Hazards Associated with $LiMnO_2$ Cells with Different Electrolytes

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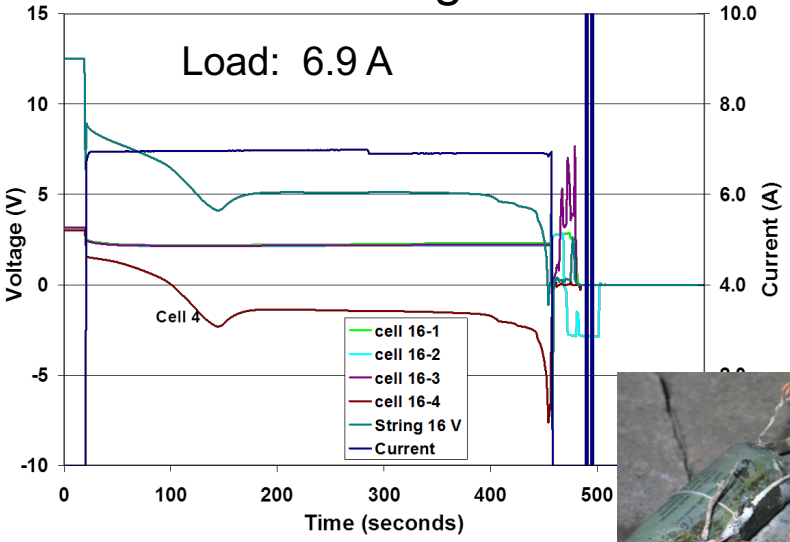
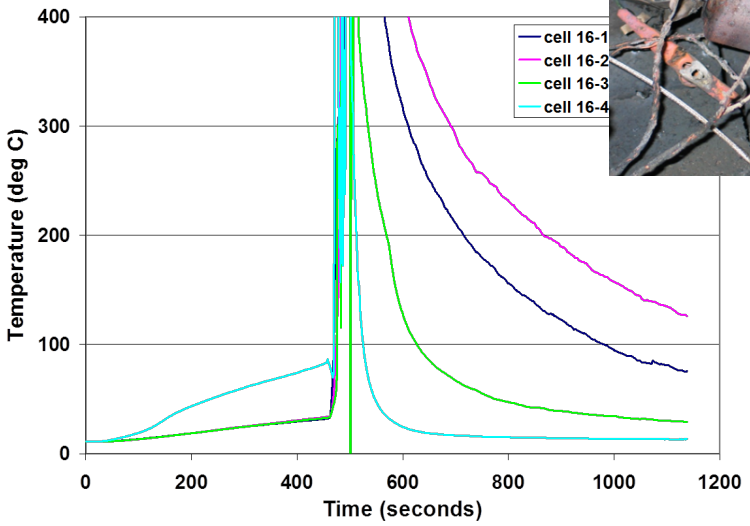
Background

- Past work at NASA- JSC showed that $LiMnO_2$ cells from different manufacturers gave different results under conditions of unbalanced overdishcarge (into reversal) and hard external short circuit conditions
  - Some were explosive and changes were made to flight hardware (ex. AED) to include two-failure tolerance to voltage reversal with two independent diodes parallel to each cell
- Unpublished data and discussions from 'government-only' meetings indicated that this was a well known, but unpublished, fact that the electrolyte salt was the cause of the difference in behavior
- Current test program was undertaken to obtain data to confirm effects of electrolyte salts on the outcome of off-nominal conditions on $LiMnO_2$ primary cells.

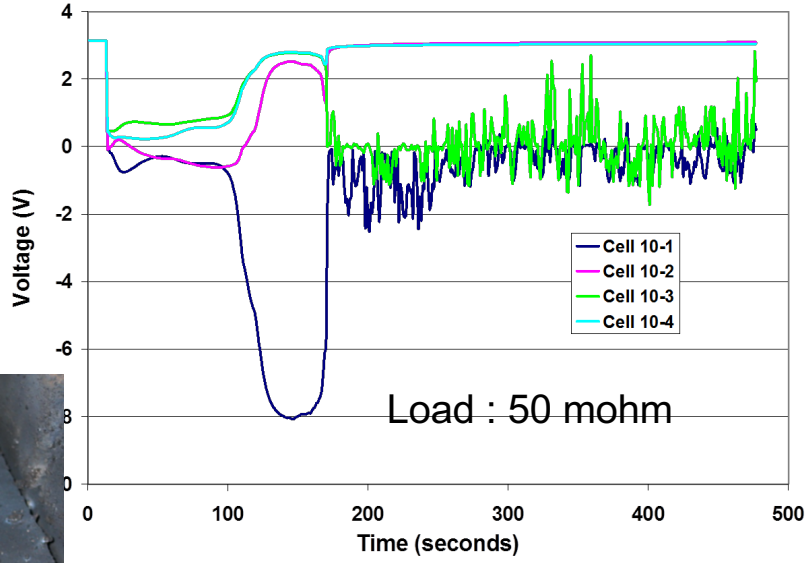
Primary Lithium Batteries: Overdischarge on Unbalanced Series String and External Short (on series string)

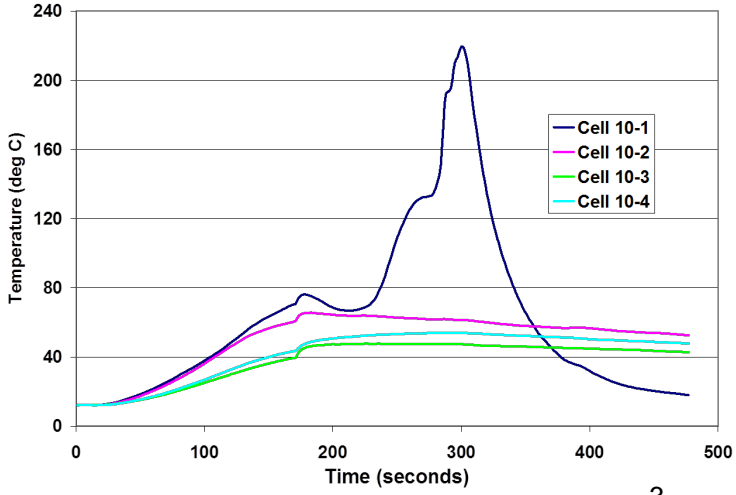
Overdischarge





External Short





Outline of Tests

- Baseline characterization
  - Cell
  - Battery (5-cell series)
- External short test
  - Cell
  - Battery (5-cell series)
- Over-discharge test
  - Cell
  - Battery (5-cell series)
    - Balanced condition
    - Unbalanced condition
- Electrolyte (salt) analysis using EDS

Test Condition

❑ Cell A CR17335

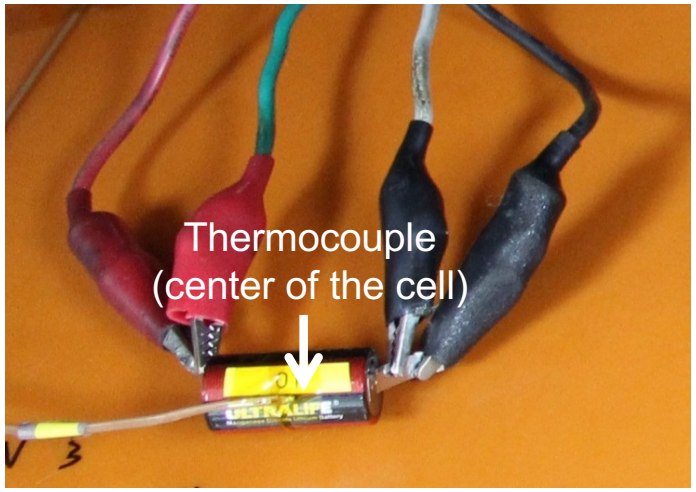
- ❑ Discharge Current 1.5A in baseline test and over-discharge test
- ❑ Unbalanced Condition of the over-discharge test
  - Unbalanced Condition 1: One cell in each series string was discharged to 25% of its baseline capacity
  - Unbalanced Condition 2: One cell in each series string was discharged to 2V, and then keep at 2V for 10 hours
- ❑ External short circuit tests using about 50 mOhm resistive load

❑ Cell B CR123

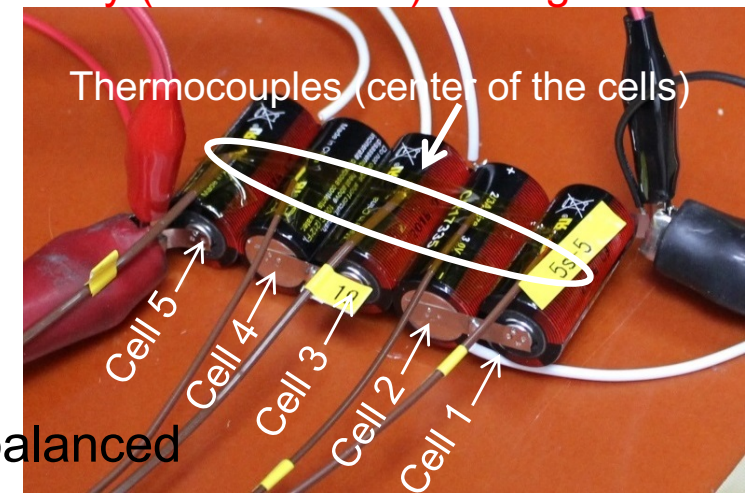
- ❑ Discharge Current 1A in baseline test and over-discharge test
- ❑ Unbalanced Condition of the over-discharge test
  - Unbalanced Condition 1: One cell in each battery will be discharged to 25% of its baseline capacity
- ❑ External short circuit tests using about 50 mOhm and 10 mOhm resistive load

