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Sonnenenergie- und Wasserstoff-Forschung
Baden-Württemberg
Gemeinnützige Stiftung

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Certified according to DIN EN ISO 9001:2008

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Dupre Minerals Limited

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23.11.2016

REPORT of Test Results

Test of fire extinguishing performance of AVD (aqueous vermiculite dispersion) applied in Lith-Ex AVD fire extinguisher for Li-batteries fire (energy content 60Wh)

Product:	Lith-Ex AVD The fire extinguishing medium AVD is specifically manufactured for this application with the product reference AVD 17_3000 was applied via an extinguisher by Dupré Minerals Ltd.
Receipt of the sample:	28.9.2016, 20.10.2016
Tested by:	ZSW/EET—ECA, 89091 Ulm, Lise-Meitner Str. 24
Project Leader:	Dr. H Döring
Test engineer 1:	Dipl. Ing. (FH) M. Wörz
Test engineer 2:	M. Sc. O. Rohozneanu
Test specification:	**fire target:** 8 Li-cells/120 Wh, (4s2p, LiC-LiCo-Oxide, pouch) each cell 4Ah//4.2V//15 Wh 13s6p stack with 18650 cells 800 Wh, each cell 2.8Ah//4.2V//10.4 Wh **ignition procedure:** Heating of one cell/segment of battery module with an electric heating element. Overcharge one cell/segment of battery **Extinguishing** the battery fire by Lith-Ex AVD Aerosol fire extinguisher (6 litre single nozzle, 40 litre 4 nozzles)
Test results:	The battery fire was extinguished quickly, re-ignition could be prevented for smaller battery units failure propagation to the neighbouring cell was delayed by the cooling effect of the AVD **test passed**

M. Wörz

Dipl. Ing. (FH) M. Wörz
(Test engineer 1)
Attachment: Test report V0.8 short

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Dr. Harry Döring
(Head of Department)

Various fire extinguisher tests on Li-ion battery packs

Under contract of

Dupré Minerals Ltd.

Report Version 0.8-short

November 2016

M. Sc. O. Rohozneanu*, Dr. H. Döring, Dipl. Ing. (FH) M. Wörz

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Competence of ZSW – the test institute carried out the tests

ZSW was established in 1988 as a non-profit foundation under the civil code. The goal of the foundation is: “to conduct and promote research and development in the field of renewable energies, energy efficiency, energy conversion and storage, with focus on solar energy and hydrogen technology and by transferring the results into industrial application”.

ZSW has two main locations in Stuttgart and Ulm, with about 230 employees. While the division in Stuttgart dealing with photovoltaics, energy policy and energy carriers, the division in Ulm is focused to electrochemical energy technologies for electrochemical energy storage and conversion. The about 120 employees in Ulm working in the groups of material for energy storage (45), pilot production of Li-batteries (15), fuel cells (fundamental, stack design, system integration and testing, 25) and the battery group (electric testing, system technique, safety testing and assessment, 25).

The battery group, established in 1992, is carrying out electric tests and evaluation of batteries, abuse and safety tests for cell manufacturer including suppliers for materials and components, producer of equipment and installations employing batteries in their products (consumer products, medical products and power tools, stationary and portable applications), manufacture of mobility and logistic applications as car manufacture, automatic transport systems, fork lifts ect..

The infrastructure of the battery groups allows electric battery tests from single cells, via modules up to complete battery packs of several 10 kWh, covering the current range up to 3000A and the voltage range up to 1000V.

In the area of safety and abuse testing the infrastructure of 3 bunkers with a volume of 100 m^3 each is suitable for testing single cells as well as modules and battery packs under a wide spectra of abuse conditions as overcharge, overdischarge, crush, short circuit, nail penetration, high temperature and fire exposition, ect.. Infrastructure is suitable to handle the processes during events (fire, emissions and explosions) as well as the treatment of the waste and emissions (3 step exhaust gas cleaning process).

For the operation of the infrastructure, carrying out the tests, data processing and reporting skilled and experienced personal mainly with the qualification engineer and technician is available. For the assessment and evaluation of the result, scientist including in particular the competence of the material group is available.

The different tests in the electric field and the abuse-safety testing are done for customers as:

- Bosch (power tools, research, battery packing group)
- Daimler, DACCU
- BMW
- VW, Audi, Porsche
- Fein, Hilti (power tools)
- Li-Tec, Leclanche, ATL, SAMSUNG (cell manufacturer)

Summary of the test results

The following table summarize the different fire-extinguishing test with AVD for different sizes of the battery as well as different sizes for the fire extinguishers.

Test No.	test object	chemistry	kind of excitation	kind of extinguisher	time start fire-ex after ignition [sec]	time to extinguish flams [sec]	duration of fire extinguisher operation [sec]	applied amount of material [lit]	re-ignition	thermal propagation
#01	4s2p120Wh	LiC-CoOx	overcharge 2 C	AVD 4 nozzle rig	25	3	30	8	no	yes, after about 3 min
#06	4s2p120Wh	LiC-CoOx	overcharge 2 C	6 lit AVD hand extinguisher	12	19	44	6	no	yes, after about 1.5 min
#02	13s6p, 800Wh	LiC-NMC	heat exposition	AVD 4 nozzle rig	5	5	20/20	32	yes	yes, to 40%
#03	13s6p, 800Wh	LiC-NMC	heat exposition	AVD 4 nozzle rig	48	2	100	30	yes	yes, to 55%

AVD is a suitable fire extinguishing agent for fire of Li-batteries. Application method like spraying (“fine mist”) is suitable.

