Analysis of Asset 459 Cell 5

CORPORATE RESEARCH

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EXECUTIVE SUMMARY

Due to the high temperature detected on the aluminum rivet of asset 459 cell 5 during APU start simulation, a further analysis was conducted in this report to investigate the root cause of the high temperature rivets, and the possible consequences of this abnormal cell.

A leakage test and cell DPA were conducted in this report followed by DPA, visual inspections and component analysis on the electrolyte. Although minor leakage was found in this cell, no evidence of corrosion or HF formation could be detected from the electrolyte analysis and visual inspections. The separator was found to have several spots with evidences of deformation due to high temperature. Further measurement on the DC resistance found much higher resistance between the aluminum current collector and the rivets. CT scans also found larger gaps between the rivet and its connecting conductors, and poor connection between the aluminum rivet and current collector on 459 cell 5.

The finding on the cause of the hot rivet has raised the safety concern of this cell. If this cell keeps operating and the cell continues to have high resistance on the electrical path between the aluminum rivet and current collector, the high temperature generated is very likely to cause further deformation or melting on the separator near the aluminum current collector, which will cause short circuit between the copper and aluminum electrode and followed by possible thermal runaway.

CONTENTS

INTRODUCTION

In the battery level tests of simulated APU start on Battery #459[1], high temperatures were recorded on the aluminum rivets (positive terminal) of cell 3 and cell 5, as shown in Figure 1. The high temperatures on cell 5 were of particular concern as the cell got even much higher temperature than cell 3. The peak temperatures measured with attached thermal couples on the positive rivet of cell 459-5 during the APU cycle test are listed in Figure 2. The cell peak temperature on the rivet has reached more than 100°C in most of the cycles, and the recorded highest temperature was 157°C, which is already beyond the melting point of the separator[2] in the LVP65 cell design.

A cell leakage test followed by destructive physical analysis for Battery 459 cell 5 were performed in this report to further investigate the cause of the heat generated during the test and its potential risks during normal operation.