Test Description

Cell (Single cell) testing

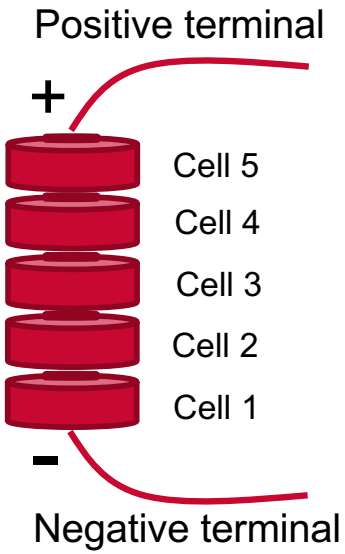


Battery (5-series cell) testing

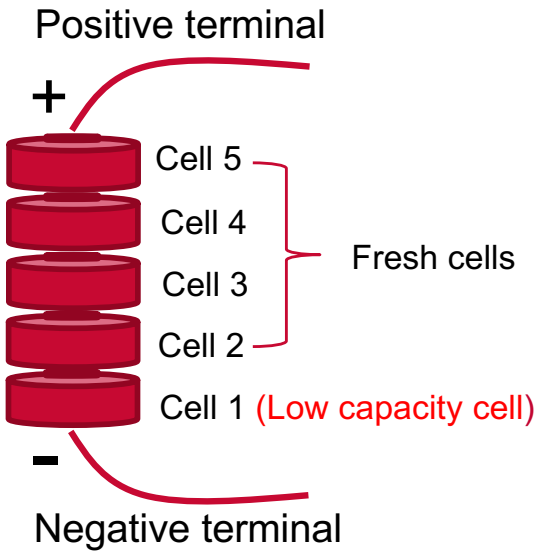


unbalanced

Battery structure



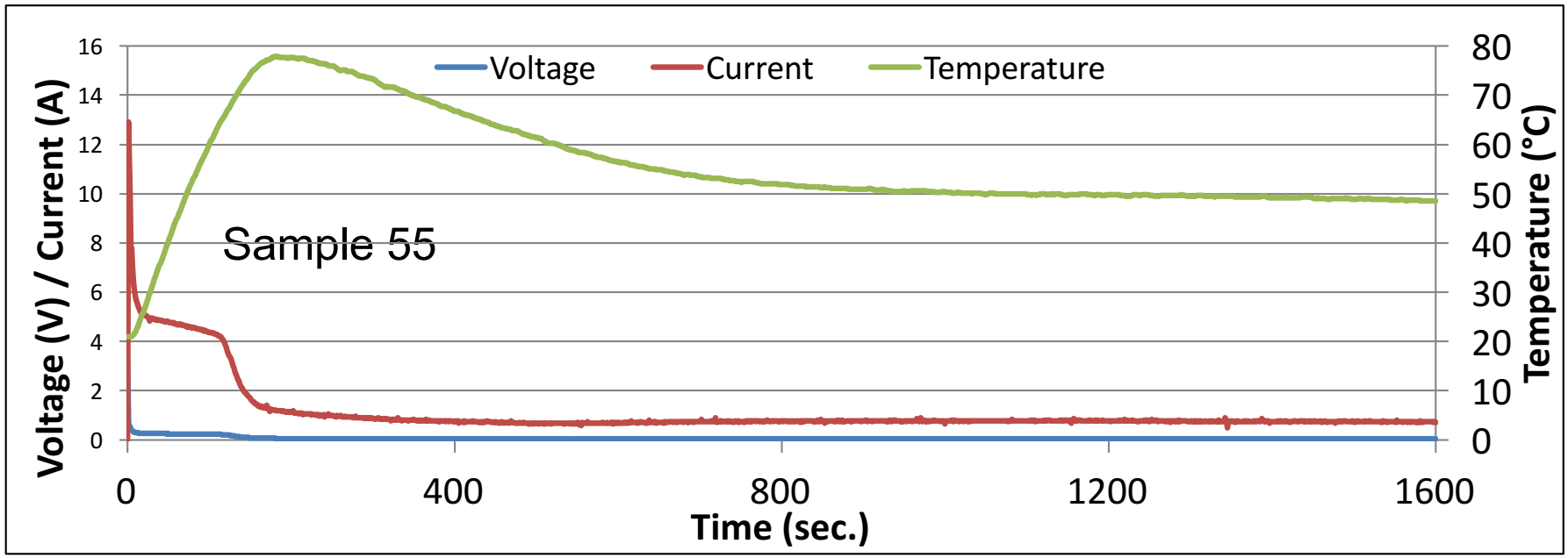
Battery structure (for unbalance testing)

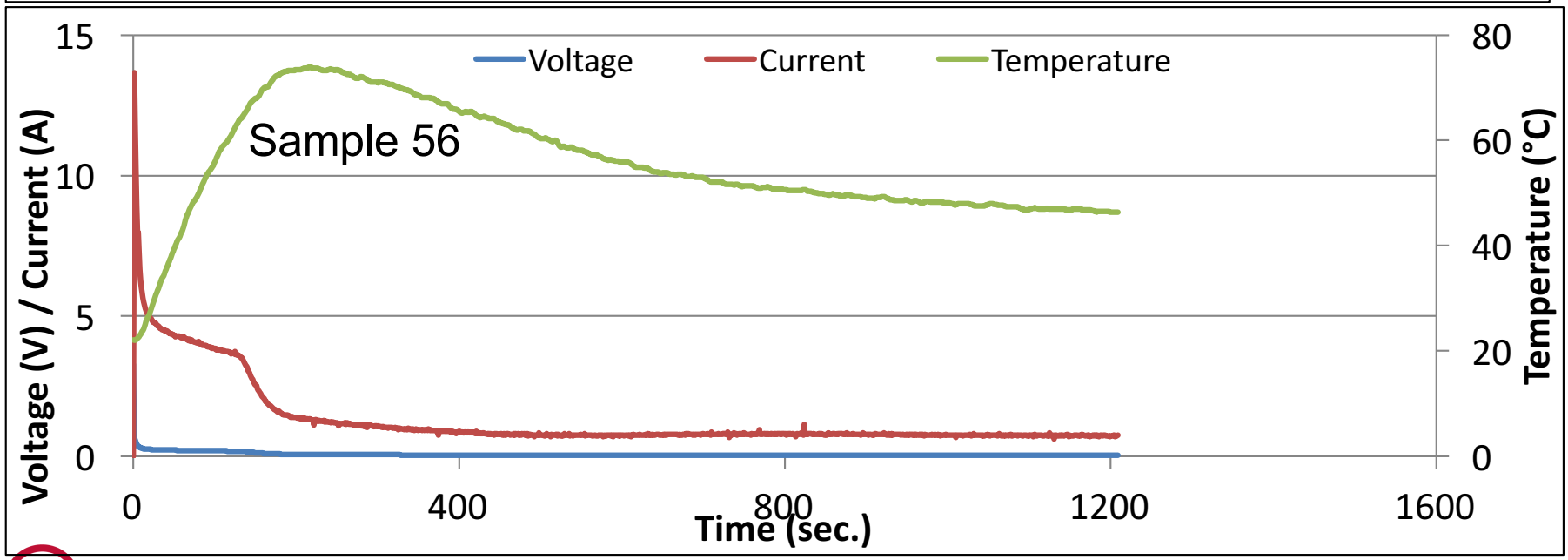


Cell A CR17335

External Short Circuit Tests - Cell

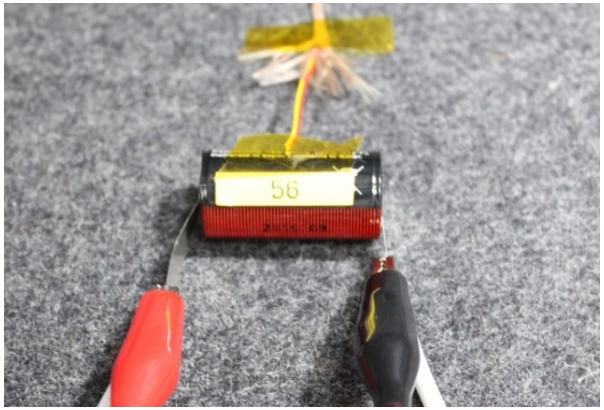
Load: 50 mOhm



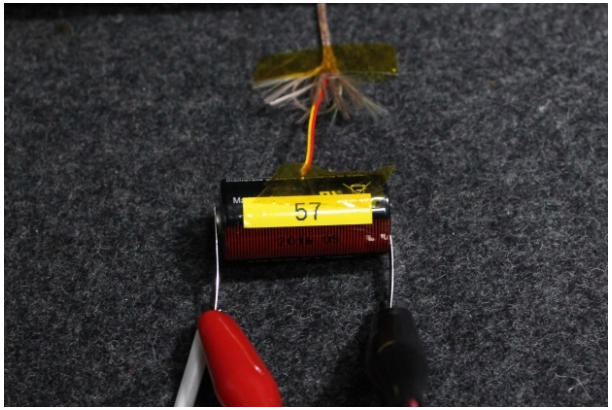


External Short Circuit Tests – Cell

Sample 55



Sample 56



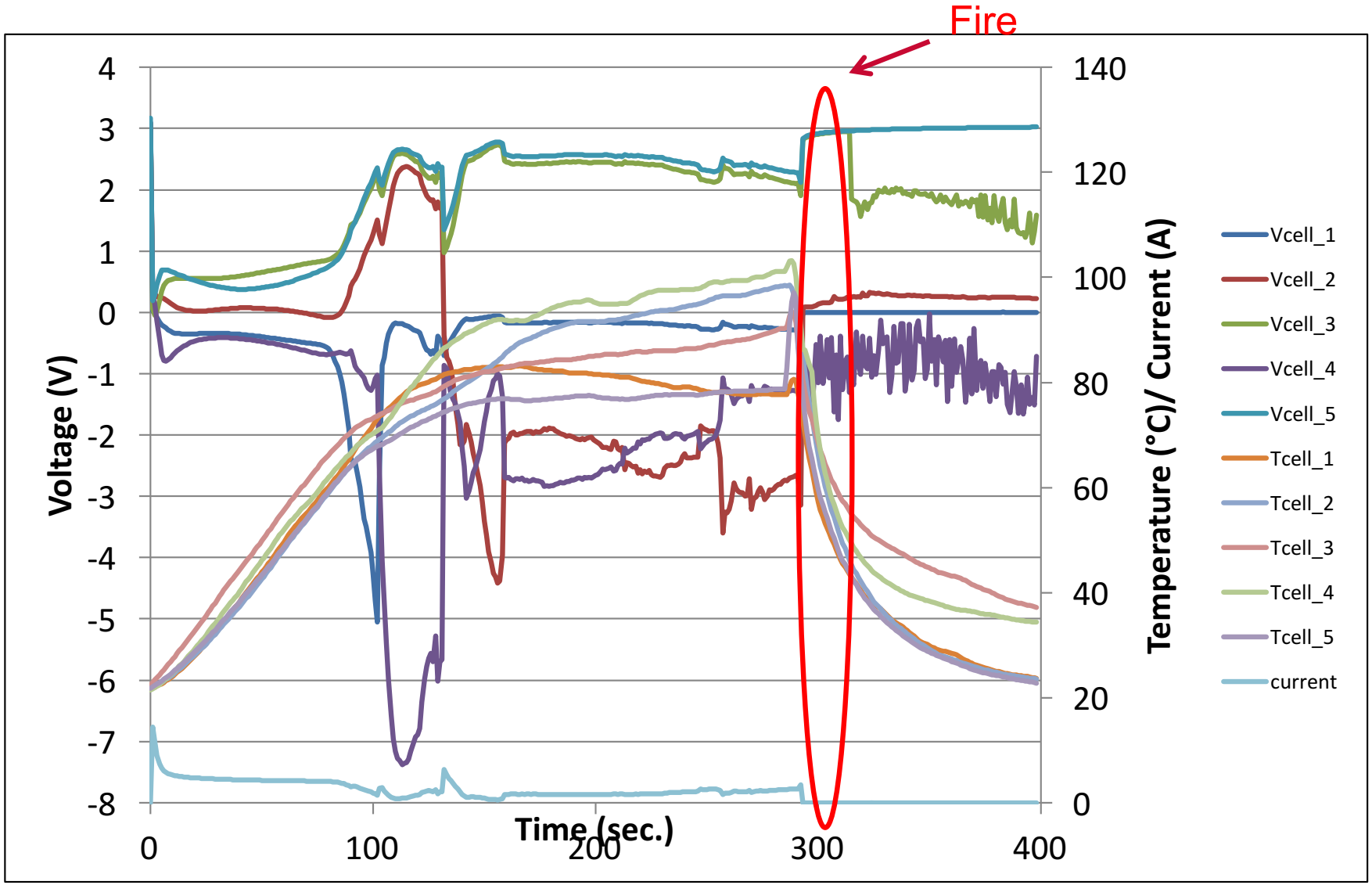
Sample 57

Parameter	Sample 55	Sample 56	Sample 57
Fire	No	No	No
Max.temperature (°C)	79.1	74.0	70.2
Max. current (A)	12.9	13.67	12.62

