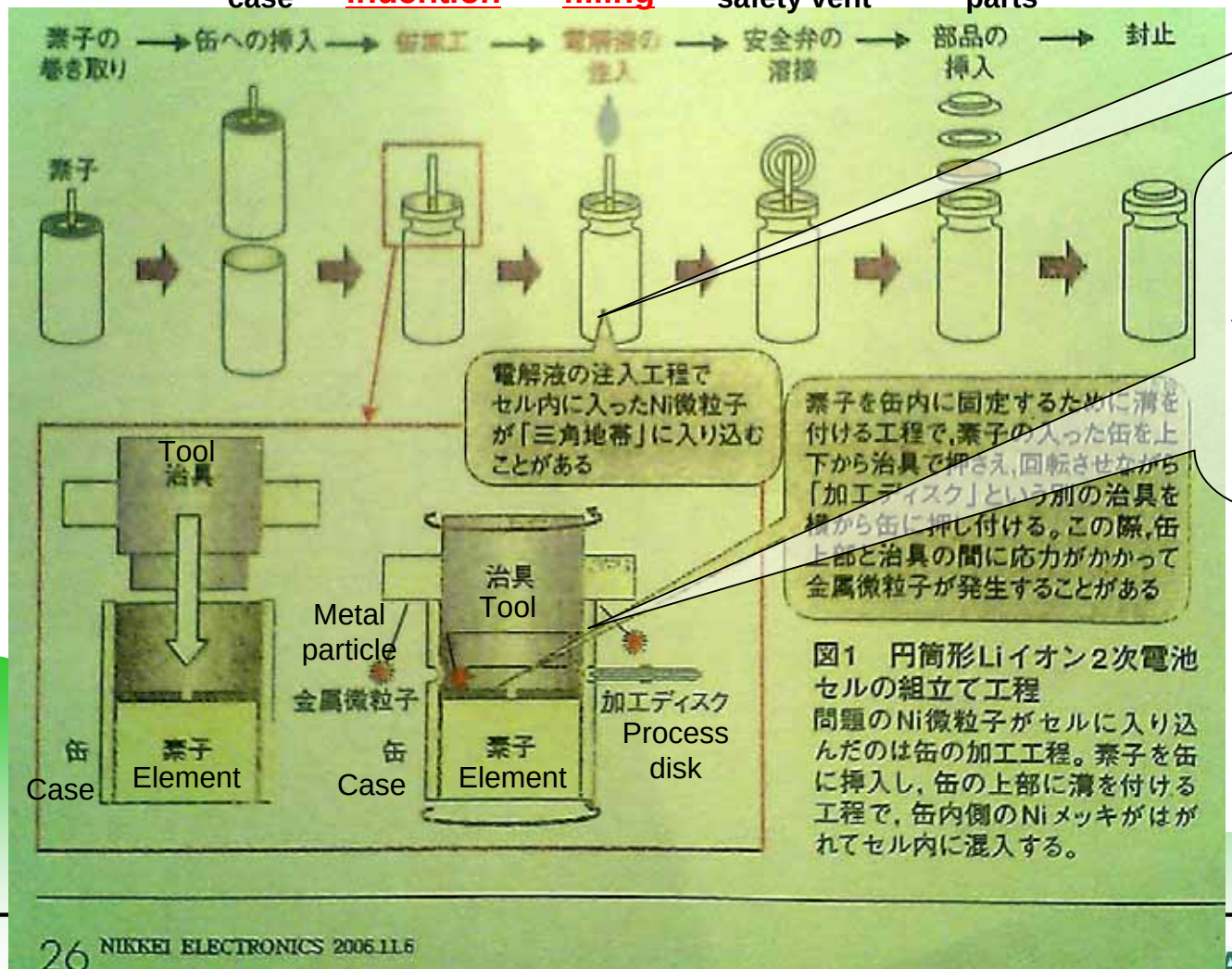
5) Cumulative incident rate: 0.000016%

Ref. http://www.sony.co.jp/SonyInfo/News/Press/200810/08-140E/index.html

Published Information (continued)

2. Assembling processes and the major reason of metal contamination published by SONY in “Nikkei Electronics, Nov. 6, 2006”.

