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Baden-Württemberg
Gemeinnützige Stiftung

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Certified according to DIN EN ISO 9001:2008

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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 Aerosol fire extinguisher for Li-batteries fire (energy content 60Wh)

Product:	Lith-Ex AVD Aerosol fire extinguisher The fire extinguishing medium AVD - Li which is specifically manufactured for this application with the product reference 1351750 was applied via an aerosol extinguisher. The composition of this extinguishing agent is according to the code 1351750 and is an aerosol manufactured by Aero-EX a division of Dupré Minerals. The container has a capacity of 794 ml and is a standard aluminium aerosol extinguisher tested according to the standards as listed in BS 6165. 400ml AVD is filled in the container and pressurised to 12 bar with Nitrogen as the propellant
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: 4 Li-cells (2x2s1p, LiC-LiCo-Oxide, pouch) each cell 4Ah//4.2V//15 Wh ignition procedure: heating below one cell with a heating cartridge 150W Extinguishing the battery fire by 400 ml Lith-Ex AVD Aerosol fire extinguisher
Test results:	The battery fire was extinguished quickly, failure propagation to the neighbouring cell was avoided by the cooling effect of the AVD

Test passed

Dipl. Ing. (FH) M. Wörz
(Test engineer 1)

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Attachment: Test protocol

Lith-Ex AVD fire extinguisher tests on Li-ion batteries

Under contract of

Dupré Minerals Ltd.

Report Version 1.0

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)

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 were subjected to 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 with pouch cells (Li-CoO_2)

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

- 2s1p max Voltage 8.4 V; capacity: 4Ah, energy 30Wh
- 2x 2s1p max Voltage 8.4 V; capacity: 4Ah, energy 60Wh

The active material of the positive electrode was CoO_2

Figure 1. Two stacks of 2s1p

Figure 2. One stack of 2s1p

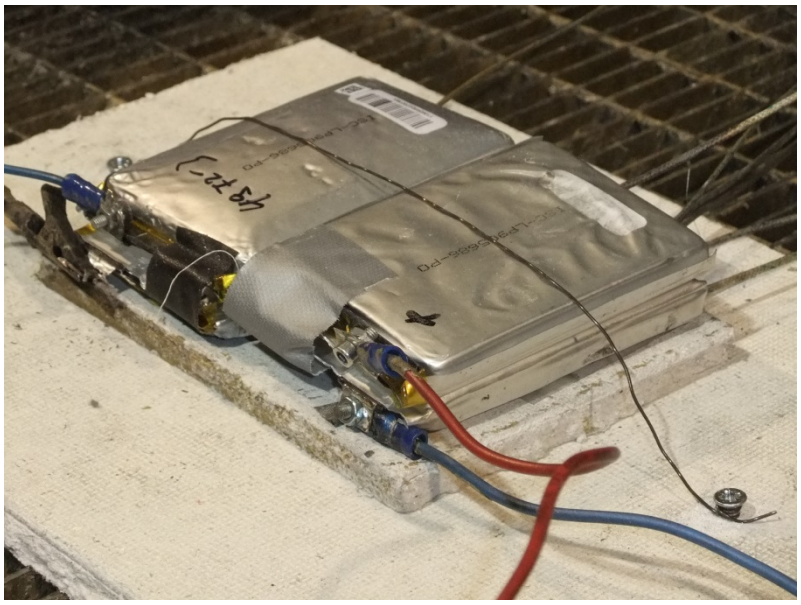

Figure 3: 2x 2s1p stacks in the test configuration all cells are in close mechanical contact

Test setup

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 heat exposition with a heating element (single rod ,150W) was used for excitation.

Set up for the fire extinguisher

The fire extinguishing medium AVD - Li which is specifically manufactured for this application with the product reference 1351750 was applied via an aerosol extinguisher. The composition of this extinguishing agent is according to the code 1351750 and is an aerosol manufactured by Aero-EX a division of Dupré Minerals.
The 400 ml aerosol fire extinguisher is pressurised to 12 bar with Nitrogen as the propellant and contains 400ml of AVD-Li in a container of capacity 794 ml. The canister is a standard aluminium aerosol extinguisher tested according to the standards as listed in BS 6165.