As in every case, fire should be extinguished as early as possible, increasing the grade of success.

By the application of the fire extinguishing agent AVD works for the extinguishing of the fire as well as for the cooling of the burning object to prevent re-ignition and failure propagation.

In particular for larger battery objects with compact packaging the success might be limited as the sprayed AVD cannot moisten all the cell surfaces.

Background

Since the use of Li-batteries is so widespread, it is sensible to test these battery cells under different conditions. Under certain relatively harsh conditions these batteries can be critically damaged and go into Thermal runaway. This may result in the propagation of heat from one cell to another causing a potentially significant fire. In order to arrest the spread of thermal runaway between the cells it is possible to quench the fire by cooling the cells to a point where the temperature is no longer critical.

Within this series of tests, Li-CoO_2 pouch cells and Li-NMC cells in a battery pack were subjected to over charging or physical overheating in order to initiate thermal runaway and to deliberately generate a fire. At this point an aerosol fire extinguisher filled with AVD-Li extinguishing agent (aqueous vermiculite dispersion) will be applied in order to extinguish the fire and to cool the adjacent battery cells. This will result in the prevention of further cells going into thermal runaway and the termination of the fire.

Test objects

Li- Battery pack 800 Wh with cylindrical 18650 cells (Li-NMC)

The basic pack configuration was a 13s6p (13 cells serial, 6 cells parallel) with a nominal energy content of 800 Wh. The single cell capacity is 2.8 Ah resulting in 16.8 Ah for the 6p configuration. The nominal voltage of a cell is 3.7V resulting in 48.1V nominal voltage for the battery pack. Charge end voltage for the pack is 54.6V (fully charged, SOC 100%). The active material of the positive electrode was NMC (Ni-Co-Mn-Oxide).

For geometric reasons a shorter battery pack was created by extracting 2s6p cell configuration from the battery block resulting in a 11s6p configuration with a nominal energy content of 680Wh.

Figure 1. Battery pack in 13s6p connection

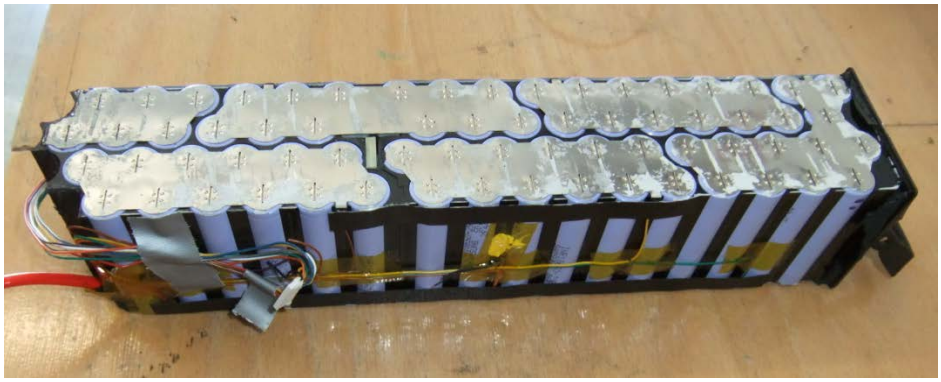
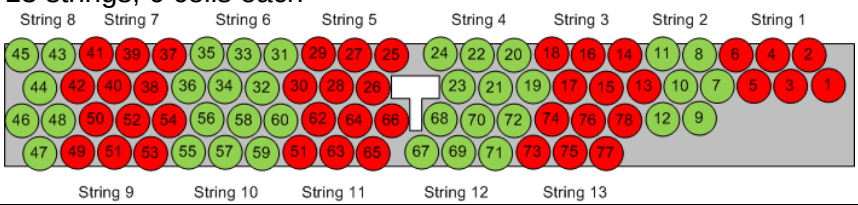


Figure 2. Battery pack in 11s6p connection

Cell connection	13S6P
String & Cell notation:	13 strings, 6 cells each 

Li- Battery pack 120Wh with pouch cells (Li-CoO_2)

The configuration of the Li pouch cell battery pack was used in different configurations

- 4s2p - max Voltage 16.8 V; capacity: 8Ah, energy 120Wh
- 2s2p - max Voltage 8.4 V; capacity: 4Ah, energy 60Wh
- 2s1p - max Voltage 8.4 V; capacity: 4Ah, energy 30Wh

The active material of the positive electrode was CoO_2

Figure 3. Two stacks of 4s2p

Figure 4. One stack of 2s1p

Test setup

The test configuration consists of 2 parts.

- Set up for initialising the thermal runaway/ignition of the Li-battery fire
- Set up for the fire extinguishing

Initializing thermal runaway/fire

Different methods are possible to initialize the thermal runaway for Li-batteries, as overcharge, short circuit, crush, nail penetration, exposition to heat.

For the tests carried out within this test program two types of excitation have been selected:

- Heat exposition (with heating elements, single rod (150W) or 2 heating rod in 2 Al plates (300W))
- Overcharge (at 2C charge rate at elevated voltages)

Set up for the fire extinguisher

The fire extinguishing medium AVD - Li which is specifically manufactured for this application. The composition of this extinguishing agent is according to the code 1351750 manufactured by Aero-EX a division of Dupré Minerals.

To perform these tests the following different setups were used:

Fixed rig with 4 nozzles

A frame with a ring tube was constructed to hold the 4 nozzles for the spraying of the fire extinguishing agent to the burning test object.