Winding → Insert to case → Case indention → Electrolyte filling → Welding of safety vent → Insertion of parts → Sealing



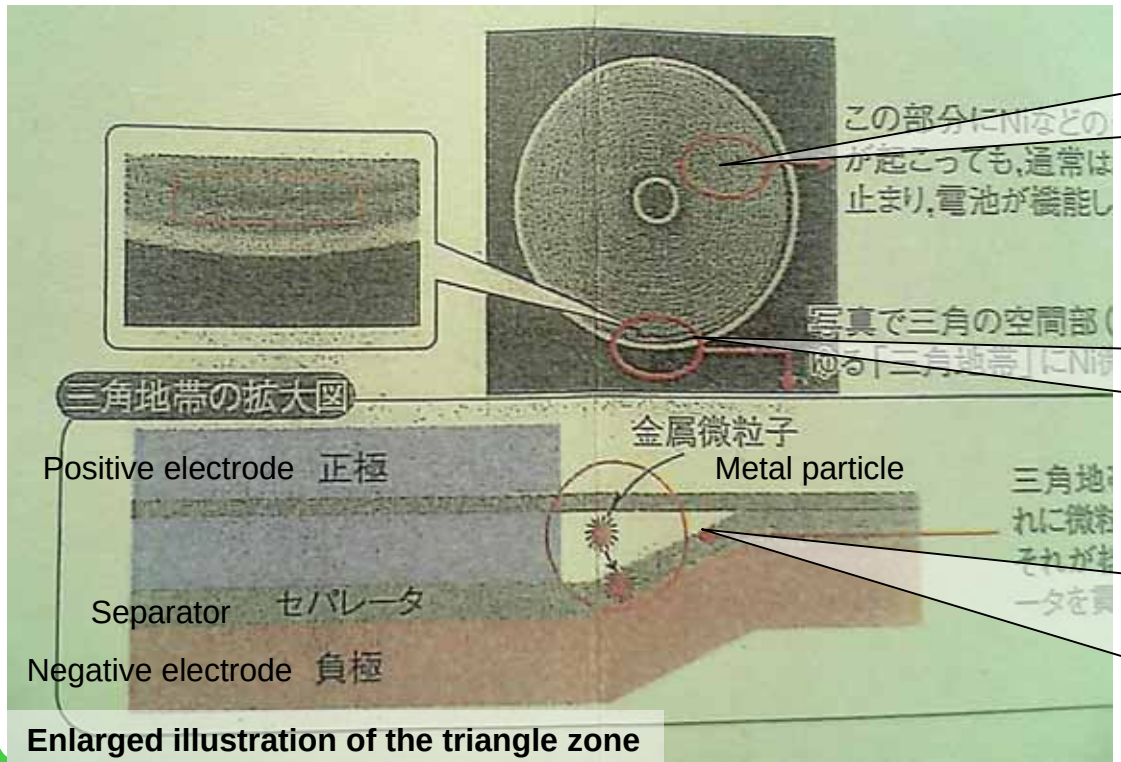
Metal particles can enter the triangle zone at the electrolyte filling process

The cell case which has element inside is clamped by a tool from upper side and rotated. Then it is pressed by the “ process disk” tool to make an indentation on the cell case to fix the inside element. At this process, metal particle can be generated by friction between the upper tool and the cell case.

Fig 1 Assembling process of cylindrical shape Li-ion cell
The process which allows contamination of metal particle is case indention process. The Nickel plating on inside of the cell case peal off and drop into the case when the process that makes an indention on the side top portion.

Published Information (continued)

3. The mechanism of the fire accident on the DELL PC / SONY Lithium Ion battery published by SONY in "Nikkei Electronics, Nov. 6, 2006".