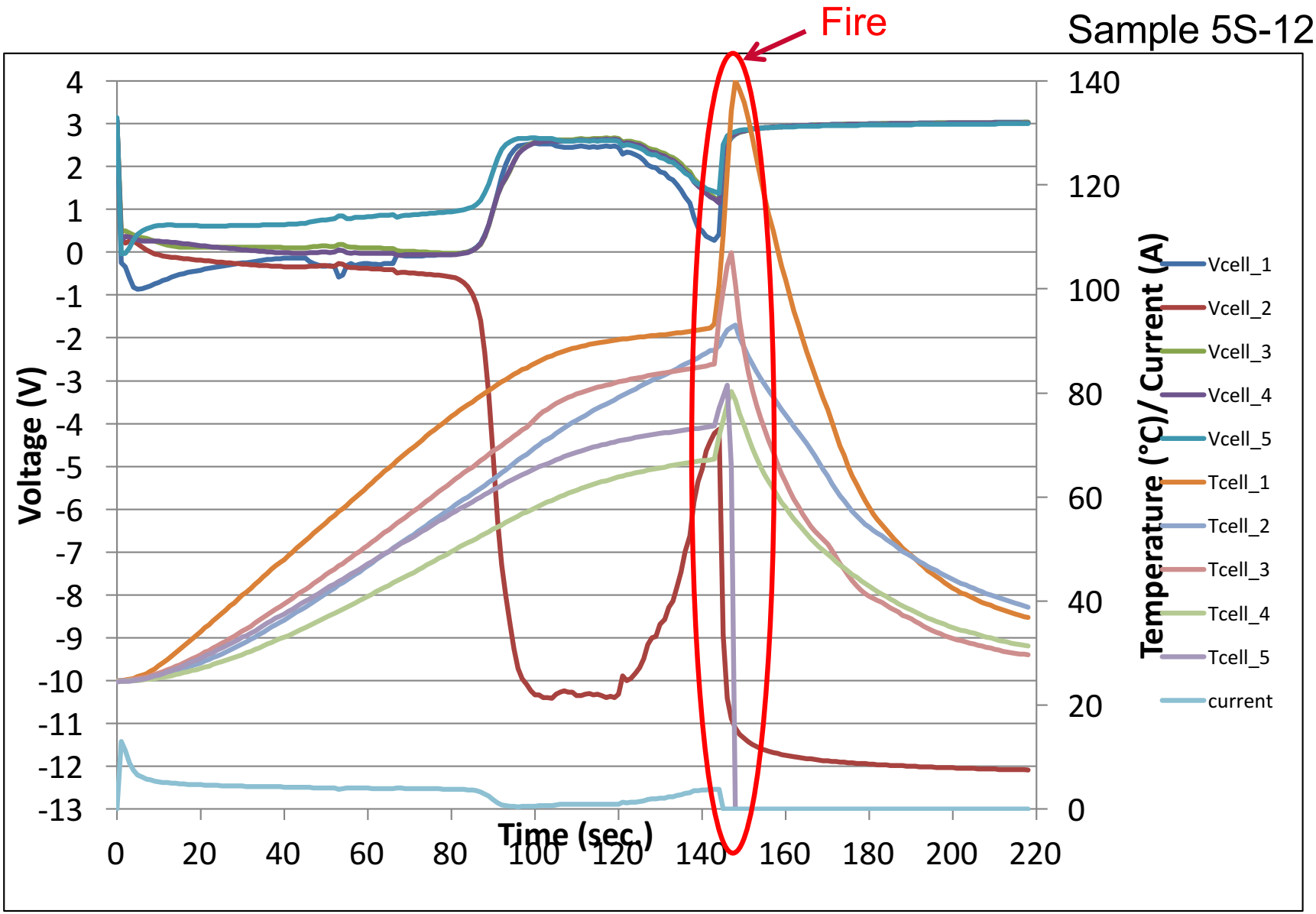
External Short Circuit Test – Battery

Sample 5S-11

Load: 50 mOhm



External Short Circuit Test – Battery (cont.)



External Short Circuit Test – Battery (cont.)

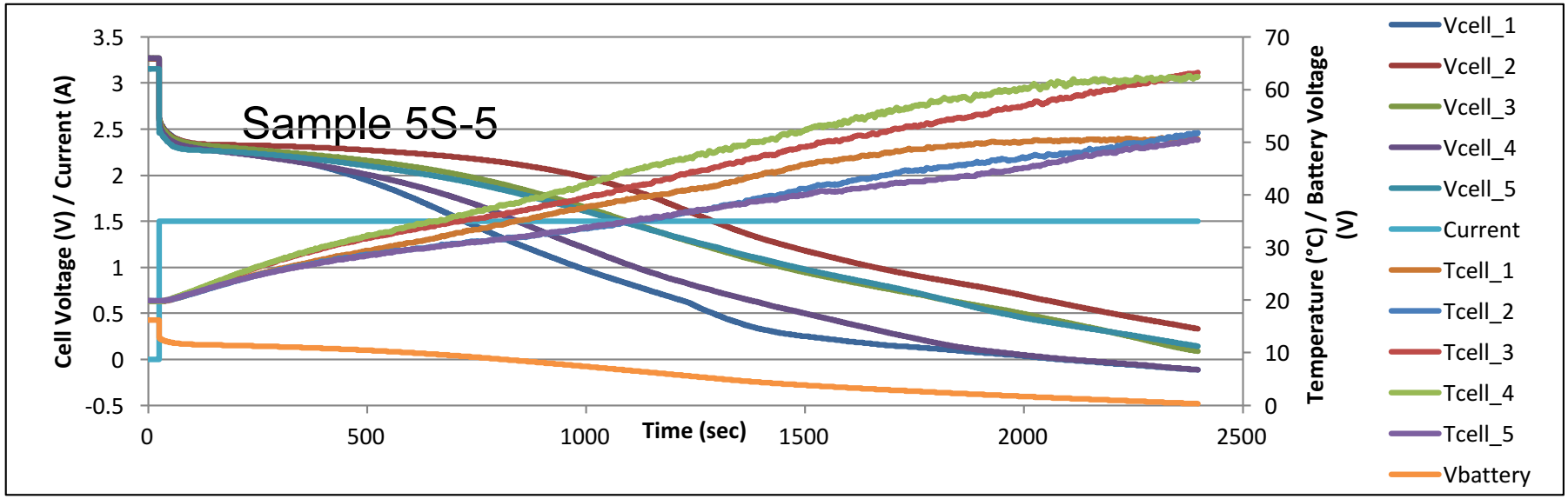
Sample 5S-11

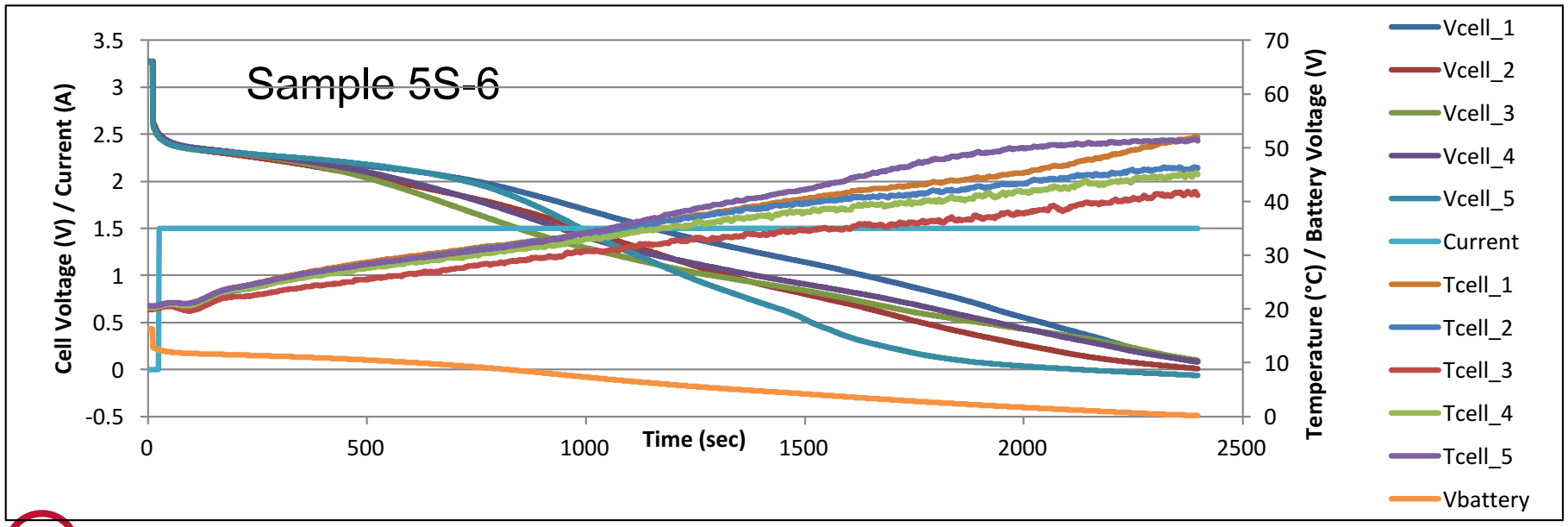
Sample 5S-12

Parameter	Sample 5S-11	Sample 5S-12
Fire	Yes	Yes
Max. temperature reading on battery (°C)	103.2	138.9
Max. current (A)	14.3	13.5
Time of thermal runaway (sec)	290	143

Over-Discharge Test – Battery (Balanced Condition)

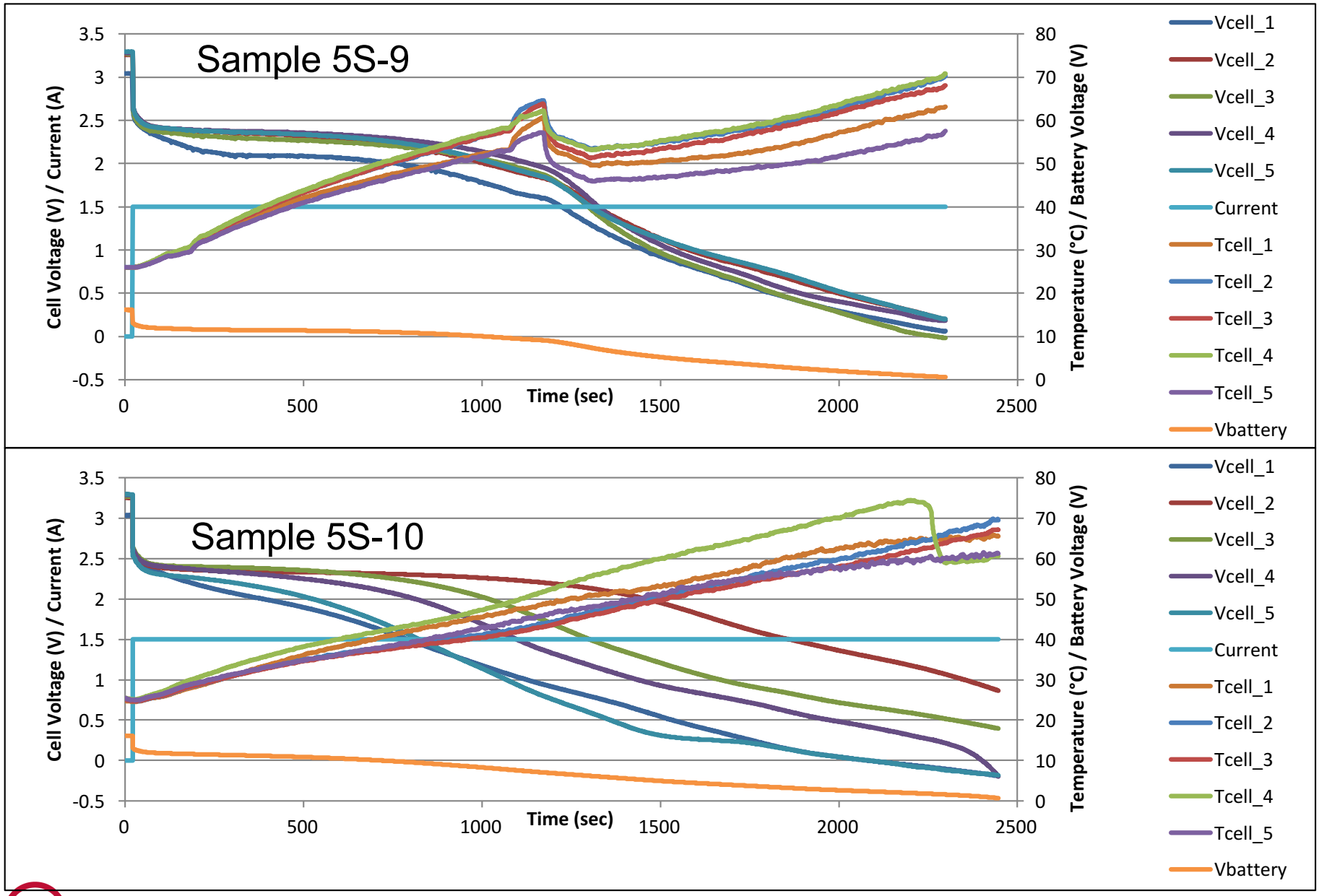
1.5A load discharge to 0V





Over-Discharge Test – Battery (Unbalanced Condition 1)