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 from left to right and back again. Figure 4 illustrates this equipment.

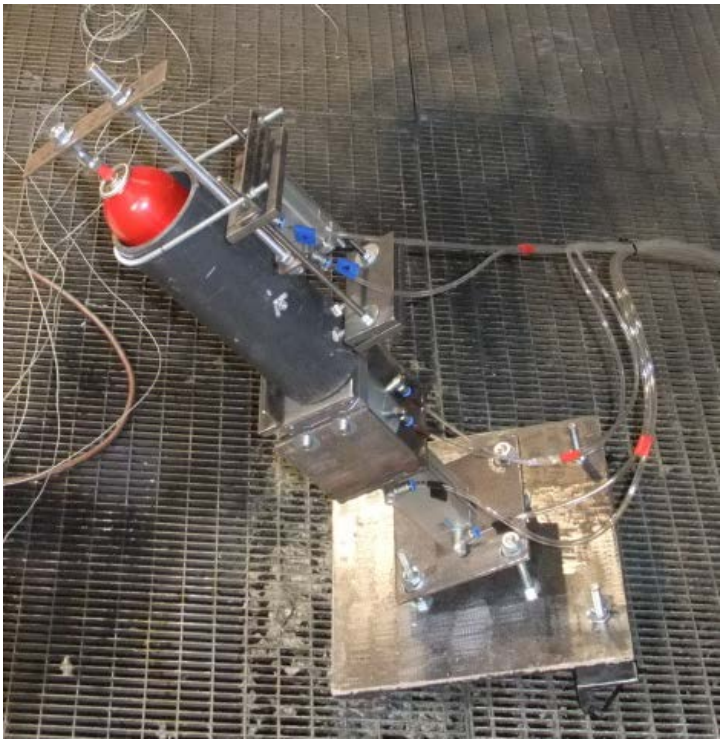

Figure 4: 400 ml Aerosol fire extinguisher filled with AVD and pressurized operated with pneumatic manipulators

Thermal stimulation with heating element	
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 cell
Parameter	• Ambient temperature 25°C ± 3°C • Cells charged to SOC ~100% • Extinguisher spray bottle 400 ml, filled with AVD • 2s1p arrangement with 4Ah pouch cells (30Wh) • Heating element (rod) 150W • 2s2p arrangement with 4Ah pouch cells (60Wh) • Heating element (rod) 150W

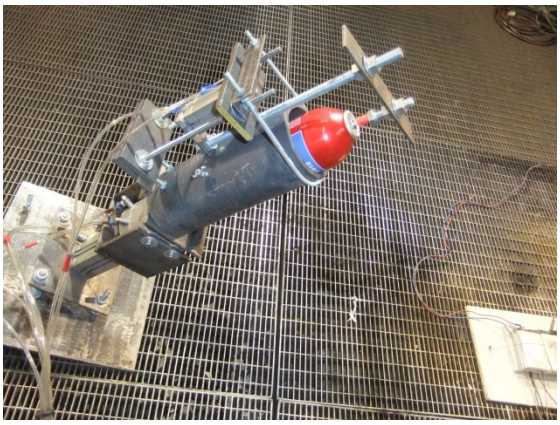

Figure 5: Set-up for fire extinguisher with 400 ml spray bottle in pneumatic manipulator

Figure 6: Set-up for fire extinguisher test for 2x2s1p configuration, below left cell is the heating rod

Test record thermal excitation 2s1p-30Wh cell assembly fire-ex: 4oo ml AVD spray bottle (Test A)