Enlarged illustration of the triangle zone

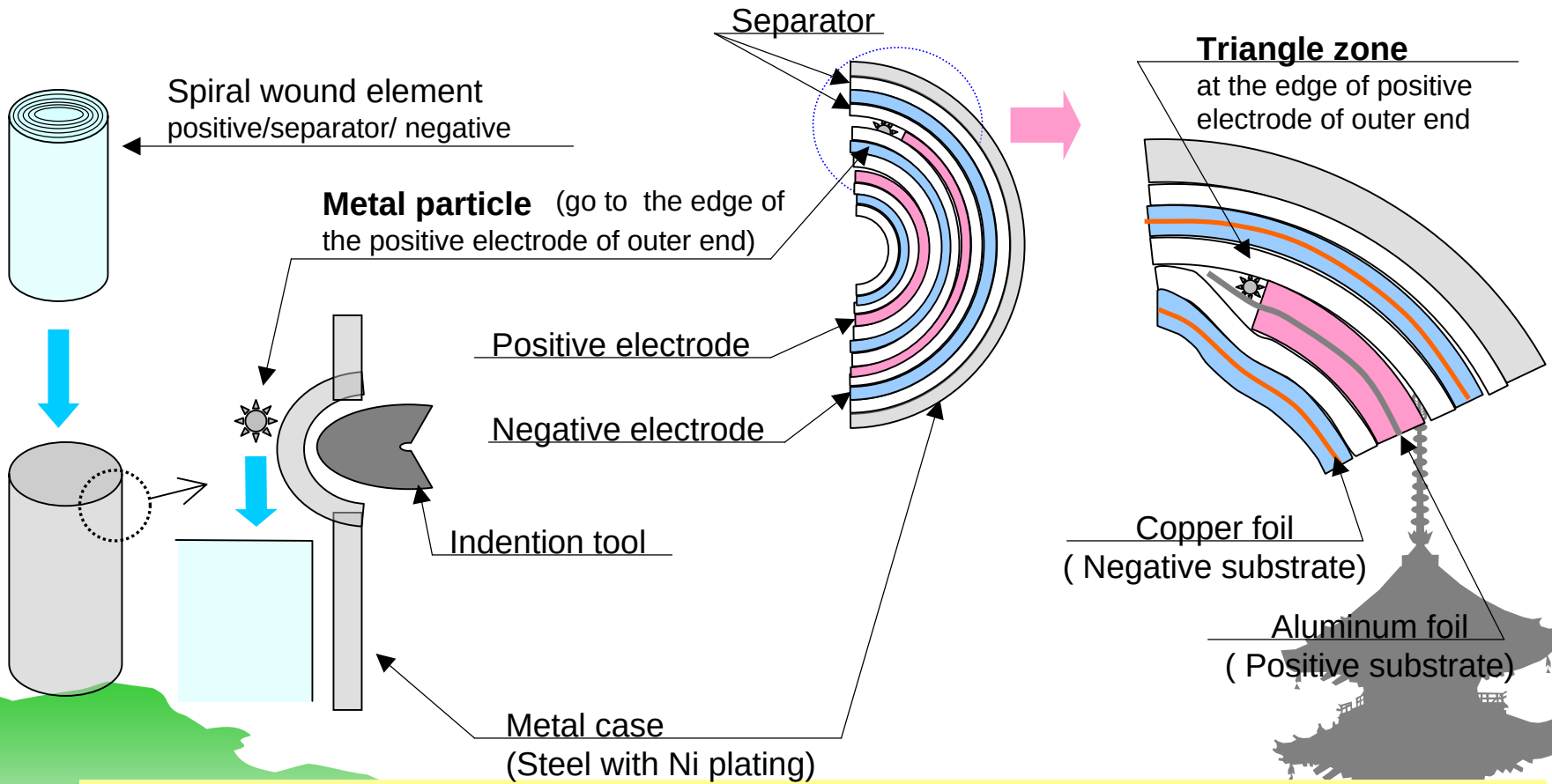
If a internal short occur because of contamination of metal particle such an Ni in this region, the cell quietly lose the function due to separator shut down.

But if a nickel particle enters the triangle zone (the edge of the positive electrode outer end) ….

If a nickel particle particle enters the triangle zone, it fairly infrequently dissolves and deposits on negative side. And then, lithium metal starts deposition on the nickel on negative electrode. Finally the deposited lithium metal go through the separator and create short circuit between negative and positive.