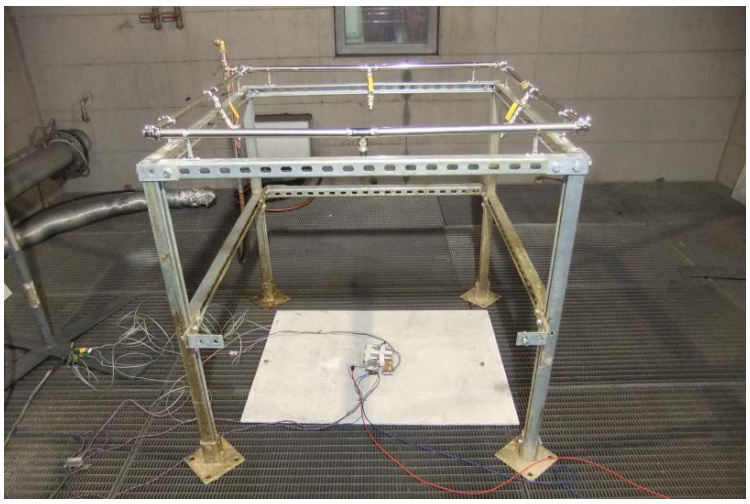


Figure 5: Mobile rig with a ring tube with 4 nozzles for spraying the dispersed vermiculite to the test object for fire extinguishing

The rig is connected by a tube with the reservoir (total volume 40 litres) filled with the fire extinguishing agent (dispersed vermiculite AVD). This reservoir was pressurized with nitrogen to have a system pressure of about 12 bars. The fire extinguisher was operated (opened and closed) by hand.

Figure 6: Pressurised reservoir for the fire extinguishing agent (AVD)

6 Litres hand fire extinguisher

A conventional fire extinguisher was modified for AVD application. The volume of the fire extinguisher was 6 litres, pressurized to 6 bars with nitrogen.

Operation of the main valve or extinguisher actuator was accomplished using an automated devise which could be manipulated from outside the test room by means of pneumatics. As a safety policy ZSW do not allow access of personnel to the test room whilst batteries are under test and for this reason an automated process was required. The system was designed to simulate the movement of a human being deploying an extinguisher in a sweeping motion. Figure 7 illustrates this equipment.

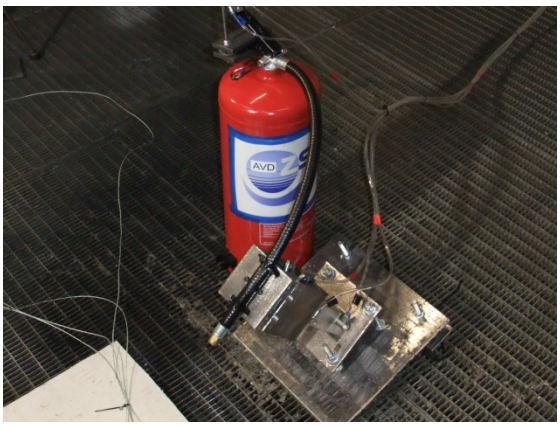


Figure 7: 6 litre hand fire extinguisher filled with AVD and pressurized operated with pneumatic manipulators

Overcharge of one cell in a two stack 4s2p pack	
Purpose	The purpose of the test was to test the functionality of the AVD product over a situation of thermal runaway with heat propagation onto the nearby battery stack
Parameter	• Module level • Two 4s2p stack fixed next to each other (120 Wh) • Ambient temperature 25°C ± 3°C • Cell charged to: 4.2 V (SOC ~100%) • Overcharge current: 15A

