Safety of Li batteries in transportation: is a protection in case of thermal runaway affordable?

C. Chanson

Nice, Sept. 25th, 2014

Recharge membership in all the Value Chain.

The European Association for Advanced Rechargeable Batteries

Saft
Panasonic
FDK
ARTS ENERGY
StanleyBlack&Decker
BOSCH
RENAULT
TOYOTA
HONDA
VARTA
UL
APPLE
MOTOROLA
MOTOROLA SOLUTIONS
VALE
Thomas&Betts
FLANDERS' DRIVE
EPTA
ICdA International Cadmium Association
SNAM FLORIDIENNE
SPECIALIZED
floridienne chimie
ERAMET
umicore
GLENCORE
ACCUREC RECYCLING GMBH
DHL

1-Li batteries transport: legislative framework

Li batteries are classified as dangerous good for transport under UN transport regulation=

No. 3480 and 3090
Lithium ion and Lithium metal batteries
Risk UN class: 9, Packing Group: II
Special Provisions : 188,230,310
Packing Instruction : P903

No. 3481 and 3091
lithium ion and Lithium metal batteries, contained in equipment, or packed with equipment,
Risk UN class: 9, Packing Group: II
Special Provisions : 188,230,310, 360
Packing Instruction : P903

1- UN Dangerous goods transport regulation

Part 1. GENERAL PROVISIONS, DEFINITIONS, TRAINING AND SECURITY

Chapter 1.1 - General provisions

1.1.1 Scope and application

1.1.1.1 These Regulations prescribe detailed requirements applicable to the transport of dangerous goods. Except as otherwise provided in these Regulations, **no person may offer or accept dangerous goods** for transport unless those goods are properly **classified, packaged, marked, labelled, placarded, described and certified on a transport document, and otherwise in a condition for transport as required by these Regulations**.

General Requirements:

- **identified products (**classification, labelling, declaration,..**)**
- **tested products (**safety test according UN *Manual of Tests and Criteria*, Part III, sub-section 38.3**)**
- **qualified packagings (UN class II)**
- **trained operators**

2.1.1_IA LITHIUM METAL CELLS (including lithium alloy cells)

Fully regulated cells UN 3090

Applies to:	Lithium metal cells with a lithium metal content in excess of 1 g/cell Lithium metal cells with a lithium metal content not exceeding 1 g/cell transported in quantities that exceed the allowance permitted in § 2.1.1_IB			
UN No., Proper Shipping Name	UN 3090, LITHIUM METAL BATTERIES			
Class	9			
Packing Group	II			
Label	• *They must have a line 5 mm inside the edge and running parallel with it.* • *Labels must be in the form of a square set at an angle of 45° (diamond-shaped) with minimum dimensions of 100 mm by 100 mm.*			
Prerequisite	➔ **Cells must meet the General Requirements of § 1.3 in particular the test requirements**			
Specific Requirements	➔ Each cell incorporates a safety venting device or is designed to preclude a violent rupture under normal conditions of carriage; ➔ Each cell is equipped with an effective means of preventing external short circuits			
Transport mode	ADR	IMDG	IATA Passenger Aircraft	Cargo
Packing instructions	P903	P903	PI 698 section IA	
	Cells must be protected against short circuit, including protection against contact with conductive materials within the same packaging which could cause a short circuit. • *Cells* must be packed so that are protected against damage caused by the movement or placement of the cells within the packaging • Use only approved packaging conforming to Packing Group II performance level.			
		•	• lithium metal cells must be placed in inner packagings that completely enclose the cell, then placed in an outer packaging. • complete package must be approved Packing Group II performance level	
			Cells must be packed: • in a rigid metal intermediate or • in a metal outer packaging Cells must be surrounded by non-combustible and non-conductive cushioning material before being placed in the metal intermediate or metal outer packaging	Packages not conforming to "Passenger Aircraft" requirements must be transported as "Cargo Aircraft Only"
Packagings	Drums (1A2, 1B2, 1N2, 1H2, 1D, 1G); Boxes (4A, 4B, 4N, 4C1, 4C2, 4D, 4F, 4G, 4H1, 4H2) Jerricans (3A2, 3B2, 3H2).		Drums (1A2, 1B2, 1N2, 1H2, 1D, 1G); Boxes (4A, 4B, 4N, 4C1, 4C2, 4D, 4F, 4G, 4H2) Jerricans (3A2, 3B2, 3H2).	
Weight limit	No limit	No limit	2.5 kg Net	35 kg Net
Tunnel code	(E)	-	-	-
Transport cat.	2	-	-	-
Exemptions	chapter 1.1.3.6 limit ≤ 333 kg Net	-	-	-
Marking	UN 3090	UN 3090, LITHIUM METAL BATTERIES	• LITHIUM METAL BATTERIES, UN 3090 • Full Name ad Address of the shipper and the consignee • Net weight (kg)	
				 Minimum dimensions: 120 × 110 mm
Overpack	"Overpack"	"Overpack"	"Overpack"	"Overpack"
Documents	Transport document	MDGF	Shipper's Declaration	