Battery	2s1p 30Wh cell assembly with 4 Ah LiC-CoOx cells
Date	29.09.2016
Test parameter	Thermal stimulation to 250°C trough heating element under the lower cell, extinguishing by 400 ml AVD spray bottle
Observations	Mass before test: 189 g, after test: 168 g, mass loss: 21 g OCV before: 8.24 V, OCV after: 0 V The heated cells entered thermal runaway after approximately 28 min from heating start (limited heat transfer from the heating element to the cell). The AVD was applied after about 3 s from presence of fire and it was sprayed for about 40 sec (empty). The fire was quenched within 2 seconds. Re-ignition and failure propagation was successfully avoided, so the second cell could survive. The maximum temperature was 250°C measured between the 2 cells.

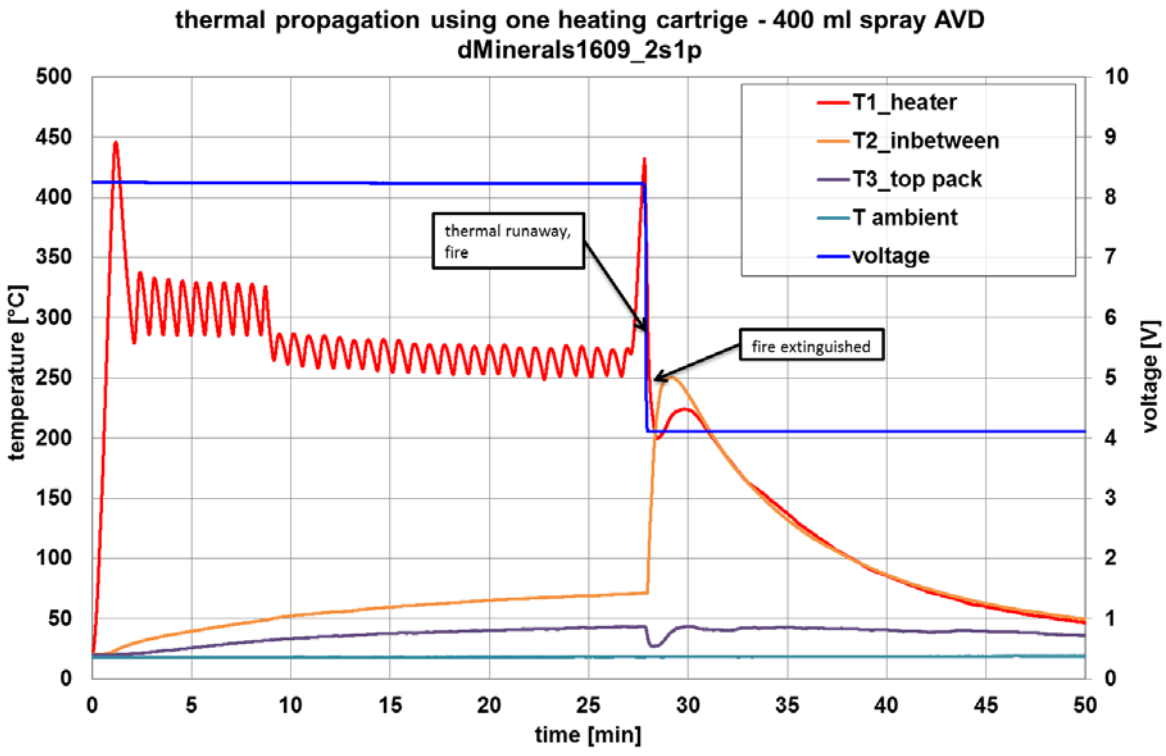

Figure 7: Temperatures and voltage during test

Figure 8: Cells after test

Figure 9: Cells after test

Test result	Mass loss of 21 g, T_{max}: 250°C Fire was quickly extinguished (2 seconds), re-ignition and failure propagation could be avoided, second cell survived

Test record Thermal stimulation 2x2s1p - 60Wh battery stacks fire-ex: Lith Ex AVD Aerosol 400ml (Test B)