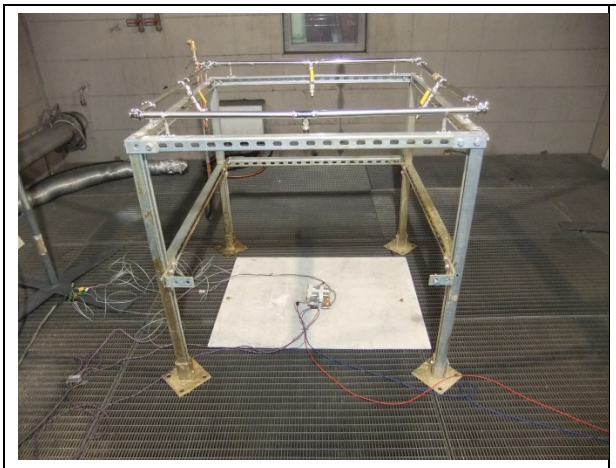


Figure 8. Overcharge with fixed rig extinguishing system

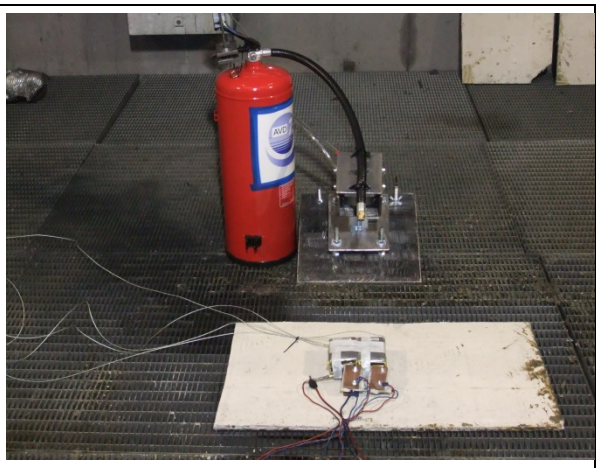


Figure 9. Overcharge setup with mobile extinguisher unit

Test record Overcharge 4s2p fire-ex: 4 nozzle rig (Test #01)	
Battery	Pouch cell pack 4s2p 120Wh, cell: Li-CoOx 4Ah
Date	28.09.2016
Test parameter	Overcharge from 100% to 200% SOC with 15A charging current
Observations	Mass before test: 988.2 g, after test: 801.9 g, mass loss: 186.3 g OCV_{cell} before: 4.09 V, OCV after: 0 V The cell entered thermal runaway at about 13.3 V and a temperature of 89°C. After 1.3 s from thermal runaway the voltage of the second stack started to decrease and after approximately 10.5 s, the bottom cells of the second stack entered thermal runaway. The fire extinguisher was applied after 25 s from presence of fire and it was sprayed for 30 s continuously. The fire was extinguished within 3 seconds and the temperatures decreased while applying AVD. However, temperature between cells kept high enough to initialise the venting of 2 more cells but there was no more fire detected. The maximum temperature was measured at stack 1 between cell no.1 (the cell overcharged) and cell no.2 with a value of 672.8°C After test inspection showed that all the cells had opened.