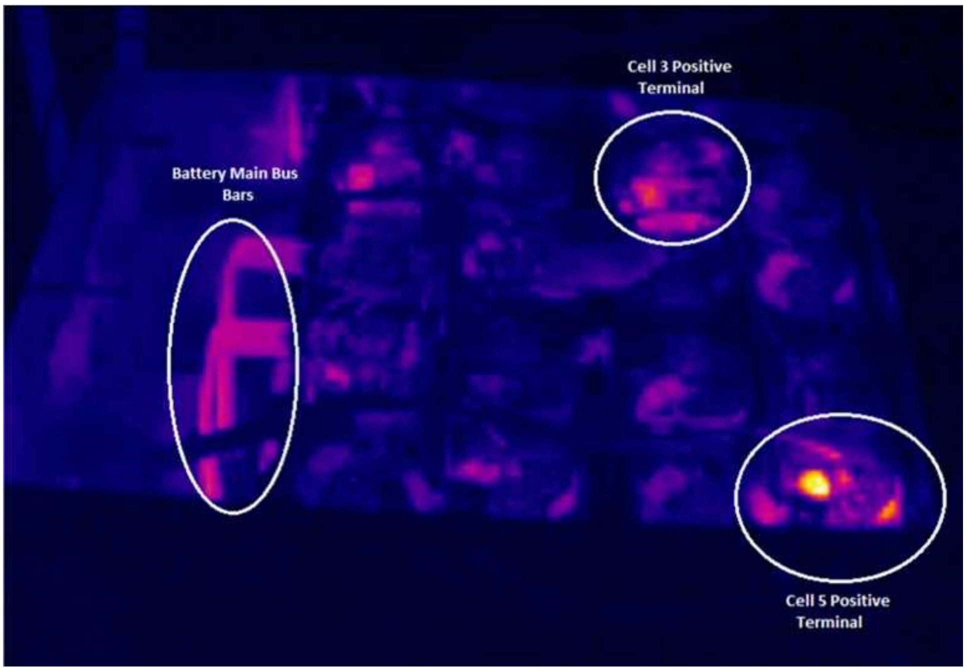

Figure 1. Infrared thermal image of Battery 459 during APU loading

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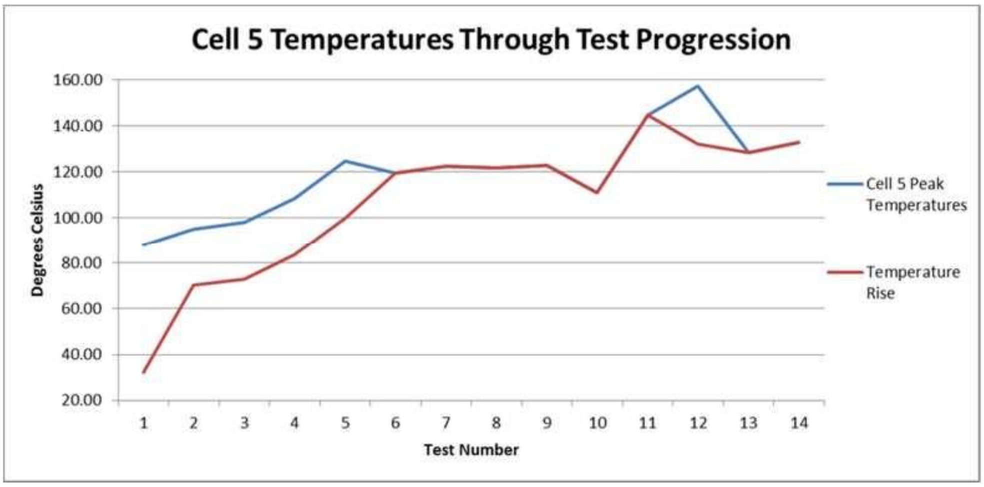
[1] UL-NTSB Contract 13CA50802

[2] The separator of LVP65 is made of [redacted] where the melting temperature of [redacted] is normally around 130°C



	Cell 5 Peak Temperature	Temp Rise
Task A.1.B, 25 C, 1 of 5	88.2 °C	63.2 °C
Task A.1.B, 25 C, 2 of 5	95.2 °C	70.2 °C
Task A.1.B, 25 C, 3 of 5	98.1 °C	73.1 °C
Task A.1.B, 25 C, 4 of 5	108.5 °C	83.5 °C
Task A.1.B, 25 C, 5 of 5	124.8 °C	99.8 °C
Task A.1.B, 0 C, 1 of 5	119.7 °C	119.7 °C
Task A.1.B, 0 C, 2 of 5	122.4 °C	122.4 °C
Task A.1.B, 0 C, 3 of 5	121.6 °C	121.6 °C
Task A.1.B, 0 C, 4 of 5	123.0 °C	123.0 °C
Task A.1.B, 0 C, 5 of 5	111.0 °C	111.0 °C
Task B, Cell Level Test, 0 C	144.7 °C	144.7 °C
Task B, Battery Level, 25 C	157.3 °C	132.3 °C
Task B, Battery Level, 0 C, 1 of 2	128.3 °C	128.3 °C
Task B, Battery Level, 0 C, 1 of 2	132.9 °C	132.9 °C

Figure 2. Temperature record of Battery 459 Cell 5

POTENTIAL ROOT CAUSES OF THE OVERHEATING RIVET

As the maximum temperature recorded from APU start tests on #459 cell 5 is 157°C, which is already beyond the shutdown and melting temperature of a [redacted] separator. Moreover, because the maximum temperature measured is on the surface of the aluminum rivet, where the heat has better dissipation comparing to the current collectors inside of the cell. It is reasonable to believe that the temperature inside of the cell could be higher to melt the separator and cause potential risks to trigger internal short-circuit (ISC) if the temperature is keep growing. Therefore it is important to understand why cell 3 and 5 are different than other cells to have higher temperature on the rivet and the possible causes and possible consequences of it.

For developing the investigation plan, one major hypothesis of this report is that the source of overheating is from the electrical path between the terminal and the current collectors.

It is very unlikely that the initial heat source to cause the overheating rivet is from the windings itself, because if the winding is the heat source, the temperature should be higher than 157°C to cause an ISC due to the melting of separator[3] and thermal runaway. As we haven't seen thermal runaway on cell 5, we assume the heating source shall be from the current path of the terminal and current collectors.

Therefore the following actions are planned in this report:

1. A leakage test on cell to check if the cell is "breathing" to cause the air to come in the cell and cause corrosion,
2. A cell DPA (destructive physical analysis) to investigate if there is any sign of corrosion in the critical current path inside the cell,
3. Visual inspection on the separator for signs of melting, deformation, and SEM to check the porosity of the separator to verify if the temperature has exceeds the shutdown temperature,
4. Component analysis on the electrolyte to see if there is any abnormal sign that can be related to the corrosion of the materials in the cell (ex. corrosion from current collector, active materials or insulation materials).
5. DC resistance measurement to check the status of conjunction points on cell top casing, and
6. CT scan to to inspect the physical connecting condition of the electrical path for gaps or signs of corrosion along to cause high temperature under high current.

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[3] The cell may still survive if the time for overheating is just within few seconds. However, as the 157°C was measured at rivet of positive terminal. It will takes at least few seconds for the heat to transfer from inside of the cell to the rivet.

Figure 3 below shows the summary of this investigation to find out the root cause(s) of this overheating rivet issue.