1.5A Discharge to 0V on unbalanced battery

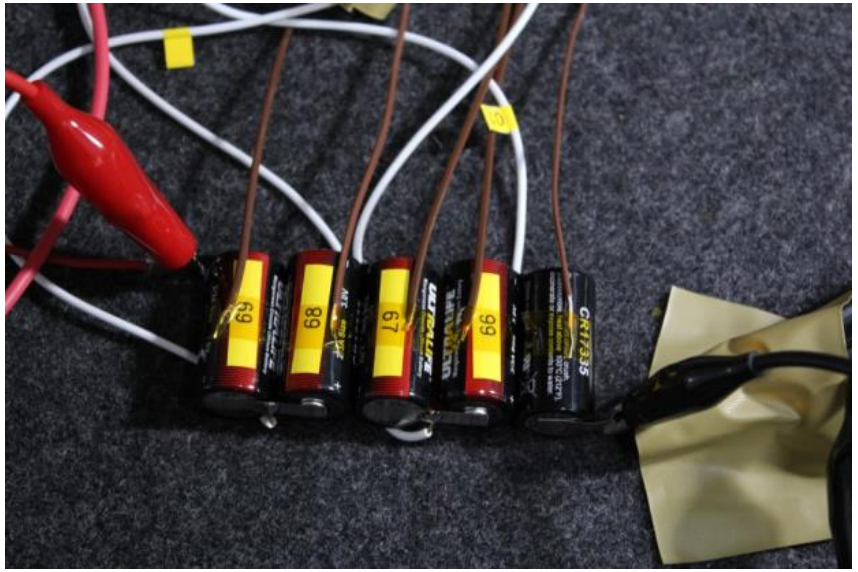


One cell in each series string was discharged to 25% of its baseline capacity

Over-Discharge Test – Battery (Unbalanced Condition 1) Summary

Sample 5S-9

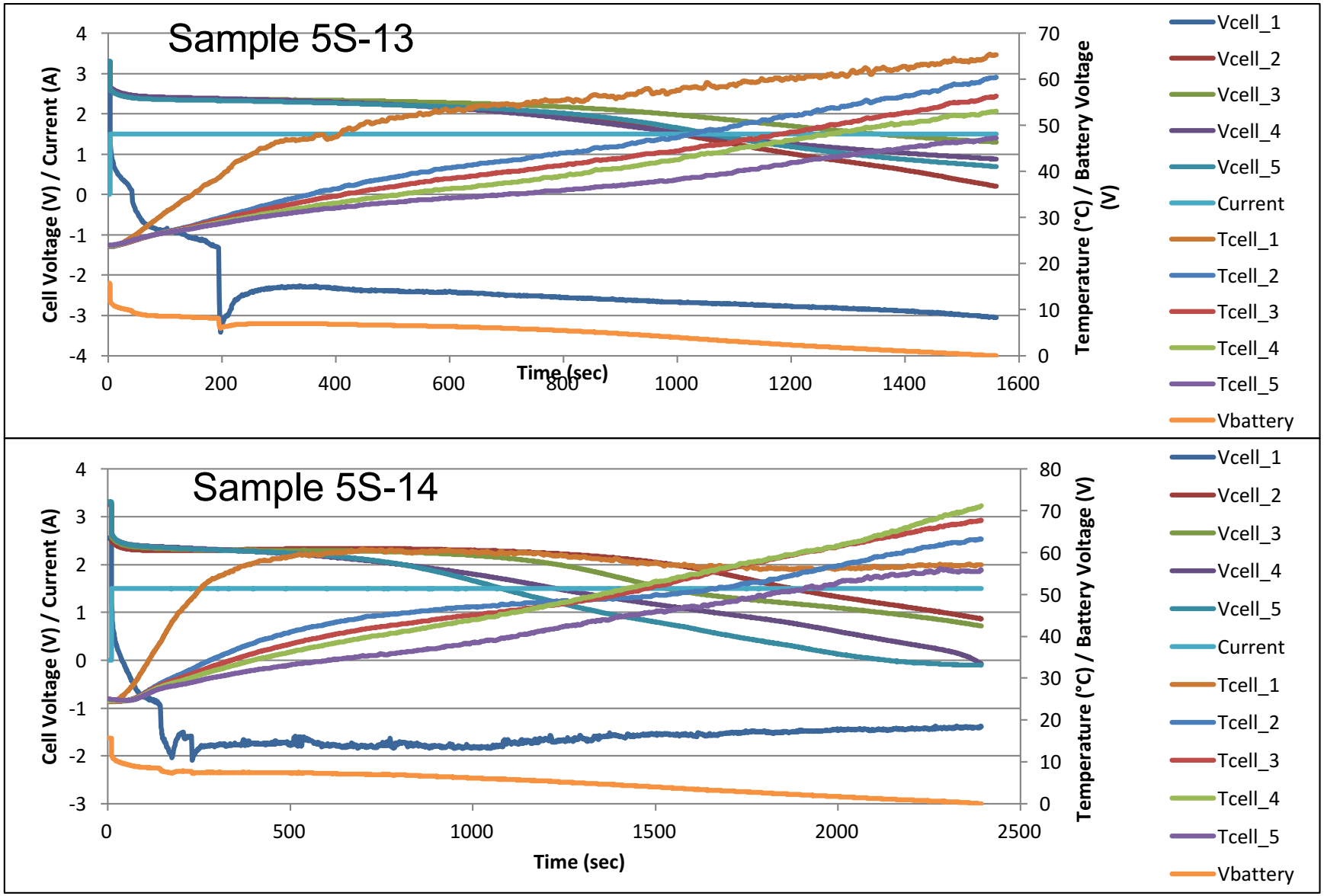
Sample 5S-10



Parameter	Sample 5S-7	Sample 5S-8	Sample 5S-9	Sample 5S-10
Fire	No	No	No	No
Max. temperature (°C)	59.6	61.7	71.7	74.6
Max. delta V between the 5 cells (V)	4.0	8.7	0.7	7.1
Capacity (mAh)	746	313	970	1013

Over-Discharge Test – Battery (Unbalanced Condition 2)

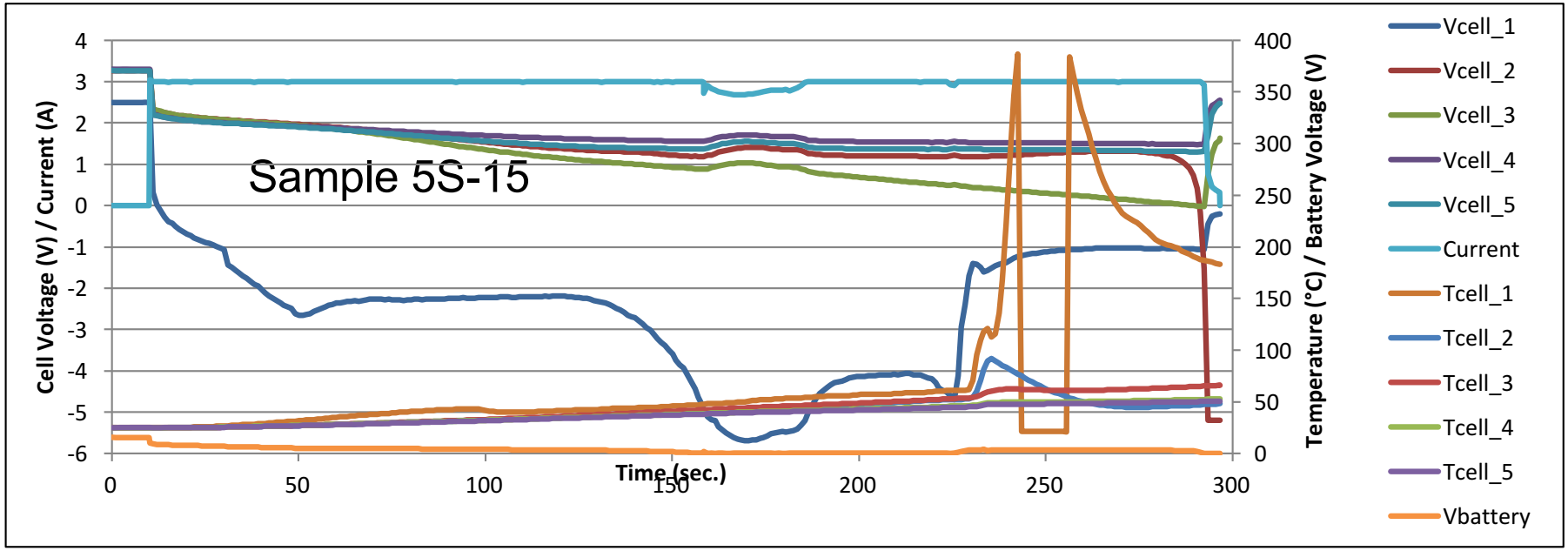
1.5A Discharge to 0V on unbalanced battery

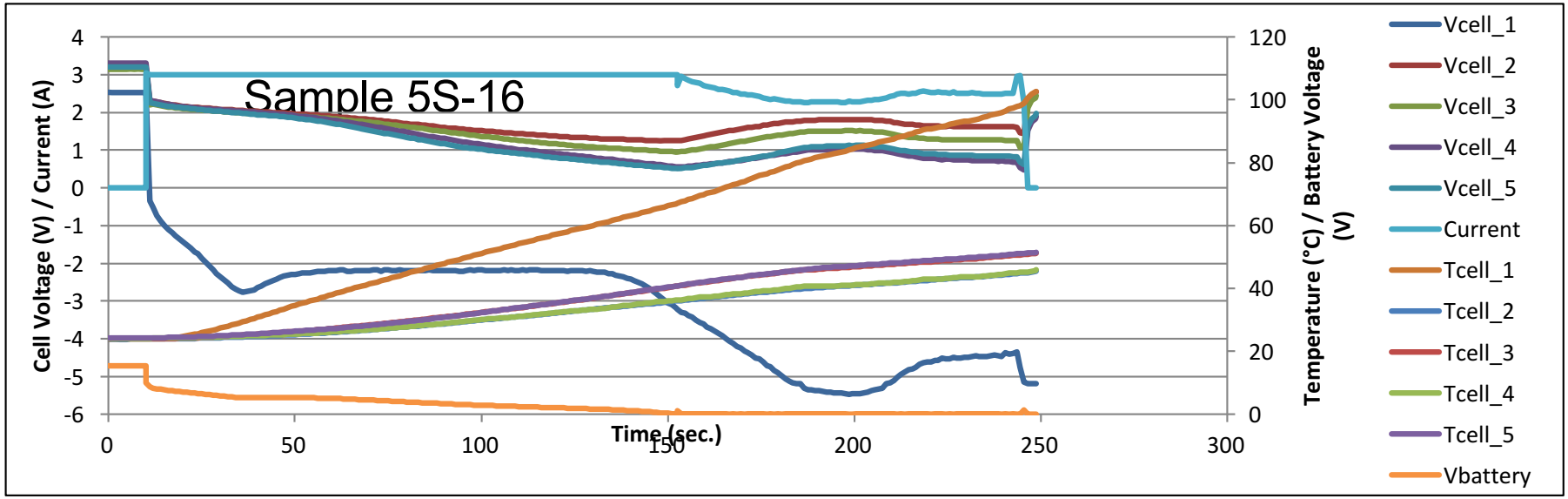


One cell discharged to 2V, and kept at 2V for10 hours; connected in series with 4 fresh cells for unbalanced condition 2

Over-Discharge Test – Battery (Unbalanced Condition 2)

3A Discharge to 0V on unbalanced battery

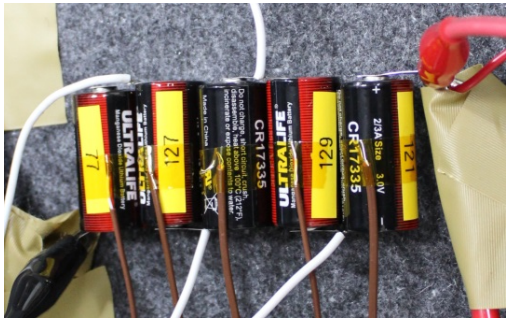




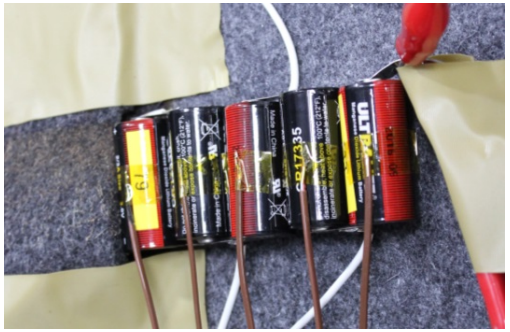
One cell discharged to 2V, and kept at 2V for10 hours; connected in series with 4 fresh cells for unbalanced condition 2