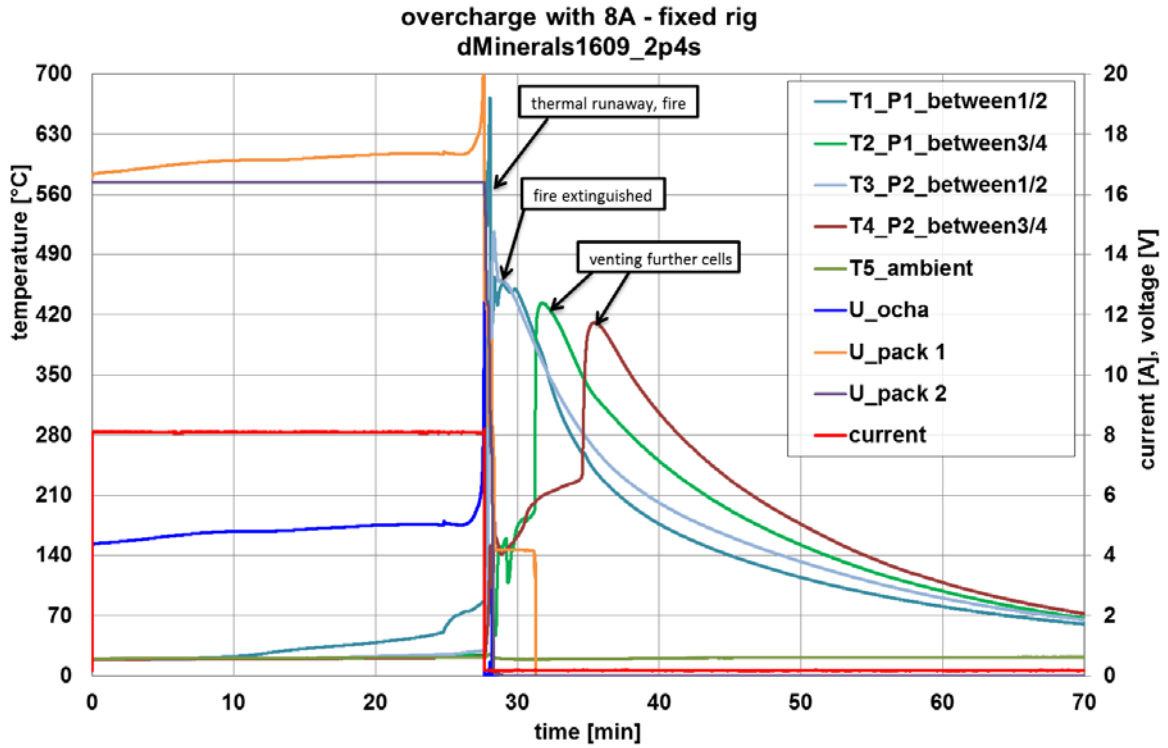


Figure 10: Temperatures, capacity, current and voltages during test

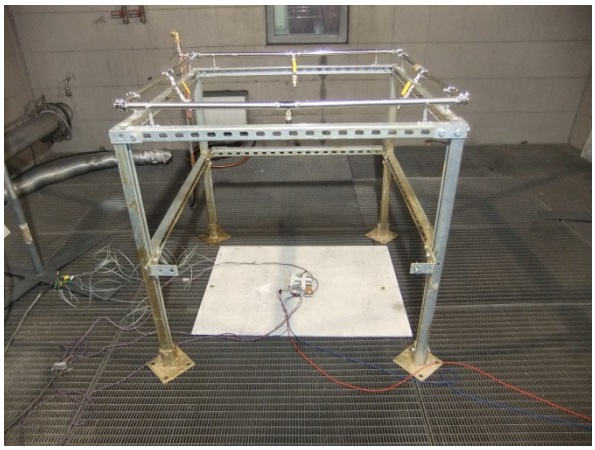


Figure 11: overall set up

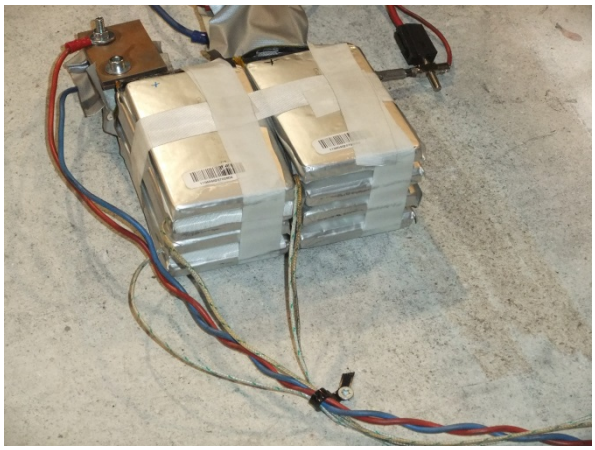


Figure 12: Cells before test front view

Figure 13: Cells after test front view

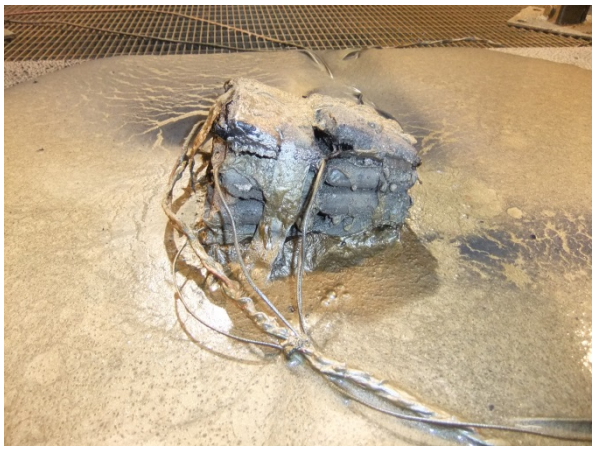


Figure 14: Cells after test rear view

Test result	Mass loss of 186.3 g, T_{max}: 672.8°C at T1_P1_between1/2. Fire was quickly extinguished but propagation was not suppressed completely as cooling inside battery pack was not efficient enough, all the cells had vented

Test record Overcharge 4s2p

Fire-ex: 6 litre mobile extinguisher, Test #06

Battery	Pouch cell pack 4s2p 120Wh, cell: Li-CoOx 4Ah
Date	30.09.2016
Test parameter	Overcharge from 100% to 200% SOC with 8A charging current
Observations	Mass before test: 993.1 g, after test: 895.3 g, mass loss: 97.8 g OCV_{cell} before: 4.009 V, OCV after: 0 V The cell entered thermal runaway at about 14 V and a temperature of 92°C. In the first 9 s, the voltage of the cells 1 and 2 from the first stack dropped to 0 V and the temperature between these two cells reached a max of 619.8°C. After 1.4 min from thermal runaway the other two cells enter thermal runaway reaching a max temperature of 478.8°C. The AVD was applied after 12 s from presence of fire and it was sprayed for 44 s continuously, i.e. the whole amount of product in the extinguisher. As result the fire was extinguished and the temperatures decreased considerably. The heat propagation to the cells with large face contact could not be avoided, so the 2 further cell vented but without flames. The propagation to the parallel side pack could successfully avoid. All of the cells in the nearby stack survived. The maximum temperature was measured at stack 1 between cell no.1 (the cell overcharged) and cell no.2 with a value of 619.8°C After test inspection showed that the all the cells of stack 1 had opened and none of the second parallel stack.