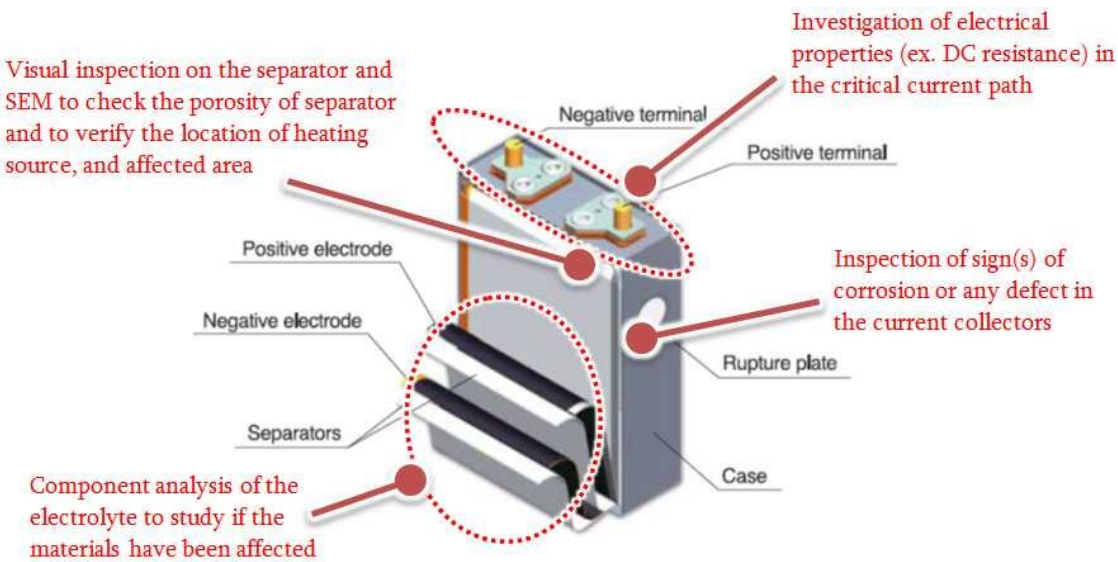

Figure 3. Stretegy to investigate the root causes of overheating in cell 5 of battery 459

Cell Examination and DPA Results

Leakage Test

From a preliminary visual inspection of Battery 459 cell 5, a gap between the connection plate and outer packing material on cell cover was discovered. A leakage test was first conducted to verify the integrity of the seal before DPA. The cell was placed in a closed glass container, vacuumed to -30 psig (comparing to the atmosphere pressure) and stayed in a temperature control environment at 40°C for 2 hours. By using the GC/MS analysis technique, the electrolyte outgassing, i.e. DMC, EMC, and EC, could be detected in the gas phase of the glass container, which confirmed the leakage of the electrolyte from cell 5. The GC/MS spectra for the leakage test are shown in Figure 4. In addition, at such specific condition (-30 psig and 40°C), the electrolyte can leak out about 6.55ul from the cell within two hours.

Figure 4. GC/MS Spectra for leakage test.

Top: blank test; middle: analysis for Battery 459 Cell 3; bottom: analysis for Battery 459 Cell 5

The leakage found on the test can be a consequence of the defect in the cell header. There should be a problem that already occured in the conjunction plane between the connection plate and outer packing material on the cell header, so the seal of the cell top casing is damaged.

Electrolyte Analysis

Since the leakage of electrolyte vapor from Battery 459 Cell 5 was confirmed from GC/MS analysis, a concern about the decomposition of electrolyte and corrosion of metallic parts might be considered once the moisture is diffused into the cell through the pathway of leakage and resulted in HF formation. A further analysis for the electrolyte was performed to investigate its constituents. The analysis includes GC/MS and ICP analysis for identifying the organic solvents and quantitatively analyzing the element contents in the electrolyte.

GC/MS Analysis on Electrolyte and Headspace Gas

Figure 5 shows the GC/MS analysis results for the electrolyte saved from Battery 459 cell 5. From the obtained MS spectrum, they are organic compounds of the electrolyte: four carbonates, including DMC, EMC, [redacted], and EC, can be ifentified, which appear to be normal. [redacted] is found from the electrolyte which is resulted from the decomposition of $LiPF_6$.