Battery	Two stacks of 2s1p pouch cells 60Wh
Date	21.10.2016
Test parameter	Thermal stimulation with heating cartridge 150W
Set up T sensors	
Observations	$m_{stack\ 1\ before\ test}$: 188.9 g, $m_{stack\ 1\ after\ test}$: 133.2 g, mass loss: 55.7 g $m_{stack\ 2\ before\ test}$: 192.2 g, $m_{stack\ 1\ after\ test}$: 192.2 g, mass loss: 0 g $OCV_{Stack\ 1\ before}$: 8.37 V, $OCV_{Stack\ 1\ after}$: 0 V $OCV_{Stack\ 2\ before}$: 8.15 V, $OCV_{Stack\ 2\ after}$: 8.15 V The voltage started to drop 1.2 min after starting heating and it caught fire 6 sec later. At this point the heater temperature was at approximately 450°C. The AVD was applied immediately from presence of fire and it was sprayed until the container was emptied, that is for about 20 sec. The fire was quenched within 11 sec without re-ignition. Failure propagation was observed only for the second cell in stack 1. This event happened after some 1 min and 20 sec from finishing spraying with AVD. Stack 2 was not affected by the thermal propagation in a critical manner. The temperature on stack 2 reaching a max of 43.8°C. As a result the fire affected only the first stack which was heated with the heating rod. Both cells in stack 1 opened, however fire was present only at the bottom cell. Stack 2 saw only a slight temperature increase but no change in voltage, both cells stayed closed. The maximum temperature at the stack level was 478.6°C .at T3.