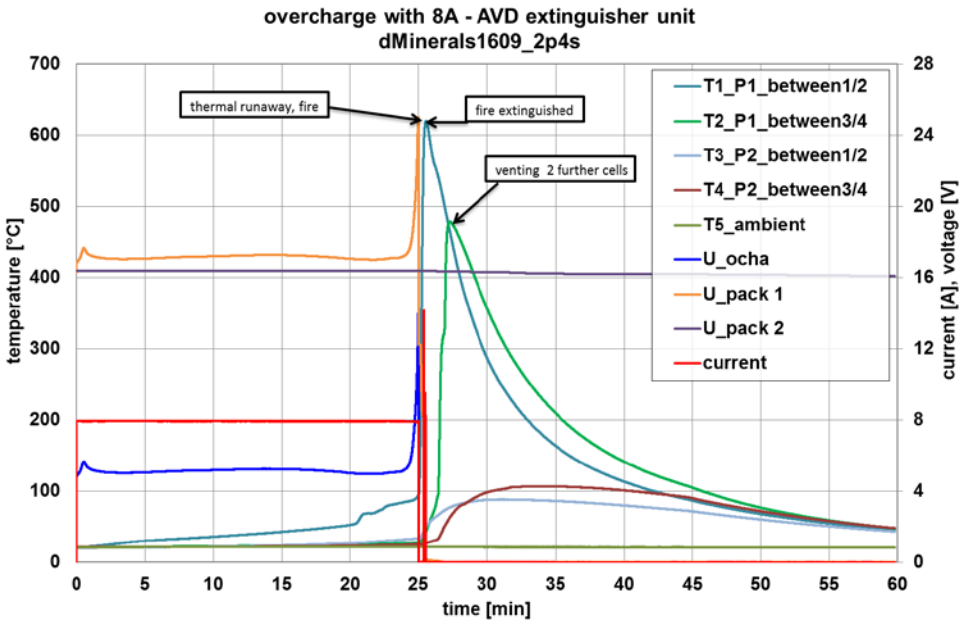


Figure 15: Temperatures, capacity, current and voltages during test

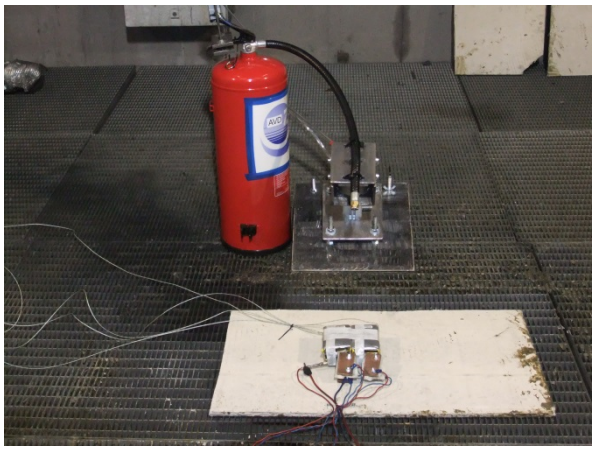


Figure 16: Overall set up

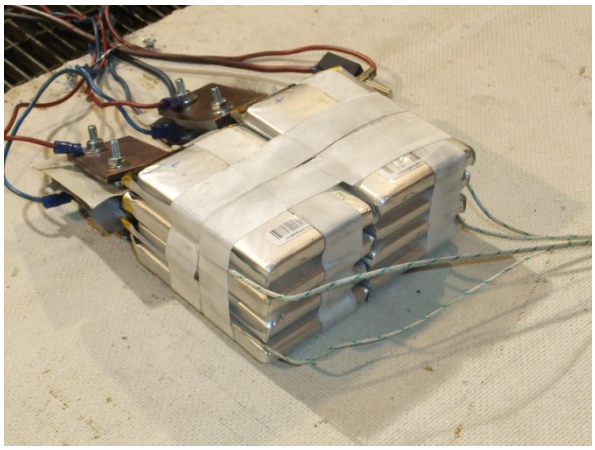


Figure 17: Cells after test front view

Figure 18: Cells after test front view

Figure 19: Cells after test rear view

Test result	Mass loss of 97.8 g, T_{max}: 619.8°C at T1_P1_between1/2. Fire was quickly extinguished (19 seconds), only the cells of the first stack had vented. Propagation over the second stack was avoided.