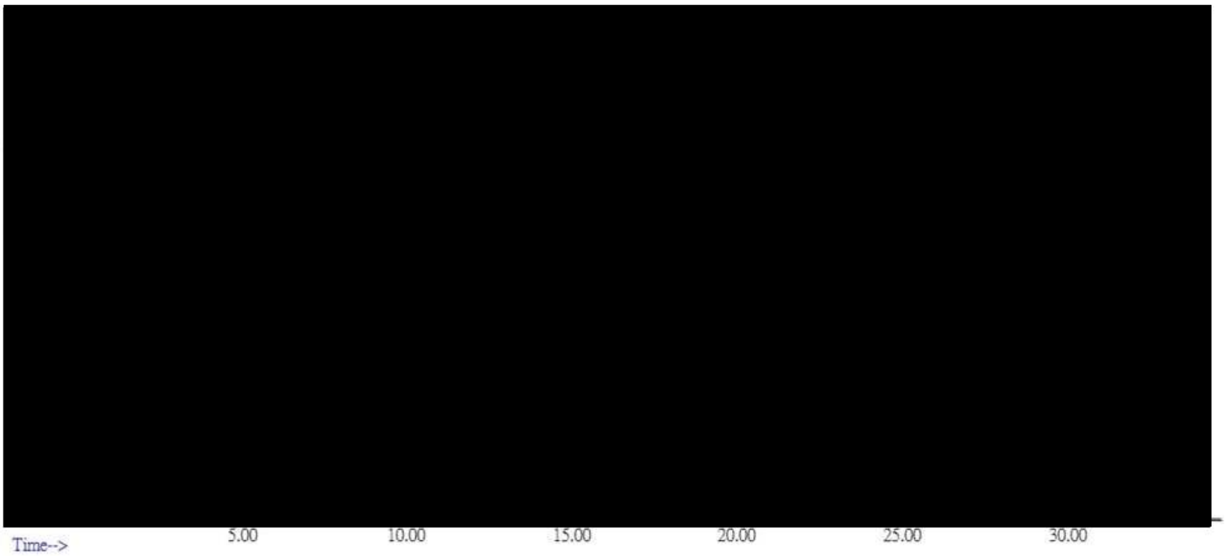

Figure 5. GC/MS anlaysis for Battery 459 cell 5. 0.2µl of electrolyte was directly injected into GC/MS.

The vapor phase in Battery 459 cell 5 headspace was also analyzed by GC/MS, as shown in Figure 6. The vapor is basically composed of the evaporation of the solvent, including DMC, EMC, and [redacted], which is normal.

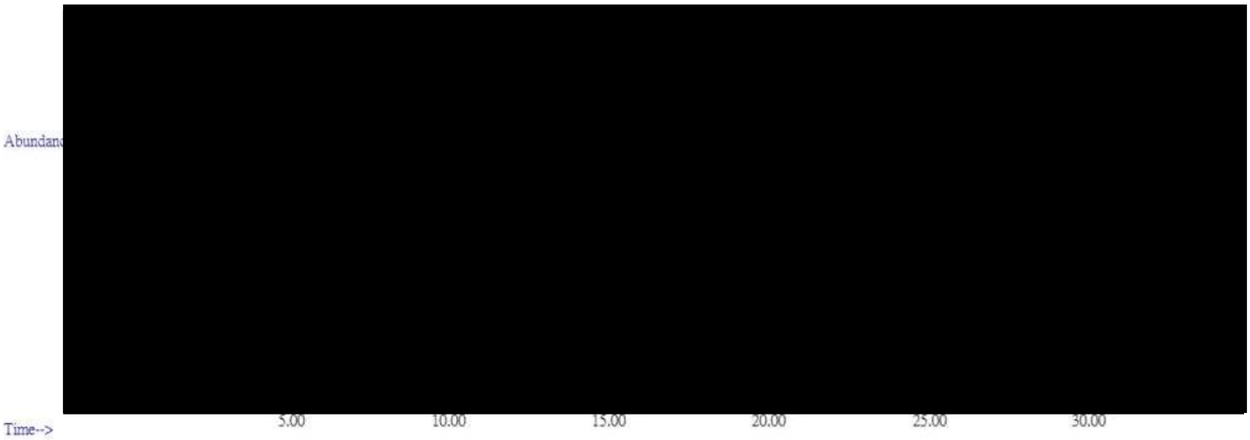

Figure 6. GC/MS anlaysis for the headspace of Battery 459 cell 5. 0.5ml of gas from headspace was directly injected into GC/MS.

ICP Analysis

The ICP analysis of the electrolyte on 459 Cell 5 is summarized in Table 1, with the comparison of Battery 412 cell 3, 5, 6. No abnormal metallic ion level was deteted in the electrolyte, which implies that the corrosion reactions have not been induced in the leaked 459-5 cell.

Table 1. ICP Elemental anlaysis of the electrolyte

	Elements in mg/L													
	Li	[redacted]	Al	Cu	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Blank	[redacted]	[redacted]	0.01	ND	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
#459-5	[redacted]	[redacted]	0.6	0.5	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Blank	[redacted]	[redacted]	0.1	0.7	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
#412-3	[redacted]	[redacted]	2.0	1.2	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
#412-5	[redacted]	[redacted]	2.4	4.0	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
#412-6	[redacted]	[redacted]	1.1	1.5	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]

	Elements in mg/L													
	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]								
Blank	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]								
#459-5	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]								
Blank	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]								
#412-3	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]								
#412-5	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]								
#412-6	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]								

According to the result of electrolyte analysis, we cannot find any significant evidence to show the corrosion issue that can potentially result from the interaction between moisture and electrolyte.