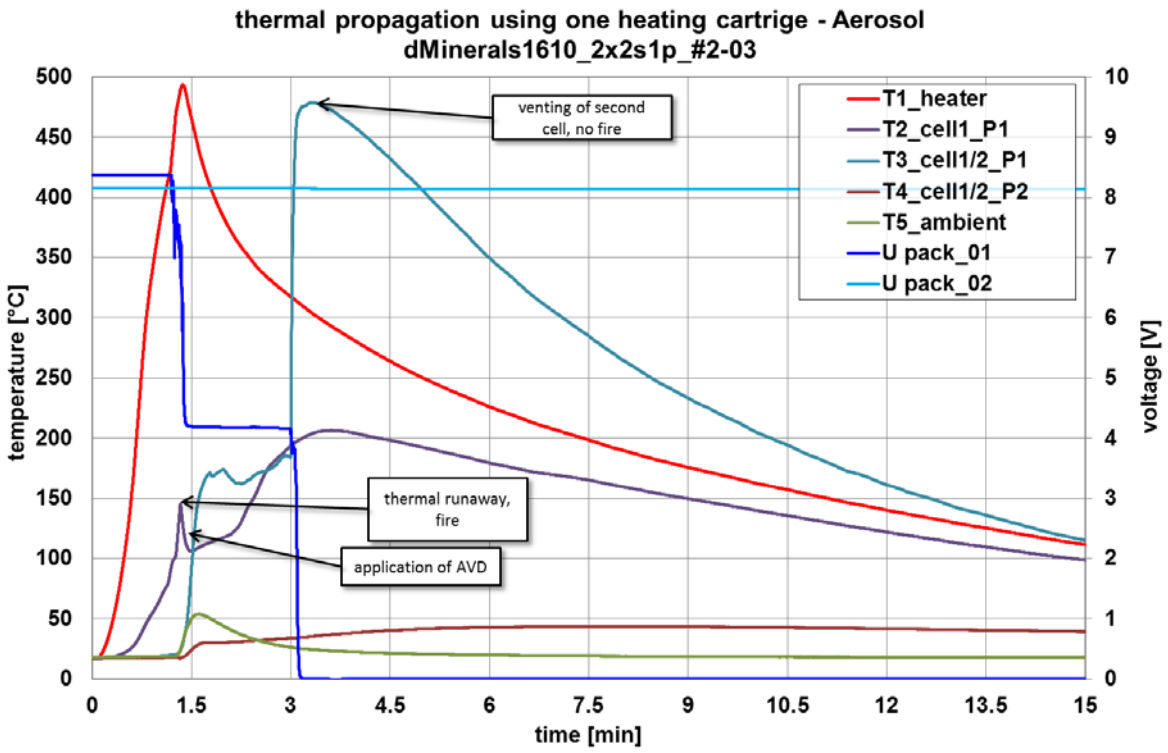

Figure 10: Temperatures and voltage during test

Figure 11: Cells after test front view

Figure 12: Cells after test rear view

Test result	Mass loss of 55.7 g, T_{max}: 478.6°C at T3. Fire was quickly extinguished within 11 seconds, no re-ignition and propagation was seen only at the second cell in the same stack. The second stack remained closed without changing in voltage.

Test record Thermal stimulation 2x2s1p - 60Wh battery stacks fire-ex: Lith Ex AVD Aerosol 400ml (Test C)	
Battery	Two stacks of 2s1p pouch cells 60Wh
Date	24.10.2016
Test parameter	Thermal stimulation with heating cartridge 150W
Observations	$m_{stack\ 1\ before\ test}$: 191.1 g, $m_{stack\ 1\ after\ test}$: 168.1 g, mass loss: 23 g $m_{stack\ 2\ before\ test}$: 191.8 g, $m_{stack\ 1\ after\ test}$: 191.8 g, mass loss: 0 g $OCV_{Stack\ 1\ before}$: 8.07 V, $OCV_{Stack\ 1\ after}$: 3.95 V $OCV_{Stack\ 2\ before}$: 8.11 V, $OCV_{Stack\ 2\ after}$: 8.11 V The voltage started to drop 1 min after starting heating and it caught fire 17 sec later. At this point the heater temperature was at approximately 425°C. The AVD was applied immediately from presence of fire and it was sprayed until the container was emptied. The fire was quenched within 2 sec without re-ignition. Failure propagation was not observed on any other cell. The top cell in the first stack had a voltage of 3.95 V after the fire was quenched and it stayed at this value over the rest of the observation time (over 60 min). Stack 2 was not affected by the thermal propagation in a critical manner. The temperature on stack 2 reaching a max of 51.4°C. As a result the fire affected critically only the cell which was directly in contact with the heating cartridge. The cell on the top remained closed despite the elevated temperature of 232.5°C at T3, between the two cells. Its voltage decreased slightly from ca.4.1 V to 3.95 V Stack 2 saw only a slight temperature increase but no change in voltage, both cells stayed closed. The maximum temperature at the stack level was 342.9°C .at T2, under the heated cell.