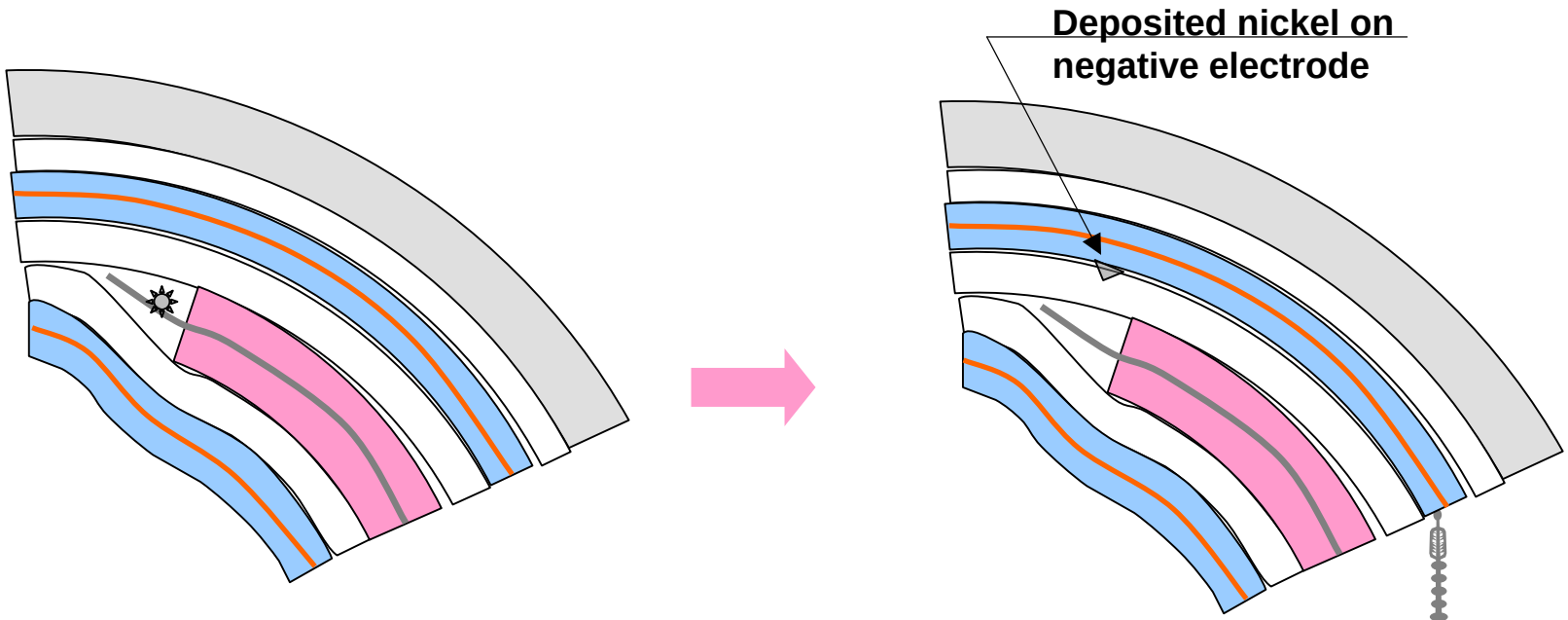
Summarized Mechanism

4. The detail mechanism of the fire accident



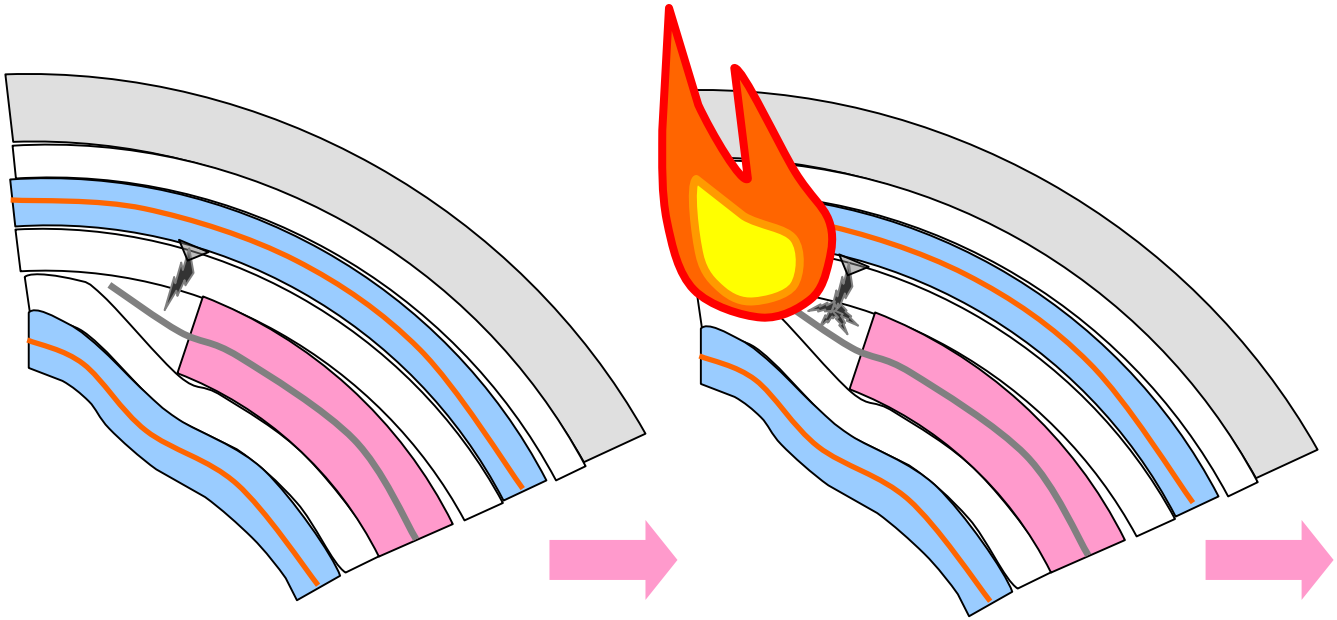
1) Metal particle can enter the cell inside and fairly infrequently locates the triangle zone after electrolyte filling process

Summarized Mechanism (continued)



2) After electrolyte filling and charge/discharge operation, the particle dissolve and deposit on negative electrode.