Although no electrolyte decomposition or metal corrosion can be detected from the electrolyte analysis, it is believed that the cell degradation will happen eventually if the leakage of Battery 459 cell 5 continues with longer charge/discharge cycles.

Visual Examination and SEM on The Separator

Since the peak temperatures on the 459-5 cell's rivet has been detected to reach over 130°C several times during APU start simulations (Figure 2), some irreversible damages might occur on the materials once the heat passed along with the current collector and down to the winding. A physical inspection was conducted to review the unwound jelly rolls. From the photos shown in Figure 7, few spots with shrunk or melted separators could be observed from visual inspection. The spots were about 1 to 2 mm wide and less than 1 mm tall. Such shrinkage might be resulted from the separator in contacting with the hot current collectors.

Typical separators used in lithium ion cell have high density of open pores for ion transportation. On the regions adjacent to these shrunk separators, however, the pores were closed, as shown in the SEM images in Figure 8. These observed shrunk separators were generally close to the welded current collector near the cell cover. It is also the evidence to show the heating source to cause the overheating is not from inside of cell (ex. windings) but from cell top casing.

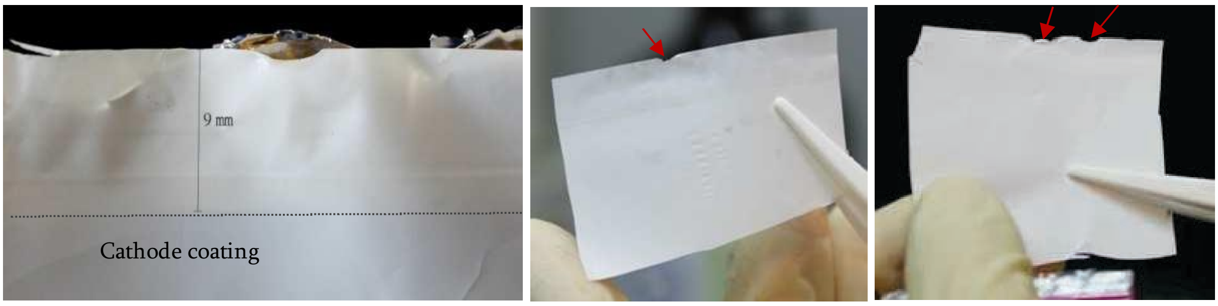

Figure 7. Shrunk separator observed in the jelly rolls in Battery 459 Cell 5

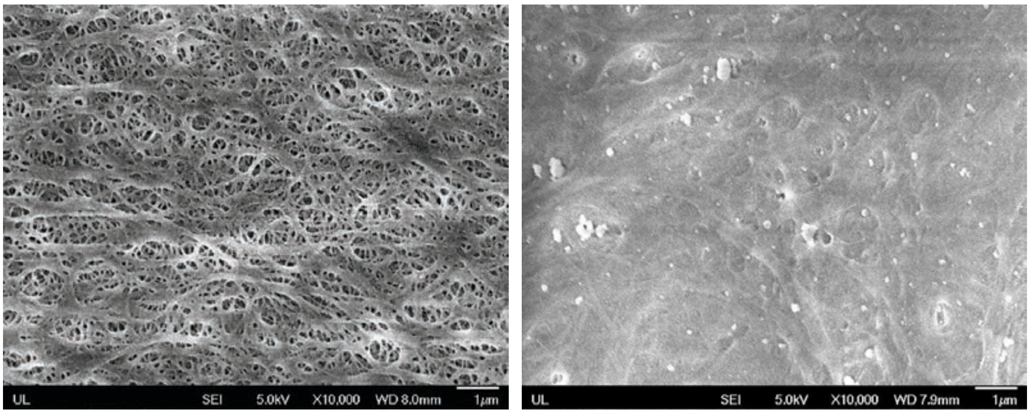

Figure 8. SEM Images of separators. Left: open pores on normal site; right: close pores near shrunk separator

Although the melted separator found in this report have not reached to the point to cause direct contact between the aluminum and copper electrodes, it is very likely that if the cell keeps operating with the high temperature near the rivet, the melting separator will continue and cause the short circuit of the electrodes then followed by thermal runaway.

DC & AC Resistance measurement

As we already confirm the heat source was not from the windings but the electrical path from the current collector to the terminal screw, DC and AC resistance measurement were conducted.

The DC and AC resistances were measured with a HIOKI RESISTANCE HiTESTER RM3543 Series DC resistance tester and a FLUKE 289 True-rms Industrial Logging Multimeter. The measurement was conducted under 25°C with 50% RH. The testing results are summarized in

Table **2**. The data of Battery 376 cell 8 is used as a reference for comparison between normal (376-8) and target (459-5) samples.