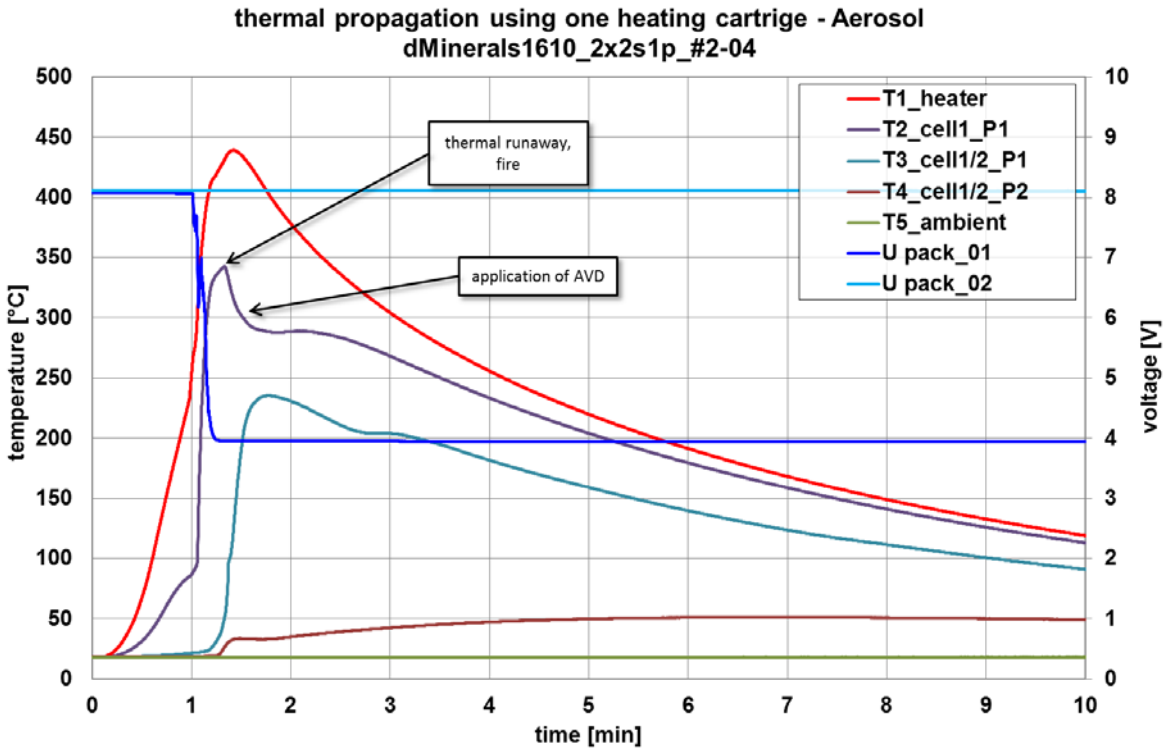

Figure 13: Temperatures and voltage during test

Figure 14: Cells after test side view

Figure 15: Cells after test rear view

Test result	Mass loss of 23 g, T_{max}: 342.9°C at T2. Fire was quickly extinguished within 2 seconds, no re-ignition, no propagation were seen at the other cells. The other three cells remained closed.

Test record Thermal stimulation 2x2s1p - 60Wh battery stacks fire-ex: Lith Ex AVD Aerosol 400ml (Test D)	
Battery	Two stacks of 2s1p pouch cells 60Wh
Date	24.10.2016
Test parameter	Thermal stimulation with heating cartridge 150W
Observations	$m_{stack\ 1\ before\ test}$: 190.3 g, $m_{stack\ 1\ after\ test}$: 138.2 g, mass loss: 52.1 g $m_{stack\ 2\ before\ test}$: 193.2 g, $m_{stack\ 1\ after\ test}$: 193.2 g, mass loss: 0 g $OCV_{Stack\ 1\ before}$: 8.26 V, $OCV_{Stack\ 1\ after}$: 0 V $OCV_{Stack\ 2\ before}$: 8.11 V, $OCV_{Stack\ 2\ after}$: 8.11 V The voltage started to drop 1.1 min after starting heating however the bottom cell did not catch fire but only vented with strong gas/electrolyte release for about 25 sec. The heating process was carried out further in other to obtain fire over the second cell. After 2.4 min from heating start, fire was obtained at the top cell of stack 1 and AVD was applied immediately. The product was sprayed until the container was emptied, that is for 27 sec. The fire was quenched within 11 sec without re-ignition. Further heat/ fire propagation was avoided. Stack 2 was not affected by the thermal propagation in a critical manner. The temperature on stack 2 reaching a max of 54°C. As a result the heater affected only the first stack with the bottom cell reaching thermal runaway but no fire and the top cell reaching thermal runaway with flames. Both cells in stack 1 opened and saw voltage drop to 0 V. Stack 2 saw only a slight temperature increase but no change in voltage, both cells stayed closed. The maximum temperature at the stack level was 500°C .at T3.