Summarized Mechanism (continued)



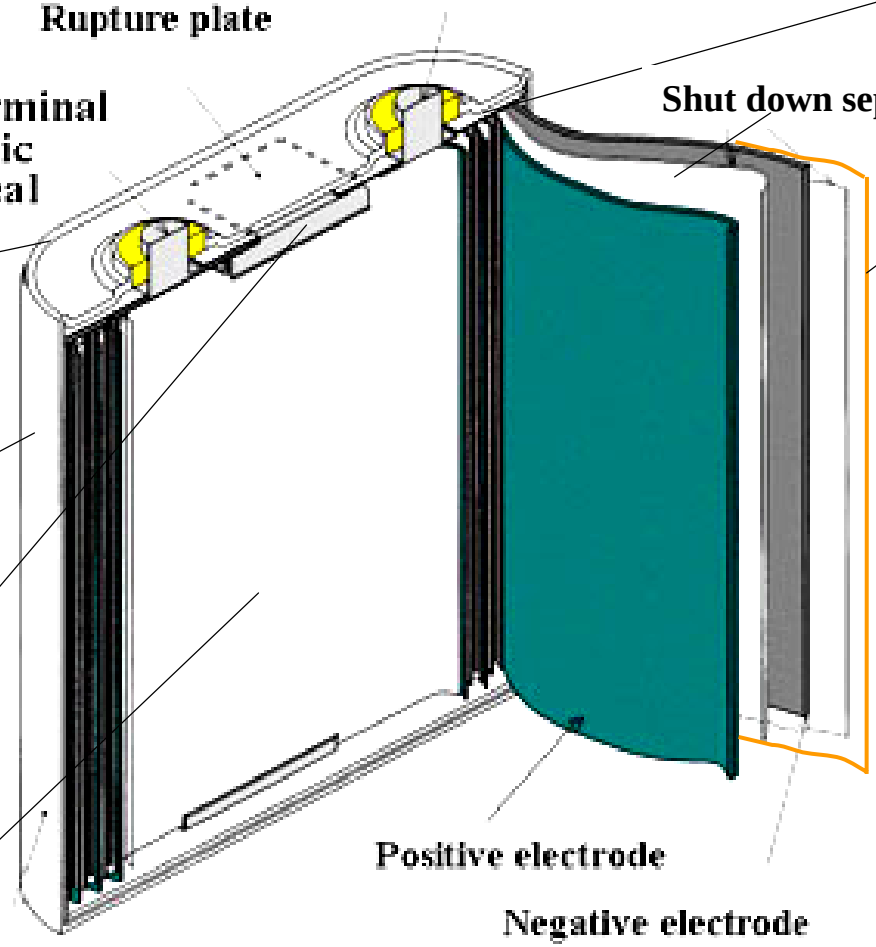
3) Lithium metal dendrite grows on the deposited nickel on negative electrode. It go through the separator and reach to the positive electrode. Finally, a short circuit path created between the negative and the positive electrode and cause fire.

The fire occurrence can be assisted by existence of thermally active metal lithium and low short circuit resistance because of direct short to aluminum foil which is positive substrate

Notes: Lithium metal dendrite can be created by only high voltage charging, very high rate charging such as more than 2C, or high rate charging under very low temperature.

If the short circuit path created on coated positive active material, it result in just consume capacity because of high short circuit resistance.

Structure of GYT Large Li-ion Cell for Satellite Application



Difference Between Commercial 18650 Cell and GYT Large Cell

	Commercial 18650	GS Yuasa Large Cell
Case material	Steel with Ni plate (or Stainless Steel) It can generate Ni particle that can dissolve on positive electrode potential and can cause the problem.	Aluminum Alloy The aluminum alloy does not dissolve on the positive electrode potential.
Case indention process	Yes. It can generate Ni particle which can fall on the inserted element.	No. The aluminum alloy case is welded without indention or any deformation process after the element insertion.
Contamination control	Depends on each manufacturer / model	Manufactured in clean room
Insulation film between case and element	No	Yes It can protect the element from metallic particle
Soft short (self discharge) inspection	Unknown	Yes, with very strict criteria
Charging voltage / algorism	Max 4.4V/cell / 3C quick pulse (an existing example)	Max 4.2V/cell / constant current (C/2) and constant voltage

Other Safety Test Data

- External short circuit

(Experiment)
100Ah Li-ion cells for satellite use were used for the tests. The cells have one rupture plate on the top and four rupture plates on the sides. Before the safety tests, the cells were charged to 100%SOC. The charge method is shown below.

Charge: 20A to 3.98V for 8hours by CC/CV method at room temperature.

The cell was clamped with the aluminum boards to simulate the environment in a battery unit.

Two kinds of condition in external short circuit tests were selected. One was a complete short circuit with only a resistance by the equipment *(0.5mohm)* (TEST I) and the other was a short circuit in which a resistance (1.4mohm) was used to control the short circuit current (TEST II).

Other Safety Test Data (continued)

(Results)

Figure 1 shows voltage, current and surface temperature of the cell on the external short circuit test (TEST I). The cell voltage became 0V after 3.6 sec. There was little temperature rise, no generation of vent gas and no explosion of the case. The reason for the voltage becoming 0V is that the electrical collector of positive electrode was melt down by joule heat.