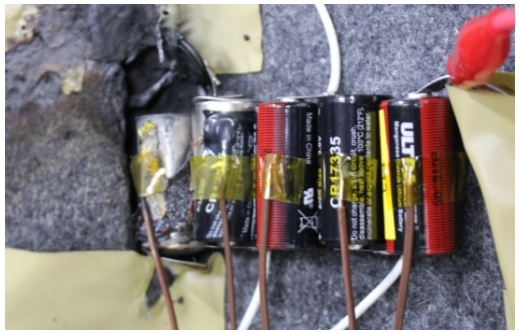
Over-Discharge Test – Battery (Unbalanced Condition 2)

Sample 5S-15



Sample 5S-16

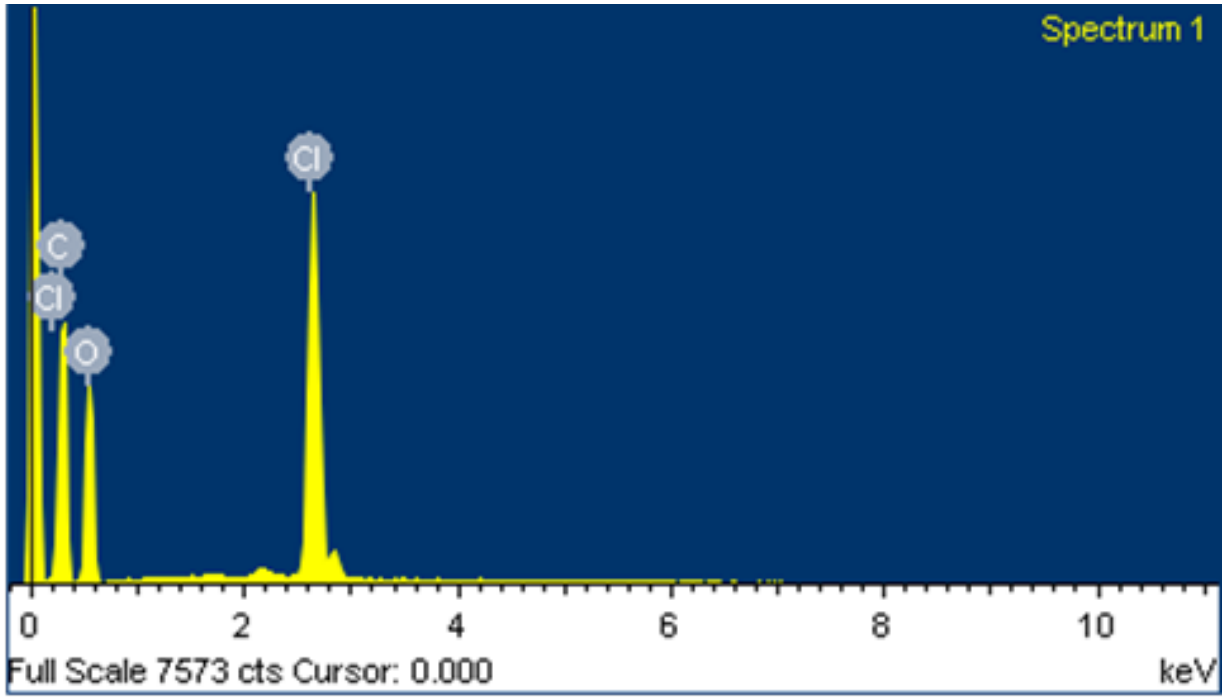




Test result

Parameter	Sample 5S-15	Sample 5S-16
Fire	Yes	Yes
Max. temperature reading on battery	386.75	102.64
Capacity (mAh)	111	64

Electrolyte Analysis with EDS



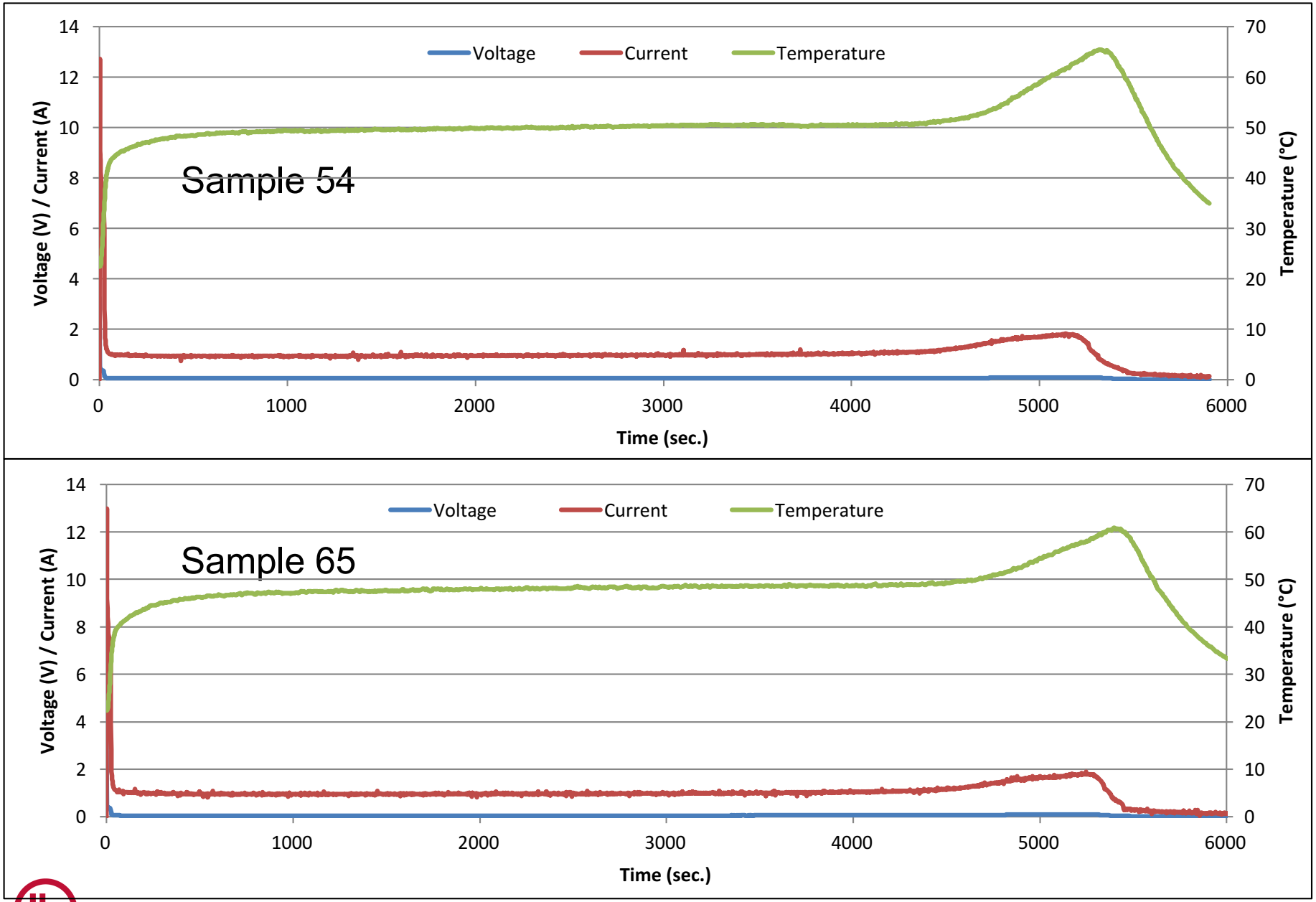
Element	Weight%	Atomic%
C K	55.04	64.57
O K	36.34	32.01
Cl K	8.62	3.43
Totals	100.00	

Cell A has a perchlorate salt (containing Cl)