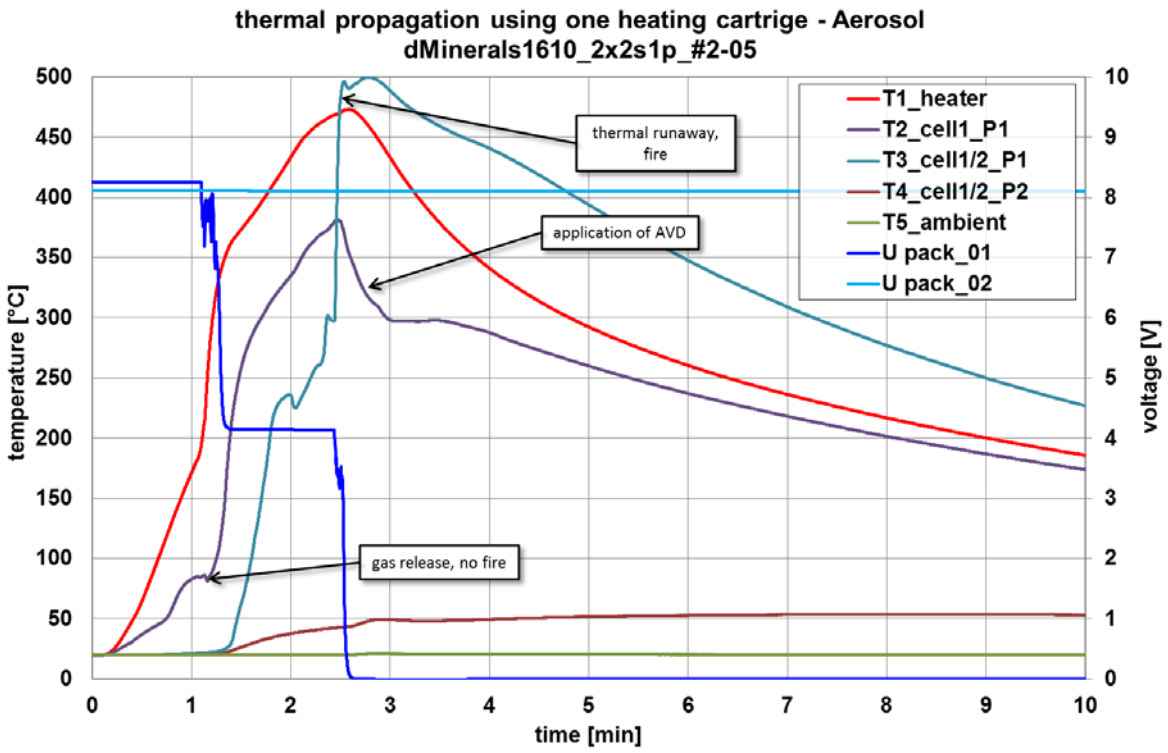

Figure 16: Temperatures and voltage during test

Figure 17: Cells after test front view

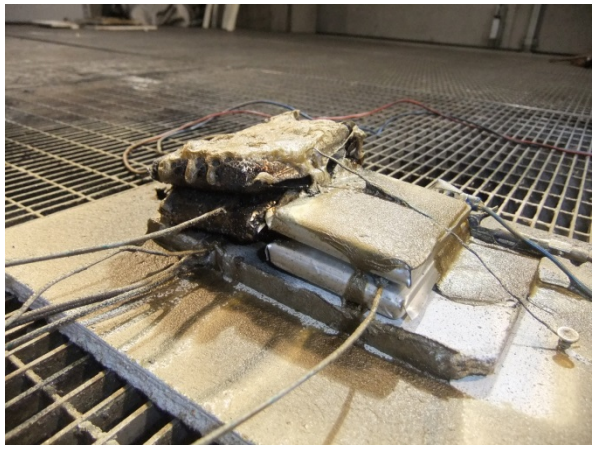

Figure 18: Cells after test rear view

Test result	Mass loss of 52.1 g, T_{max}: 499.7°C at T3. Fire was quickly extinguished within 11 seconds, no re-ignition or further propagation. The second stack remained closed without changing in voltage.