Figure 2 shows voltage, current and surface temperature of the cell on the external short circuit test (TEST II). The maximum current of the test was 2200A. The cell surface temperature raised up gradually to 86 degree C. There was electrolyte leakage from rupture plate on the top. There was no generation of vent gas and no explosion of the case.

Other Safety Test Data (continued)

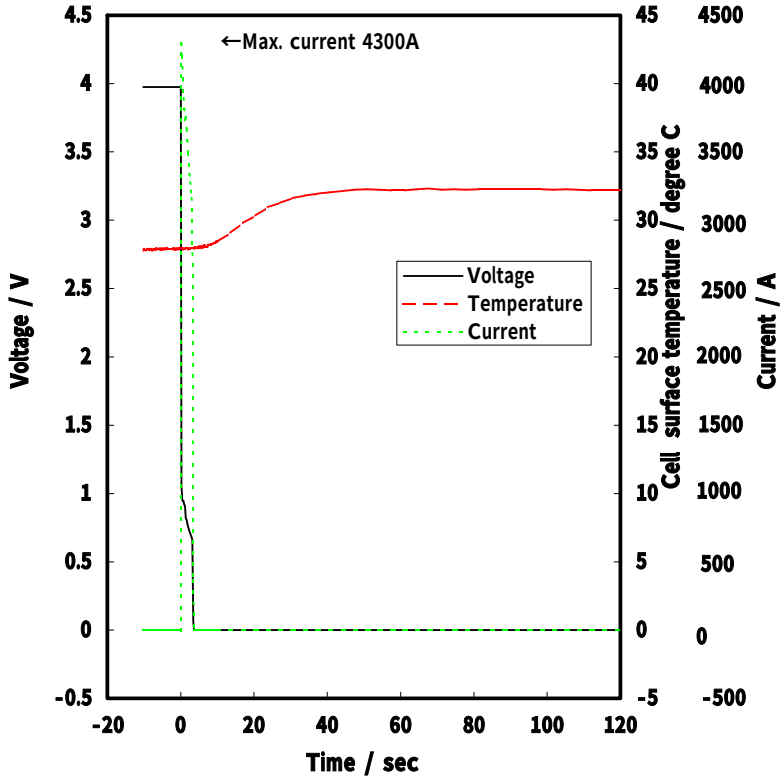


Fig. 1. Changes in voltage, current, and surface temperature of 100Ah Li-ion cell or the external short circuit test with *0.5mohm* resistance. (TEST I)

Charge before the external short circuit test:
20A to3.98V for 8hours by CC/CV method at 25°C

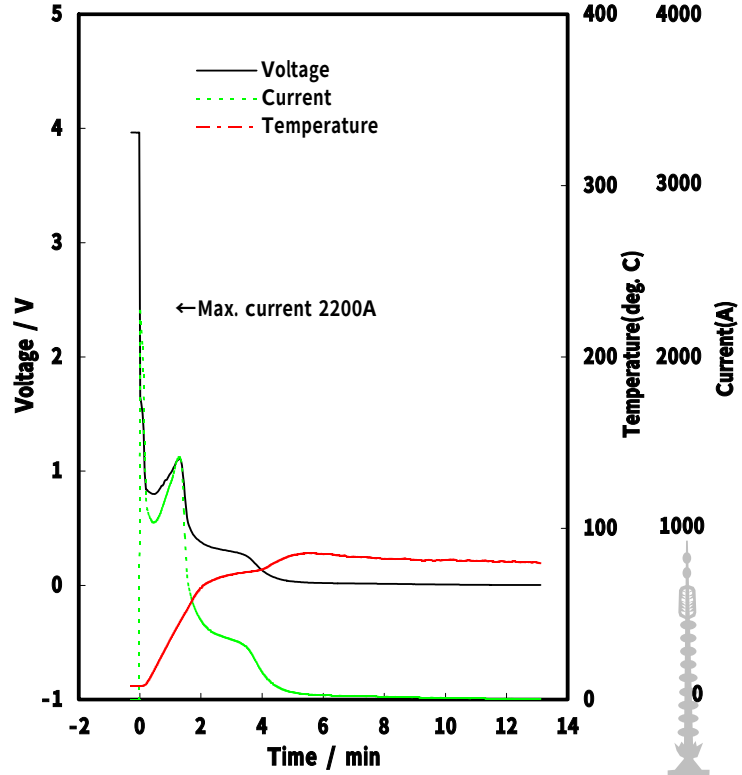


Fig. 2. Changes in voltage, current and surface temperature of a 100Ah Li-ion cell on the external short circuit test with a 1.4 mohm resistance. (TEST II)

Charge before the external short circuit test:
20A to3.98V for 8hours by CC/CV method at 25°C

Other Safety Test Data (continued)

- Over discharge

(Experiment)
A 100Ah Li-ion cell for satellite use was used for the over discharge test. The cell has a rupture plate on the cover plate and four rupture plates on the narrow side of the case.
At the starting, the cell was fully discharged state.
The over discharge test condition is shown as follows.