Li battery transport
Author Marco Ottaviani
New edition 2014

A booklet can be used to identify the applicable packaging (Recharge and Hyper) on line demo:

http://www.rechargebatteries.org/knowledge-base/transport/

- **Information describing all modes of transport**
  - White: all modes of transport
  - Orange: specific to Road
  - Violet: specific to Maritime
  - Blue: specific to Air
- **Pictures for packaging and labelling**

Li battery transport, M. Ottaviani: New edition 2014

2.1.1_IA LITHIUM METAL CELLS (including lithium alloy cells)
Fully regulated cells UN 3090

Applies to:	Lithium metal cells with a lithium metal content in excess of 1 g/cell Lithium metal cells with a lithium metal content not exceeding 1 g/cell transported in quantities that exceed the allowance permitted in § 2.1.1_IB			
UN No., Proper Shipping Name	UN 3090, LITHIUM METAL BATTERIES			
Class	9			
Packing Group	II			
Label	• *They must have a line 5 mm inside the edge and running parallel with it.* • *Labels must be in the form of a square set at an angle of 45° (diamond-shaped) with minimum dimensions of 100 mm by 100 mm.*			
Prerequisite	→ **Cells must meet the General Requirements of § 1.3 in particular the test requirements**			
Specific Requirements	→ Each cell incorporates a safety venting device or is designed to preclude a violent rupture under normal conditions of carriage; → Each cell is equipped with an effective means of preventing external short circuits			
Transport mode	ADR	IMDG	IATA	
			Passenger Aircraft	Cargo
Packing instructions	P903	P903	PI 698 section IA	
	Cells must be protected against short circuit, including protection against contact with conductive materials within the same packaging which could cause a short circuit. • *Cells* must be packed so that are protected against damage caused by the movement or placement of the cells within the packaging • Use only approved packaging conforming to Packing Group II performance level.			
		•	• lithium metal cells must be placed in inner packagings that completely enclose the cell, then placed in an outer packaging. • complete package must be approved Packing Group II performance level	
			Cells must be packed: • in a rigid metal intermediate or • in a metal outer packaging Cells must be surrounded by non-combustible and non-conductive cushioning material before being placed in the metal intermediate or metal outer packaging	Packages not conforming to "Passenger Aircraft" requirements must be transported as "Cargo Aircraft Only"
Packagings	Drums (1A2, 1B2, 1N2, 1H2, 1D, 1G); Boxes (4A, 4B, 4N, 4C1, 4C2, 4D, 4F, 4G, 4H1, 4H2) Jerricans (3A2, 3B2, 3H2).		Drums (1A2, 1B2, 1N2, 1H2, 1D, 1G); Boxes (4A, 4B, 4N, 4C1, 4C2, 4D, 4F, 4G, 4H2) Jerricans (3A2, 3B2, 3H2).	
Weight limit	No limit	No limit	2.5 kg Net	35 kg Net
Tunnel code	(E)	-	-	-
Transport cat.	2	-	-	-
Exemptions	chapter 1.1.3.6 limit ≤ 333 kg Net	-	-	-
Marking	UN 3090	UN 3090, LITHIUM METAL BATTERIES	• LITHIUM METAL BATTERIES, UN 3090 • Full Name ad Address of the shipper and the consignee • Net weight (kg)	
				CARGO AIRCRAFT ONLY FORBIDDEN IN PASSENGER AIRCRAFT Minimum dimensions: 120 × 110 mm
Overpack	"Overpack"	"Overpack"	"Overpack"	"Overpack"
Documents	Transport document	MDGF	Shipper's Declaration	

2.1.1_IA LITHIUM METAL CELLS (including lithium alloy cells)
Fully regulated cells

Practical example of packaging, marking and labelling of packages containing lithium content 1.5 g/cell - Net weight 15 kg

On line preview: http://www.rechargebatteries.org/knowledge-base/transport/

RECHARGE

1-Li batteries transport: cushioning requirement

- The packaging instructions P908, applicable for damaged and defective cells and batteries, requires the use of cushioning material:

  "2. Each inner packaging shall be surrounded by sufficient non-combustible and non-conductive thermal insulation material to protect against a dangerous evolution of heat."