Table 2. Electrical test data

Cell	**459-5**				
Copper Side	DC Res (mΩ)	AC Res (Ω)	Aluminum Side	DC Res (mΩ)	AC Res (Ω)
Rivet → Rivet	0.0067	0.16	Rivet → Rivet	0.025	0.15
	0.0059	0.16		0.024	0.16
Rivet → Plate	0.0075	0.17	Rivet → Plate	0.017	0.14
	0.0083	0.16		0.019	0.2
Rivet → Screw	4.12	0.16	Rivet → Screw	3.21	0.17

	3.15	0.17		2.15	0.14
Collector → Rivet	0.02	0.16	Collector → Rivet	74.02	0.22
	0.017	0.16		74.53	0.26
Collector → Plate	0.019	0.15	Collector → Plate	74.56	0.21
	0.018	0.15		74.83	0.23
Collector → Screw	4.72	0.17	Collector → Screw	75.62	0.21
	6.39	0.17		75.87	0.2

Cell	376-8				
Copper Side	DC Res (mΩ)	AC Res (Ω)	Aluminum Side	DC Res (mΩ)	AC Res (Ω)
Rivet → Rivet	0.0011	0.14	Rivet → Rivet	0.0039	0.24
	0.0015	0.14		0.0038	0.23
Rivet → Plate	0.0075	0.14	Rivet → Plate	0.019	0.21
	0.0079	0.14		0.017	0.24
Rivet → Screw	1.32	0.15	Rivet → Screw	3.12	0.24
	1.42	0.15		3.54	0.25
Collector → Rivet	0.012	0.14	Collector → Rivet	0.03	0.24
	0.012	0.14		0.03	0.23
Collector → Plate	0.017	0.13	Collector → Plate	0.039	0.23
	0.017	0.13		0.039	0.24
Collector → Screw	1.49	0.14	Collector → Screw	39	0.23
	1.39	0.14		34	0.23

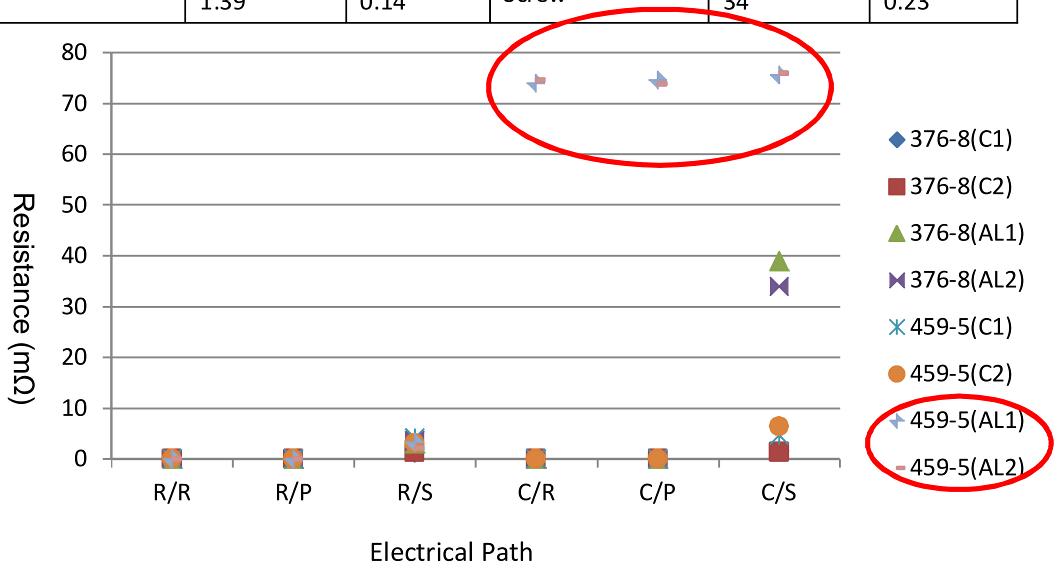

Figure 9. Plot of the electrical resistance for various contact path

According to the results, the paths from rivet to rivet and from rivet to plate have very low resistance, which suggests there is no deterioration or interruption in the path for both Cell 376-8 and Cell 459-5. The resistance from rivet to the terminal screw is higher than rivet to others because the screw should be fixed by a nut to form a good ohmic contact. In Figure 9, we can find that the resistances of 459-5(AL1) and 459-5(AL2) are higher than 376-8(AL1) and 376-8(AL2). Because the path from AL rivet to Cu terminal screw is good, therefore the problem contributing to the high resistance is between AL current collector and AL rivet.