Discharge: 100A for 1 hour (100% over discharge)

(Result)
Figure 4 shows the voltage and temperature profiles at the over discharge test.. The maximum temperature was 48.5 degrees C after 17 min.
There was no electrolyte leakage. No rupture plate operated.

Other Safety Test Data (continued)

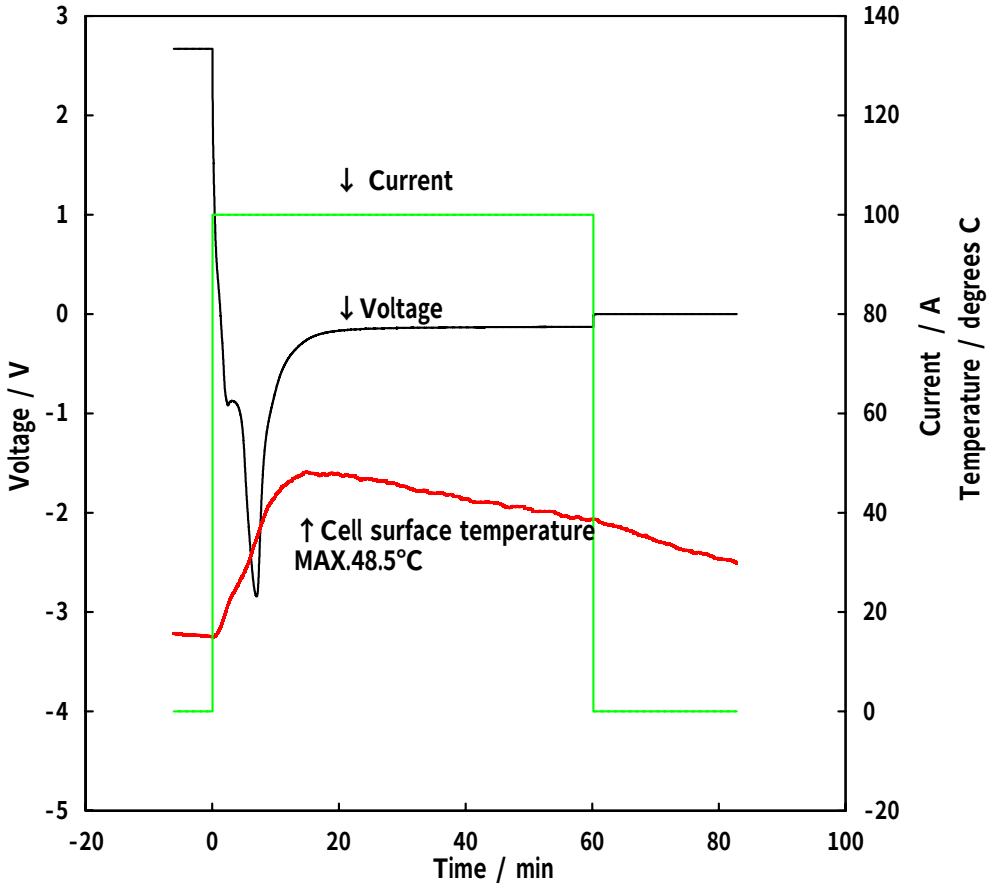


Fig. 4. Voltage and temperature profiles of the 100Ah Li-ion cell at the over discharge test.

Over discharge condition
Constant current at 100A for 1hour

Other Safety Test Data (continued)

- Press with load

(Experiment)
100Ah lithium ion cells were pressed by a round plate (r=10mm). The press loads were 2800kg from oil pressure pump. It is approximately 1000 times as the cell weight. When the load reached 2800kg, the cell was immediately released from the load. The each test time was within 5 sec.
We performed the tests for 4 cells. Each cell was pressed only at one time. The test condition is shown in Table 1.
The illustration of the tests is shown in Fig. 5.
During the test, we monitored the cell voltage and the situation.

Table 1. Test condition.

	Direction of the press
10Ah charged state	X, Y axes (1 press / 1 cell)
100% SOC	X, Y axes (1 press / 1 cell)

(Result)
For X axis, the electrolyte leakage, the voltage drop and the temperature rise were not observed.
The change of the cell shape was a little.
For Y axis, the cell shape changed largely. There was the electrolyte leakage from rupture plate of a cell case. But, the voltage drop and the temperature rise were not observed.