- It is the responsability of the shipper to define the sufficient amount of cushioning material, but no more information is provided.

There is a need of practical tests and models to provide valid information to the professionnels shipping batteries.

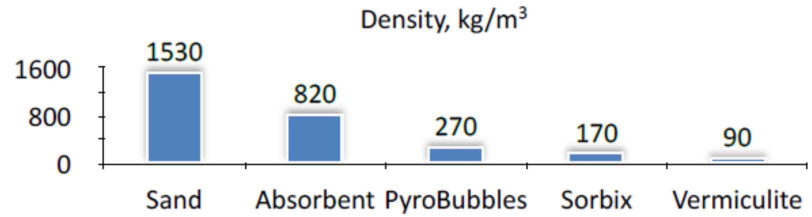
2- ACCUREC Experimental study: materials

ACCUREC has tested several cushioning materials to compare their effectiveness in protecting in case of Li-ion battery thermal runaway (ref. 1).

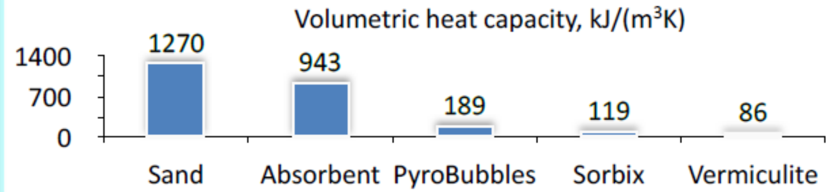
- At first, the thermal properties of the selected materials were measured

- **Electrical insulation:** All of these materials are non-electrical conductive

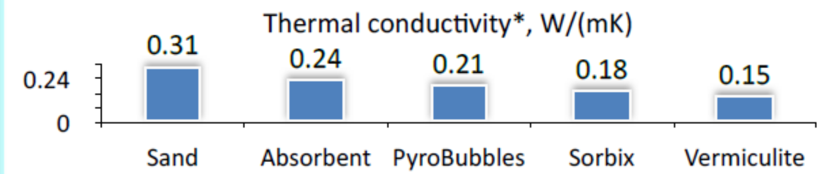
- **Density**:



- **Volumetric heat capacity:**



- **Thermal insulation**:

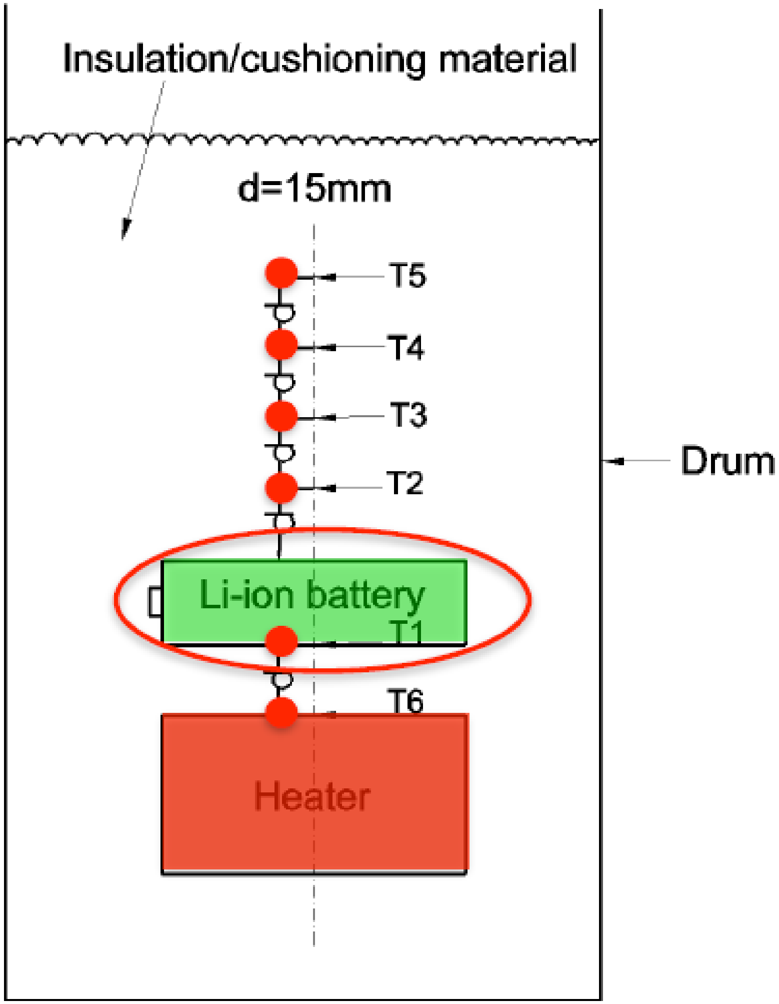


Ref 1. : ACCUREC, Investigation on packaging materials for safe transport of spent Li-ion batteries, March 4- 2014.

2- ACCUREC Experimental study: testing configuration

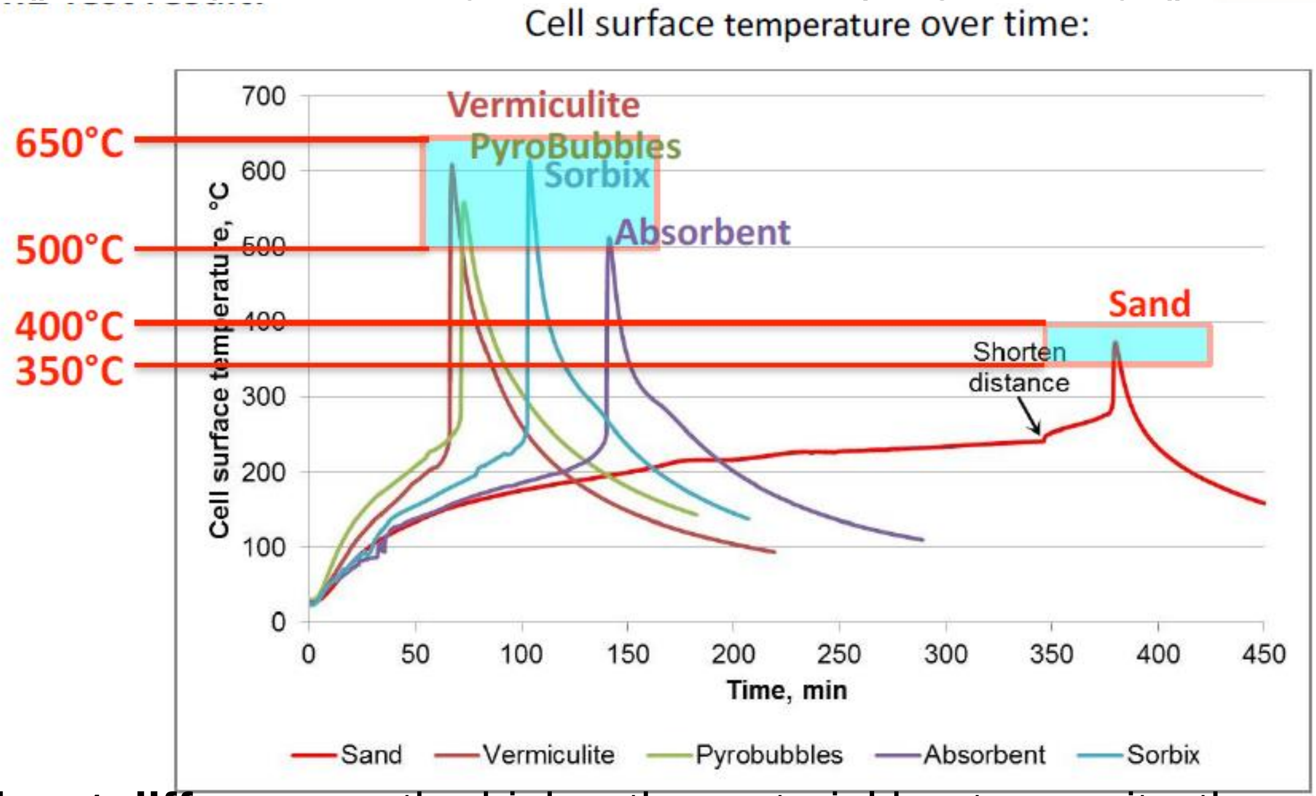
- One Li-ion single cell (18650) was placed in a drum filled with cushioning material. A heater was placed at 15 mm to cause a run-away.