Cell B CR123

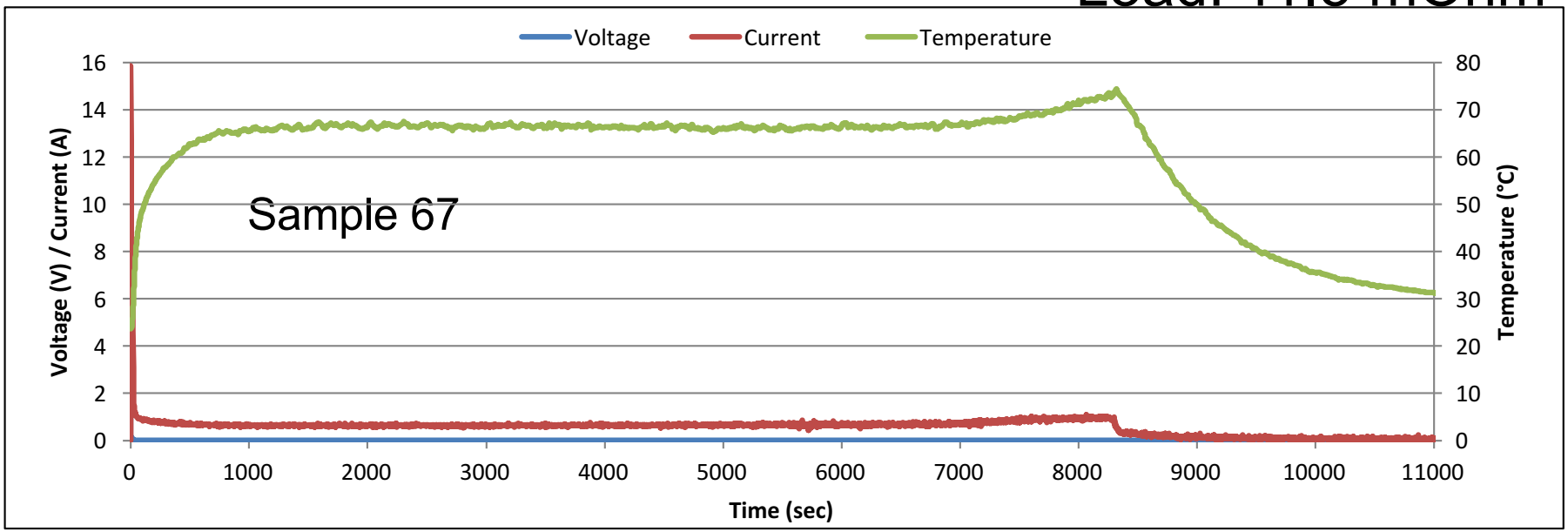
External Short Circuit Test - Cell

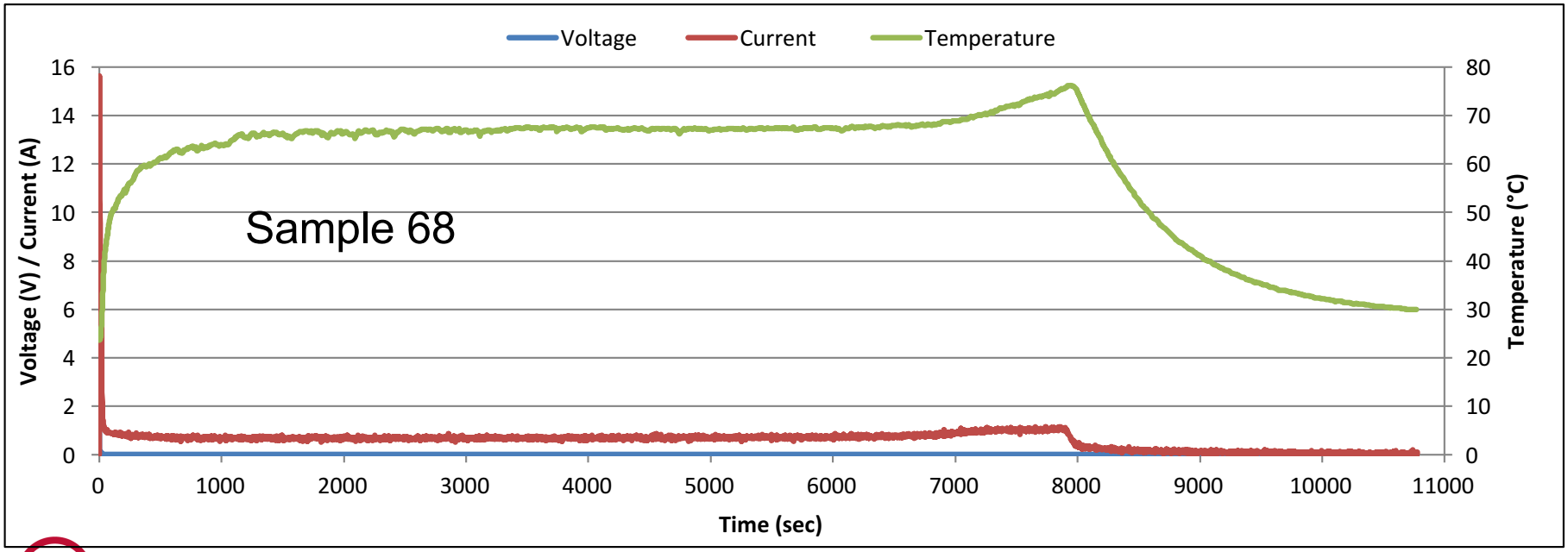
Load: 50 mOhm



External Short Circuit Test - Cell

Load: 11.5 mOhm

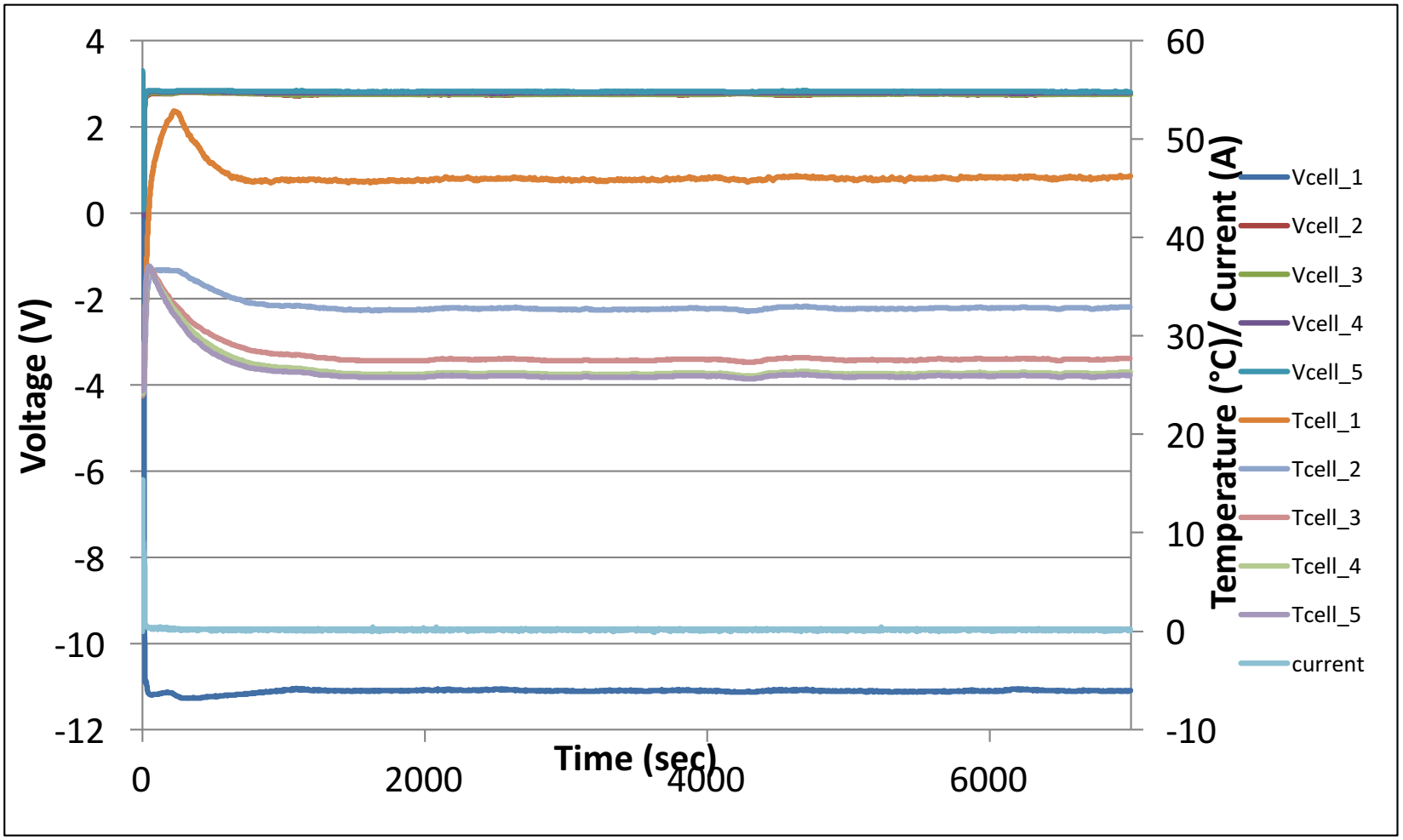




External Short Circuit Test – Battery

Load: 50 mOhm

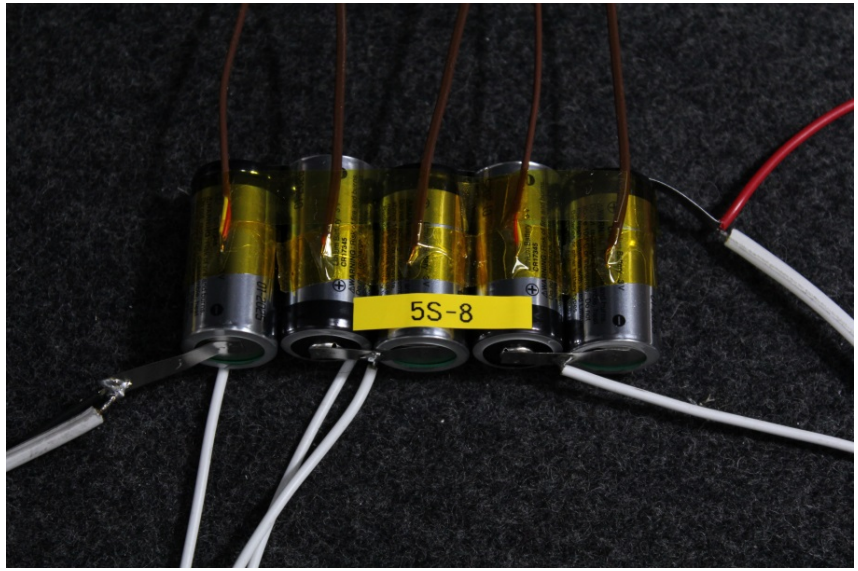
Sample 5S-8



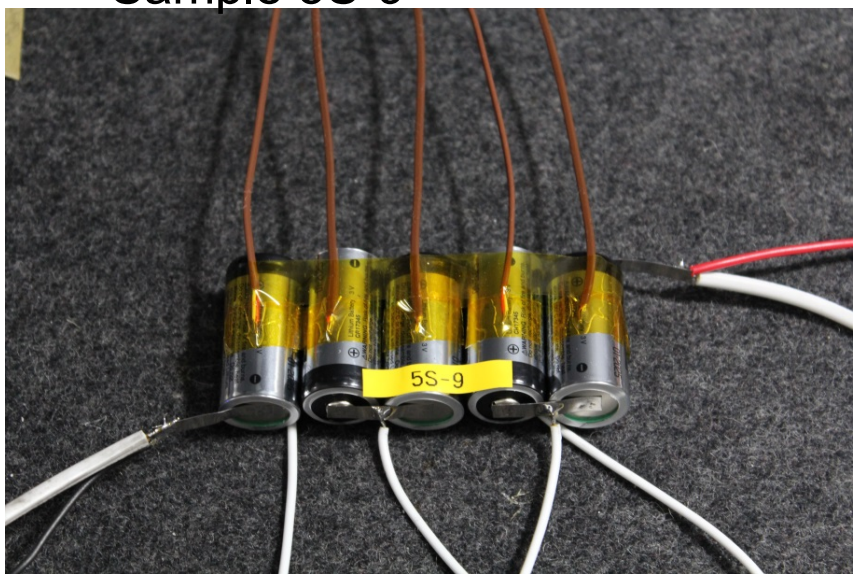
External Short Circuit Test - Battery

Load: 50 mOhm

Sample 5S-8



Sample 5S-9



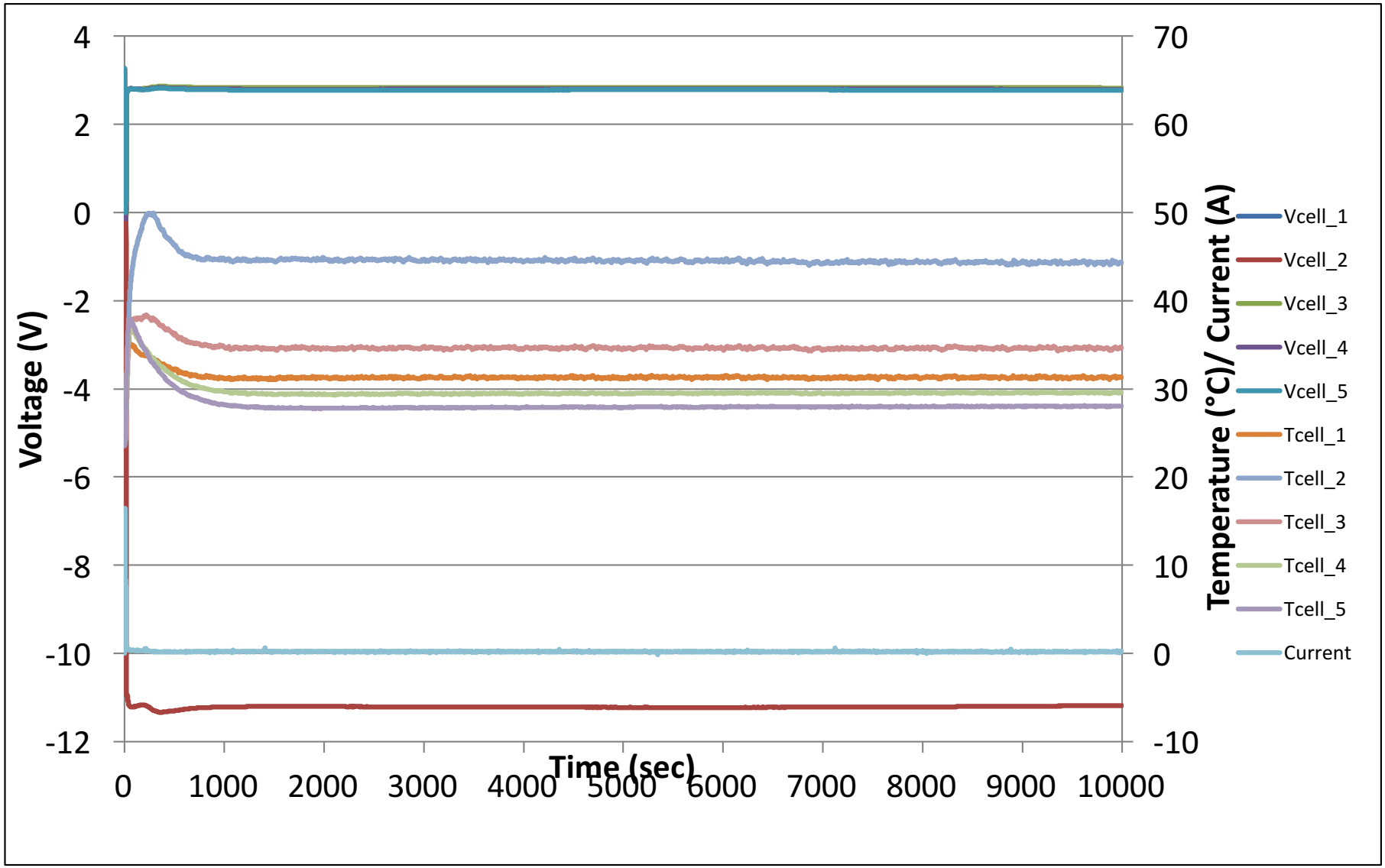
Summary

Parameter	Sample 5S-8	Sample 5S-9
Fire	No	No
Max. temperature reading on battery (°C)	52.2	48.1
Max. current (A)	15.4	15.5