Thermal stimulation with heating plates	
Purpose	The purpose of the test was to test the functionality of the AVD product over a situation of thermal runaway with heat propagation onto the nearby battery stack
Parameter	• Pack level • 13s6p stack with 18650 cells • Ambient temperature 25°C ± 3°C • Cell charged to: 4.2 V (SOC ~100%)

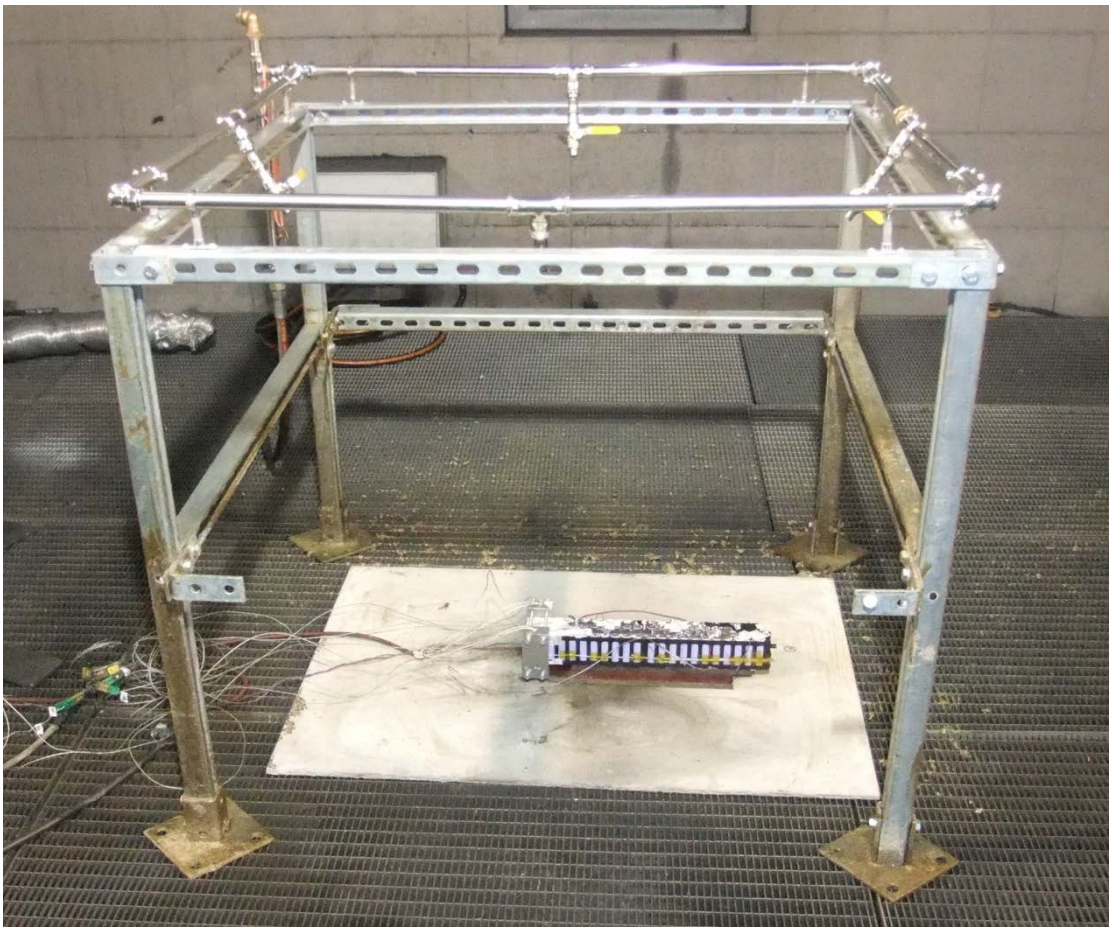
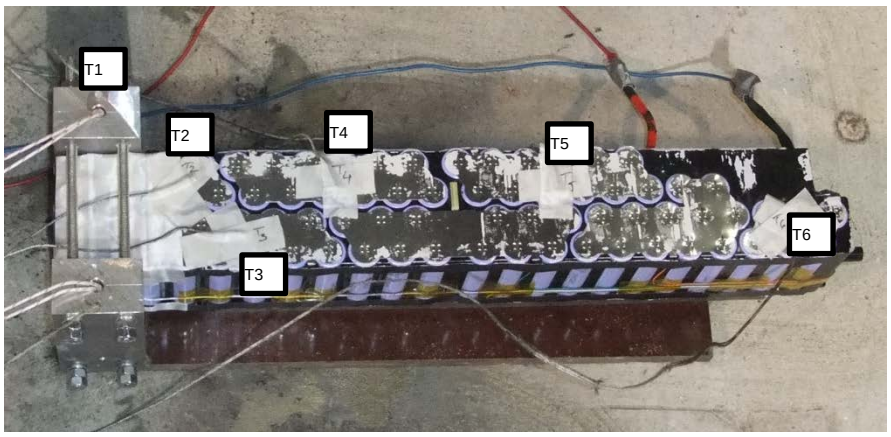