Physical Inspection for Cell Cover

Microscope inspection for cell cover

From the microscope inspection of the cell cover disassembled from DPA as shown in Figure 10 and Figure 11, the insulation material for the negative and positive terminals, [redacted] revealed deformation near the cover plate. As the glass transition region for the [redacted] is around 80 ~110°C, we can see that the overheat during the APU start tests have induced irreversible damage on [redacted] material. The deformation of the packing material may result in potential risk of cell leakage.

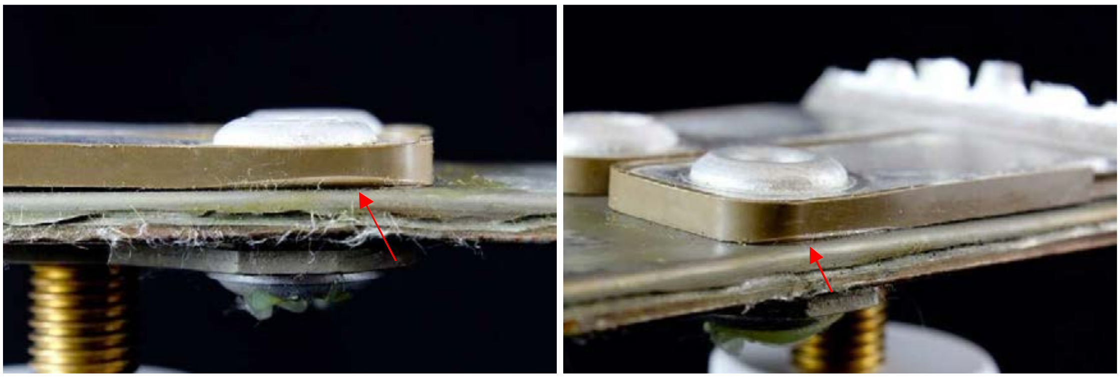

Figure 10. Images of positive terminal, showing deformed [redacted] insulator

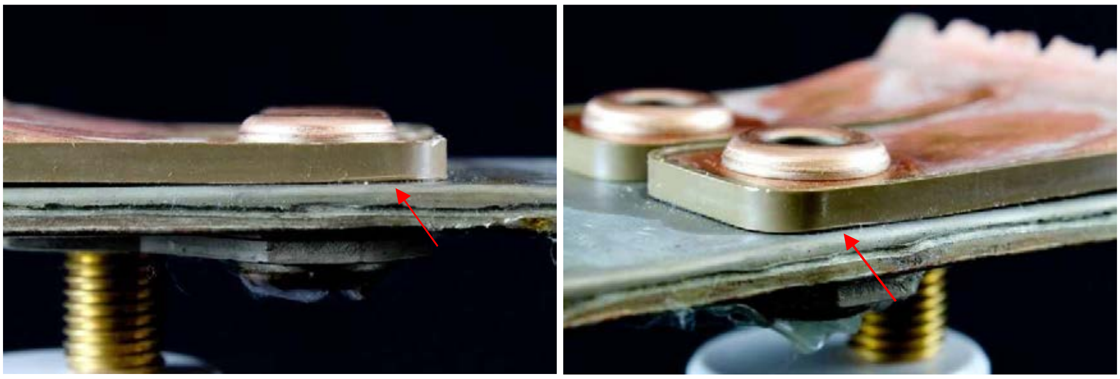

Figure 11. Images of negative terminal, showing deformed [redacted] insulator

Preliminary inspection with CT Scan

The CT scan images of cell rivets for Battery 459 Cell 5 and another normal Battery 376 Cell 8 as a reference are shown in Figure 12. Comparing the cross-sectional images of the rivet, bigger gaps can be observed from the contact interface of the rivet and current collector of Battery 459 cell 5 and the conjunction line is more obvious than a normal sample, which may result in high contact resistance due to poor connection and create localized hot spots during charge/discharge cycling.

A closer view of the right-side marked area in Figure 12 that is further showin in Figure 13. We can see more clearly about the difference between the reference (376-8) and this abnormal (459-5) samples.