External Short Circuit Test – Battery

Load: 10 mOhm

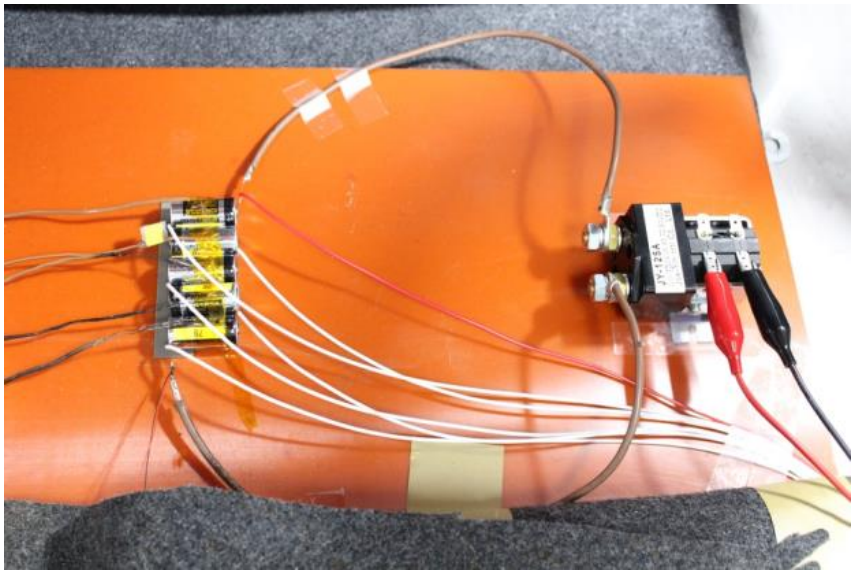
Sample 5S-10



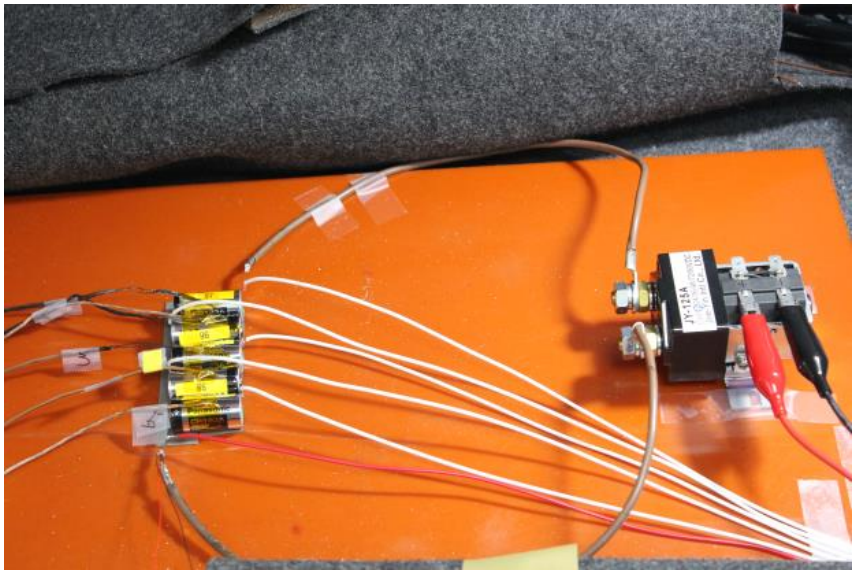
External Short Circuit Test - Battery

Load: 10 mOhm

Sample 5S-10



Sample 5S-11

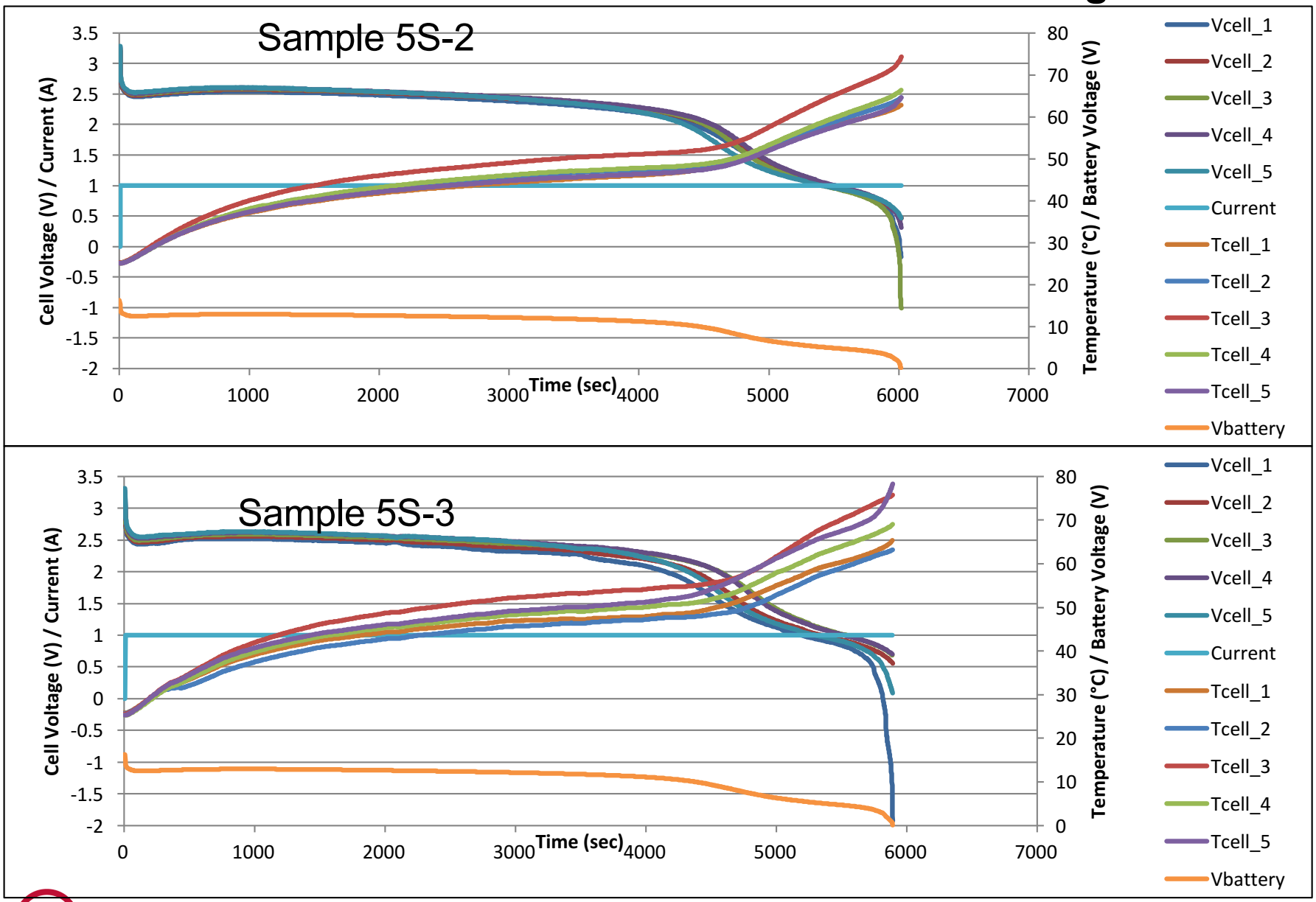


Summary

Parameter	Sample 5S-10	Sample 5S-11
Fire	No	No
Max. temperature reading on battery (°C)	49.9	58.7
Max. current (A)	16.5	16.3

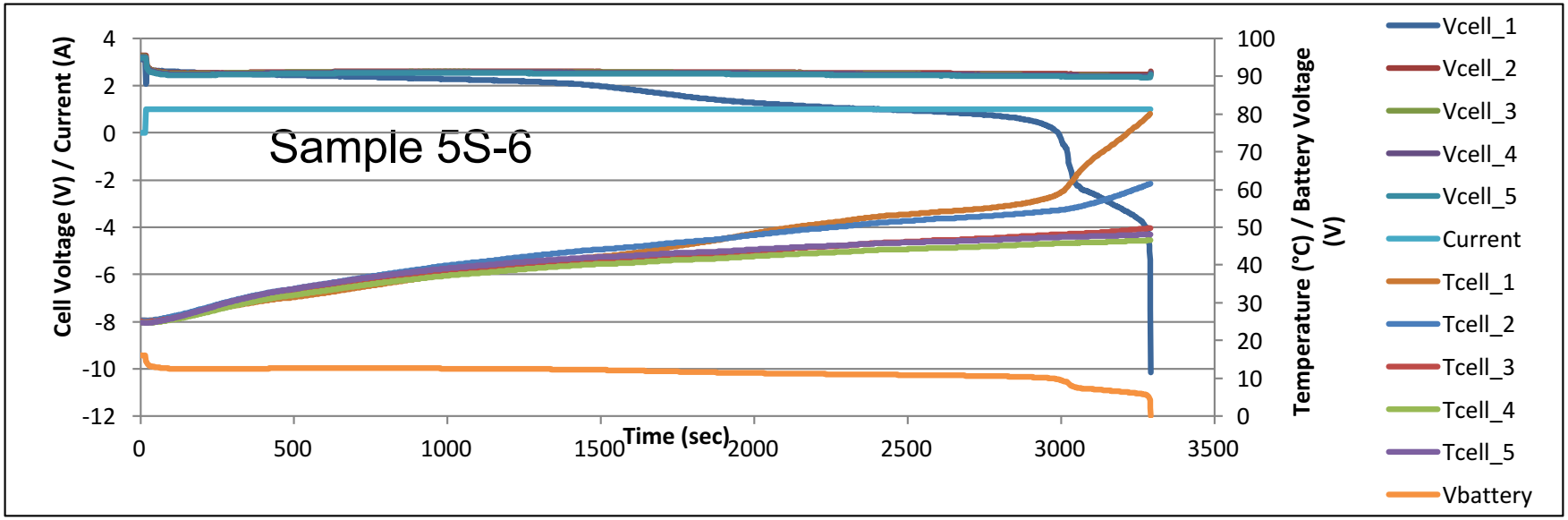
Over-Discharge Test – Battery (Balanced Condition)

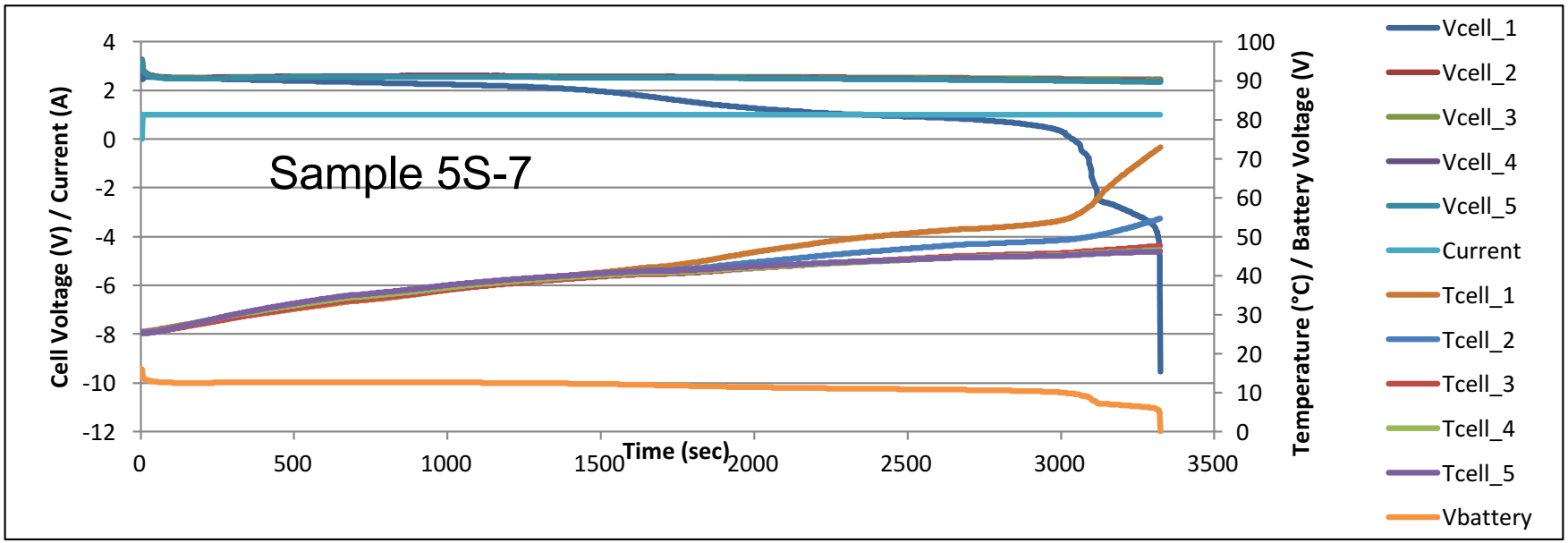
1A Discharge to 0V



Over-Discharge Test – Battery (Unbalanced Condition 1)