Figure 20: Example of set-up for thermal stimulation

Test record Thermal excitation 13s6p-800Wh battery pack fire-ex: 4 nozzle rig (Test #02)	
Battery	13s6p 800Wh battery pack with cylindrical 18650 Li-ion cells each cell 2.8Ah
Date	28.09.2016
Test parameter	Thermal stimulation to 250°C trough heating plates at one side of the module
Thermocouple distribution	
Observations	Mass before test: 4039.3 g, after test: 3167.7 g, mass loss: 871.6 g OCV before: 54.14 V, OCV after: 0 V The heated cells entered thermal runaway after approximately 17 min from heating start. At this point the heater temperature was already in the plateaued at 250°C. The AVD was applied after about 5 s from presence of fire and it was sprayed for 20 sec. The fire was quenched within 5 seconds, however, re-ignition and failure propagation was observed. This was caused by heat propagation onto the nearby cells which entered thermal runaway. AVD was applied again continuously until the container was emptied (about 32 litters AVD). So re-ignition was observed for about 5.5 minutes. As a result the fire affected only part of the module, 5 units of 6p configurations from 13, so the failure did not propagate completely through the battery pack. The maximum temperature was 845.2°C measured at T3. T6 was damaged, not useful values.

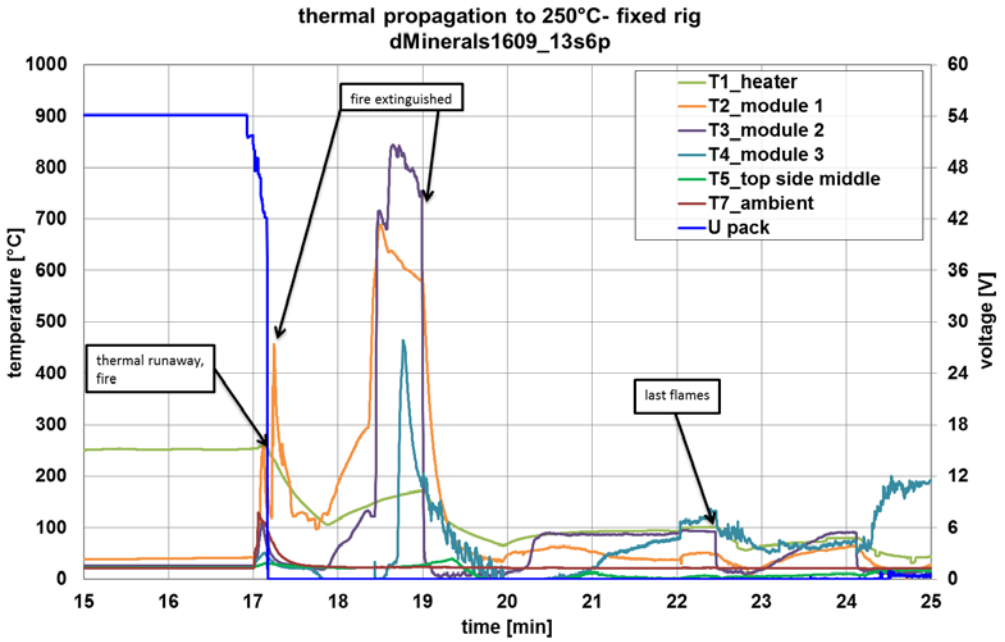


Figure 21: Temperatures and voltage during test

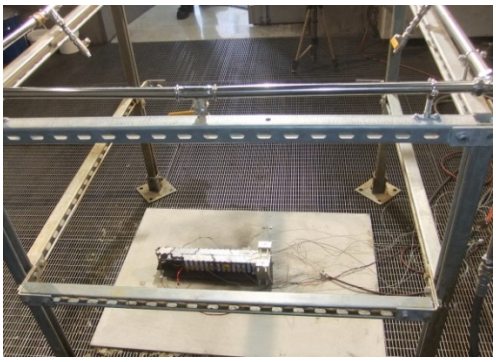


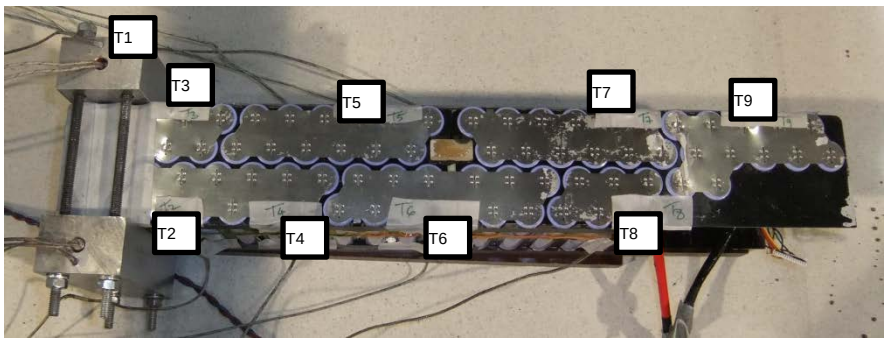
Figure 22: overall set up

Figure 23: pack before test

Figure 24: Cells after test front view

Figure 25: Cells after test side view

Test result	Mass loss of 861.6 g, T_{max}: 845.2°C at T3. Fire was quickly extinguished (5 seconds), however, re-ignition and failure propagation was observed for about 5.5 minutes, propagation could be limited to 5 units of 6p configurations (about 40% of the battery pack)

Test record Thermal excitation 13s6p-800Wh battery pack fire-ex: 4 nozzle rig (Test #03)	
Battery	13s6p 800Wh battery pack with cylindrical 18650 Li-ion cells each cell 2.8Ah
Date	28.09.2016
Test parameter	Thermal stimulation to 250°C trough heating plates at one side of the module
Thermocouple distribution	
Observations	Mass before test: 4035.7 g, after test: 3134.4 g, mass loss: 901.3 g OCV before: 54.17 V, OCV after: 0 V The heated cells entered thermal runaway after approximately 15 min from heating start. At this point the heater temperature was about 245°C. The AVD was applied after about 48 s from presence of fire and it was sprayed for 100 sec. The fire was quenched within 2 seconds, however, re-ignition and failure propagation was observed continuously even the AVD spraying was still active. So flames have been observed until 4:40 min after the start of the event. As a result the fire affected only part of the module, 7 units of 6p configurations from 13, so the failure did not propagate completely through the battery pack. The maximum temperature was around 1000°C measured at T3.

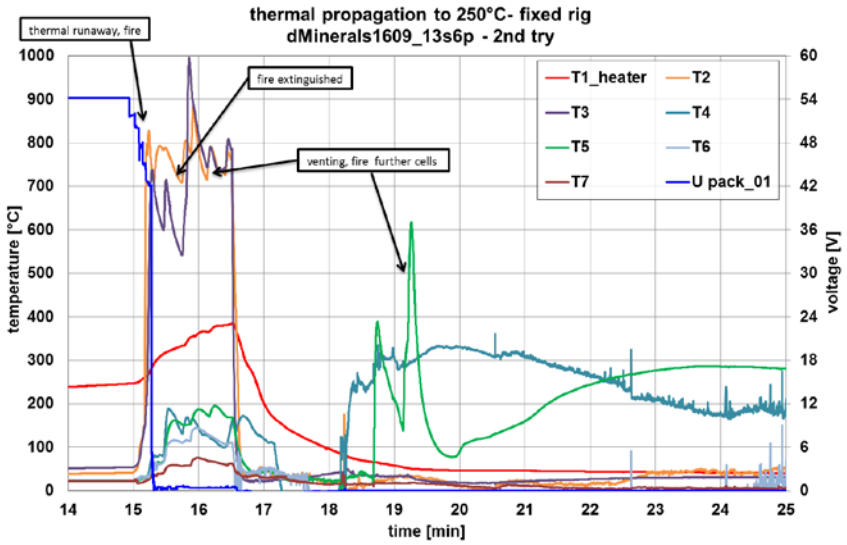


Figure 26: Temperatures and voltage during test

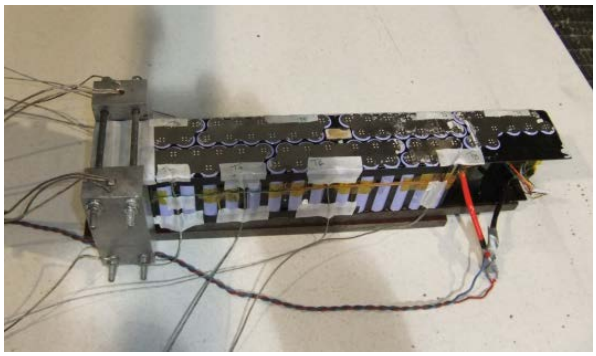


Figure 27: pack before test

Figure 28: overall set up after test

Figure 29: Pack after test front view

Figure 30: Pack after test side view

Test result	Mass loss of 901 g, T_{max}: 1000°C at T3. Fire was quickly extinguished (2 seconds), however, re-ignition and failure propagation was observed for about 4:40 minutes, propagation was limited to 7 units of 6p configurations (about 55% of the battery pack) Delay of fire extinguishing reduces the efficiency as a higher fraction of the battery got already in a critical temperature status.