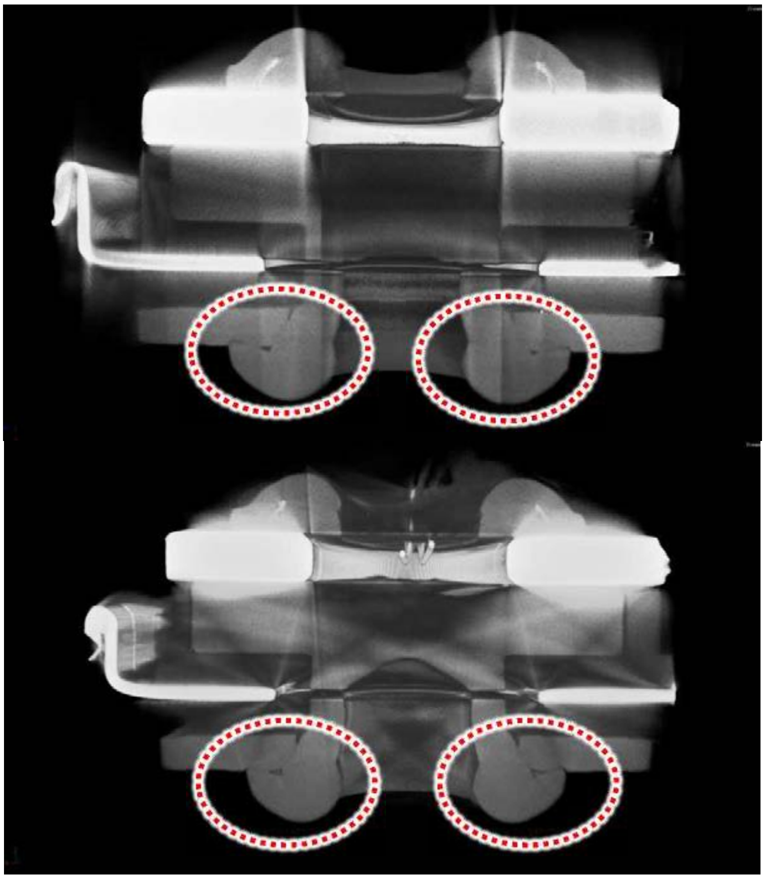

Figure 12. CT Scan image of negative terminal on Battery 459 cell 5 (Top: The crosscection view of conjunction between rivet and current collector and positive terminal in cell 376-8, which is normal sample; Bottom: The crosscection view of conjunction between rivet and current collector and positive terminal in cell 459-5, which is the abnormal sample)

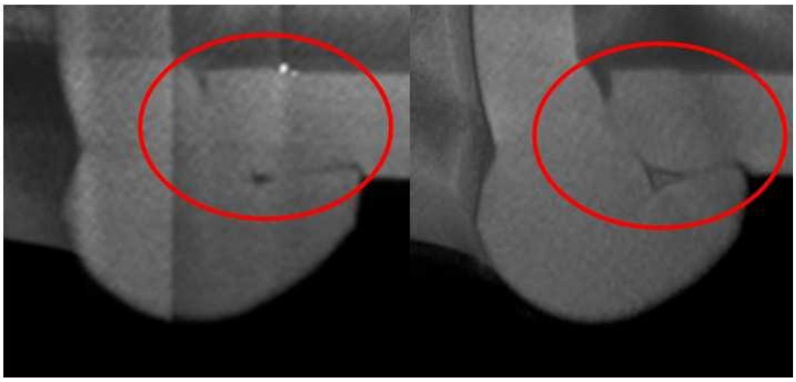

Figure 13. Closer view of Figure 13 (Left: normal sample, cell 376-8; Right abnormal sample, cell 459-5)

CONCLUSION

From the leakage test and DC resistance measurements on cell 459-5, we can confirm the seal of the cell has been damaged and the current path between the cathode current collector and rivet has much higher DC resistance (i.e. 74mΩ) than a normal cell (i.e. 0.03mΩ). The CT scan analysis can also provide evidence to show the poor physical contact between rivet and cathode current collector in cell 459-5 than a normal cell.

The partial melting in the separator close to the current collector has provided a direct evidence to show the heating souce to cause the overheating rivet is not from the winding. It is a consequence of the high resistance between the rivet and current collector on the cathode side. It also shows that if the cell continues to operate with such a high resistance on the electrical path, the heat will cause further deformation of the separator and eventually it is very likely to cause direct contact (short circuit) between aluminum and copper electrode then thermal runaway. Especially when the battery is operating under lower temperature, the higher current will make the resistance heat more severe.

Although there is no evidence of corrosion or interference from the moisture to cell electrolyte according to the result of DPA and the forensic analysis of electrolyte in cell 459-5, due to the leakage of the cell, it is believed that if the cell continues to operate, the humidity goes into the cell will cause further corrosion and power degradation, which will be a safety concern for the cell.

With the analysis of this report, one major concern is the design of using rivets in this cell. Due to the nature of the rivet, especially for aluminum which is easier to deform, and the fact that in this cell design, the rivets have not been well considered about the possible poor connections[4], the contact between the parts (rivets and conductors) will become a major issue. The high resistance, poor connections, and the melting separator detected by this report have all shown high possibility of this cell to go thermal runaway if such situation exists while performing more APU starts.

[4] For example, UL857 (Standards for Safety For Busways) specifically stated the requirements for riveted connection for aluminum: "At a riveted connection of current-carrying parts involving aluminum, each rivet shall have a spring washer at one end and either a spring washer or a flat washer at the other end. Other constructions may be used if they have been investigated and determined to be acceptable"