1A Discharge to 0 V

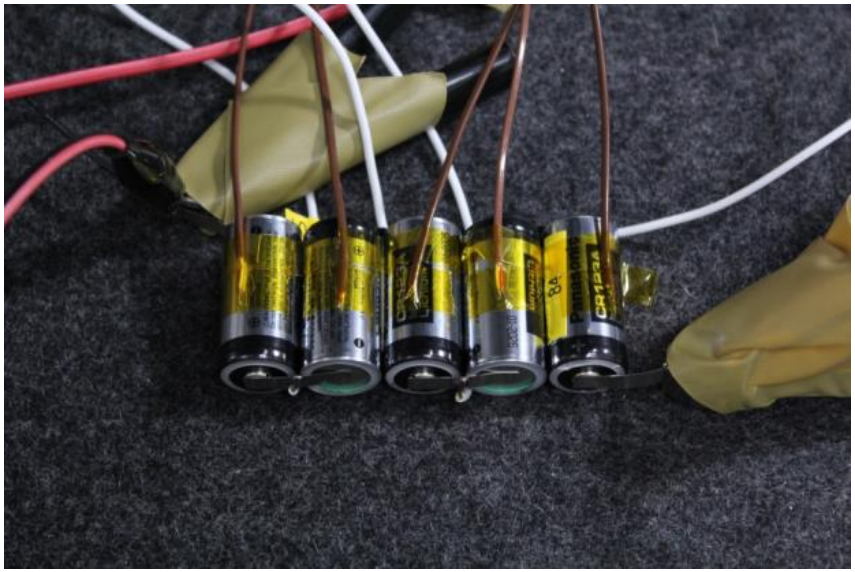




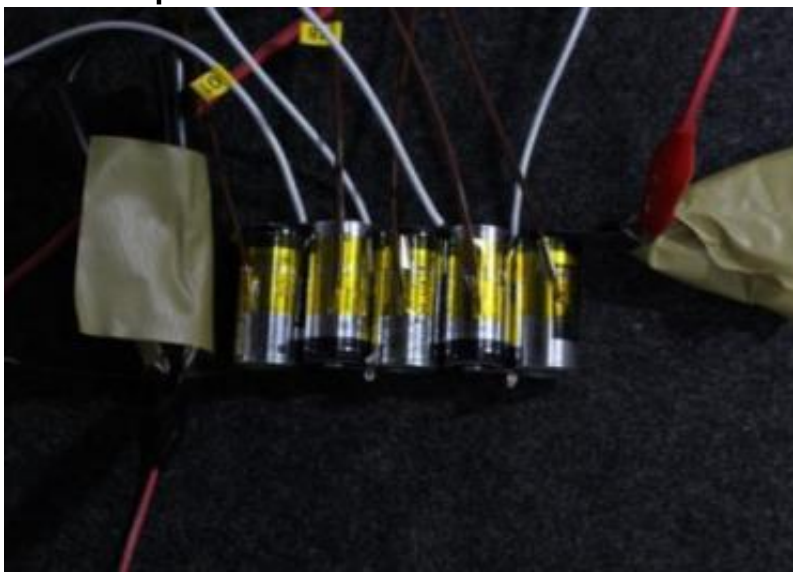
One cell at 25% SOC connected in series with 4 fresh cells

Over-Discharge Test – Battery (Unbalanced Condition 1)

Sample 5S-12



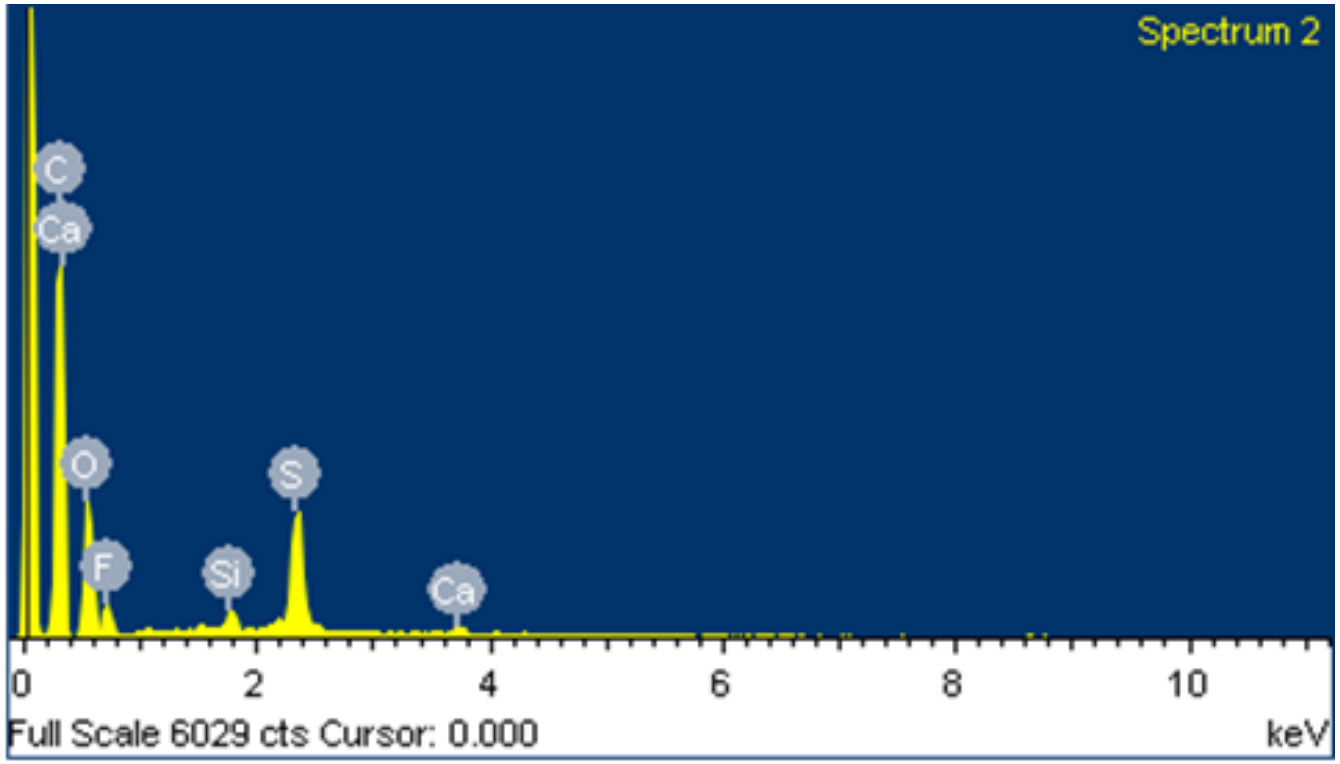
Sample 5S-13



Summary

Parameter	Sample 5S-6	Sample 5S-7	Sample 5S-12	Sample 5S-13
Fire	No	No	No	No
Max. temperature (°C)	80.0	72.7	98.3	79.3
Max. delta V between the 5 cells (V)	12.4	12.0	11.3	12.5
Capacity (mAh)	913	919	967	933

Electrolyte Analysis with EDS



Element	Weight%	Atomic%
C K	56.69	65.40
O K	30.26	26.20
F K	9.25	6.75
Si K	0.47	0.23
S K	3.07	1.33
Ca K	0.27	0.09
Totals	100.00	

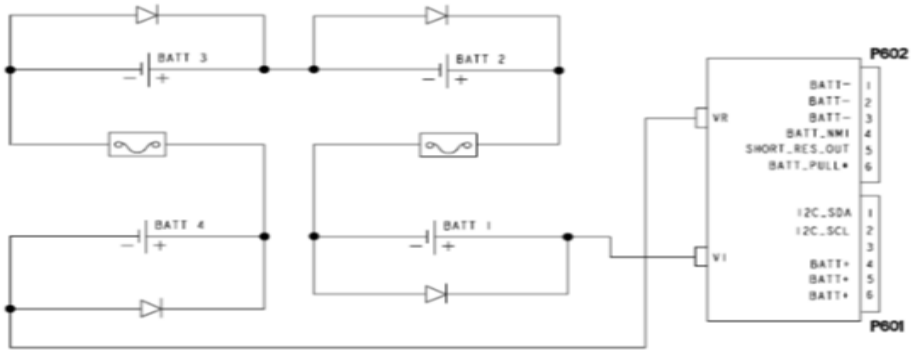
Cell B has a triflate salt (containing F and S)

Summary

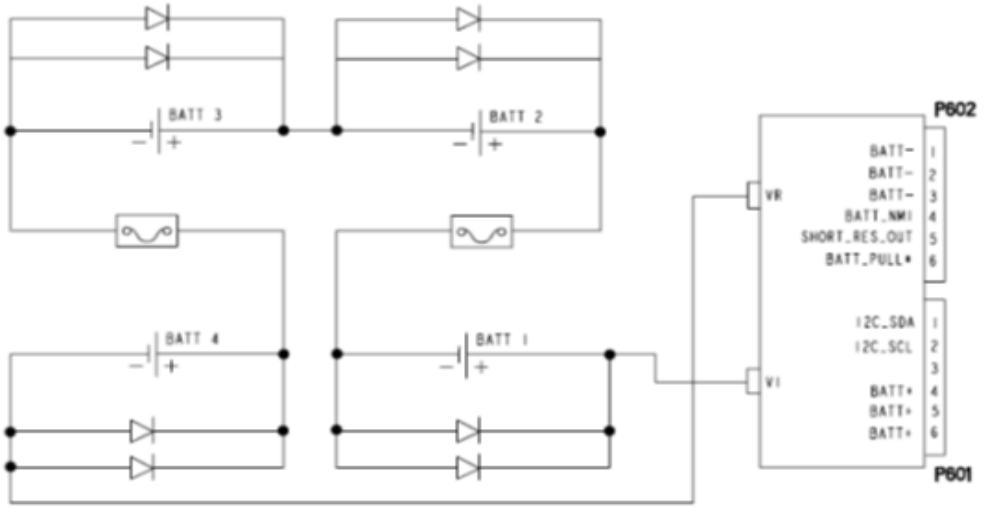
- The internal resistance (R_e) of Cell A CR17335 is 0.34 to 0.41 Ohm, and Cell B CR123 is 0.020 to 0.027 Ohm; considerable differences in R_e.
- Over-discharge tests (cells, balanced and unbalanced strings) did not exhibit fire or thermal runaway at medium rates; high current load (2C rate) test on CR17335 exhibited fire and thermal runaway.
- Short Circuit tests:
  - With 50 mohm resistive load condition, all tests with series strings of Cell A CR17335 samples exhibited fire, but none of the Cell B CR123 samples resulted in a fire; With 10 mohm resistive load condition, none of the Cell B CR123 samples resulted in a fire.
- In the EDS analysis of electrolyte it was confirmed that Cell A contains the perchlorate salt (ClO4) and Cell B contains the triflate salt (trifluorosulphonate).
- Perchlorate ion is known to react violently with organic solvents especially under conditions of high temperatures (and/or high current loads); it is said to form explosive mixtures with organic compounds
- Recommendation is to provide redundant (two-failure tolerant) protection against overdischarge into reversal – cells can go into reversal under unbalanced conditions or under external short conditions
- Test in **relevant configuration** and **environment** to **characterize** as well as understand the **tolerance limits/failure** points

Design Change as Recommended by NASA Battery Safety

Original AED Battery Design



NASA JSC AED Battery Design (currently on ISS)



Slide Courtesy: 2013 NASA Battery Workshop (J. Jeevarajan)

Acknowledgment

Dr. Carl Wang, Alvin Wu and David Chao for the numerous tests run in the UL Taiwan labs.

Thank you!