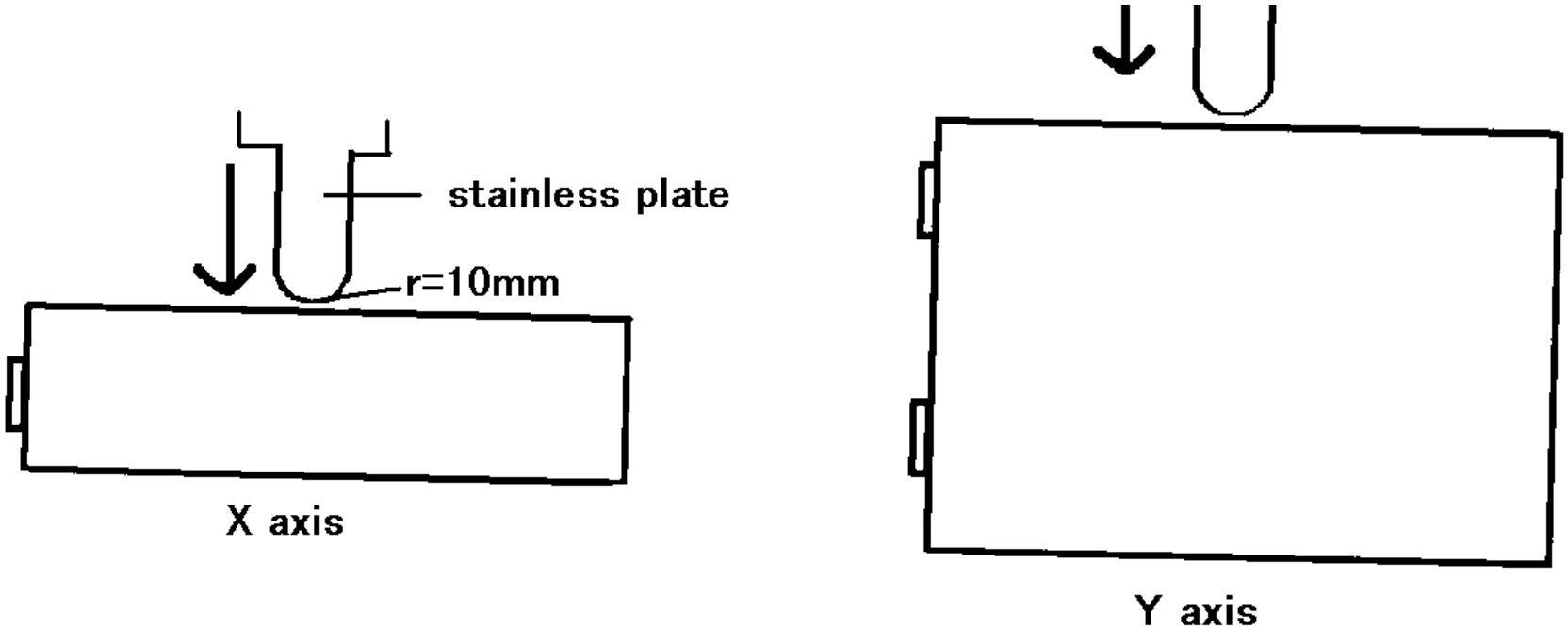


Fig. 5. Illustration of the press tests

Result of 190Ah cells

The representative pictures after the tests are shown

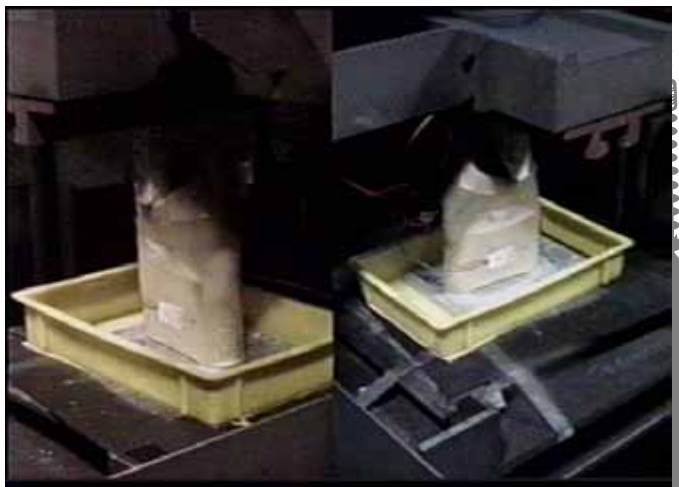
For Y axis and Z axis tests, there were electrolyte leakage from rupture plate.

In all tests, voltage drop and temperature rise were not observed.

It is suggested that <u>internal short circuit didn't happen at the tests.</u>

X axis

Y axis



Z axis

Conclusion

1. Fire accidents on commercial small cell related to indention process, cell structure, and operational condition such as charging.

2. GYT large Li-ion cells are designed in view of above points. They have never showed internal short accident through more than 10 years production. (>5000 cells)

3. GYT large Li-ion cells showed good result on external short circuit, over discharge and press with load test.