- Thermocouples were placed on the heater, the cell, and in the cushioning material at 15 mm distance to measure the thermal propagation.



2- ACCUREC Experimental study: testing results

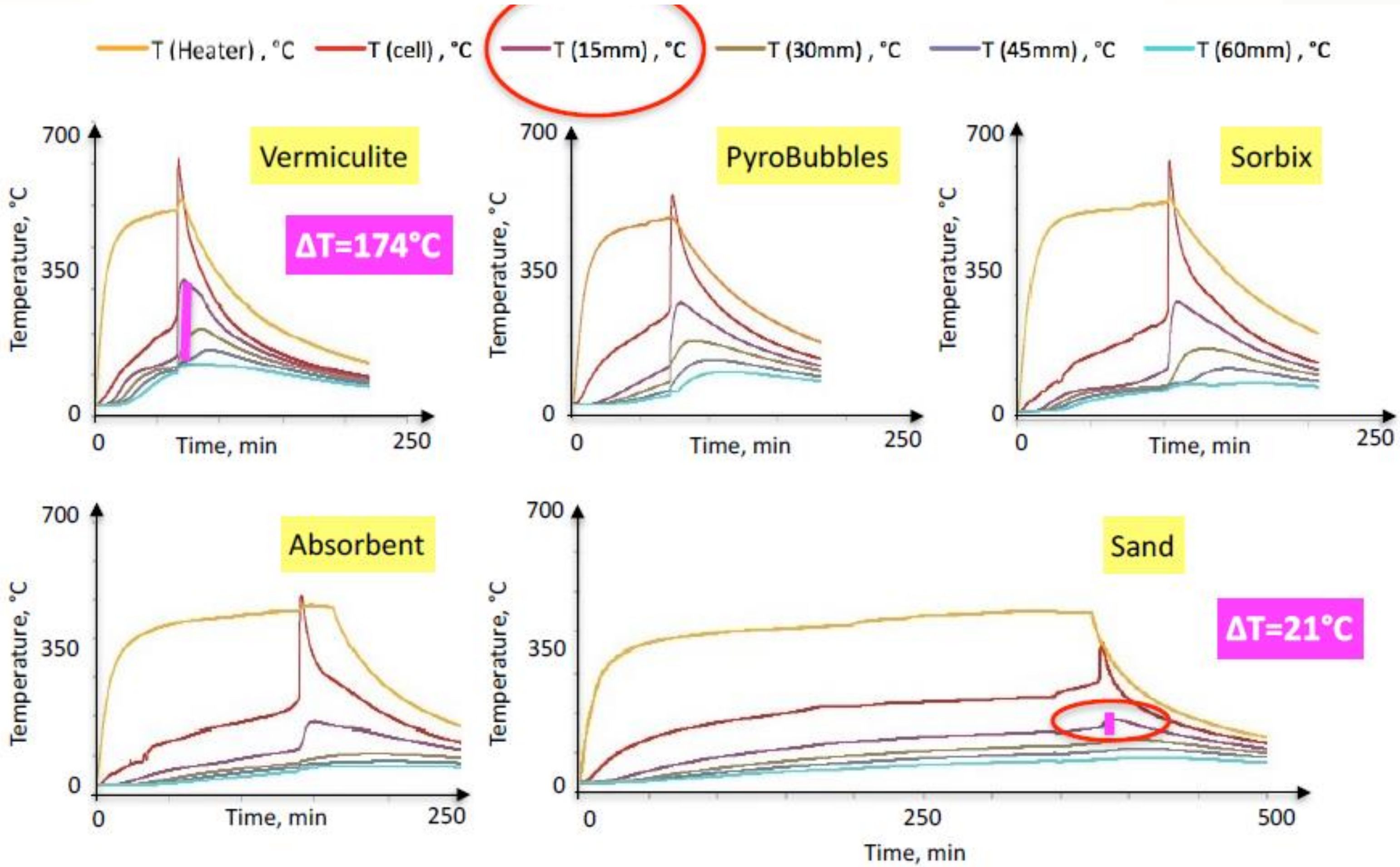
- **Similar behavior** was observed in all materials: after the heating phase up to about 200°C (phase A), the cell temperature increases abruptly due to the runaway (phase B), then the system cools down progressively (phase C).



- **significant differences**: the higher the material heat capacity, the longer the heating phase A, and the lower the runaway max. temperature during phase B.

2-ACCUREC experimental study: thermal diffusion

- The temperature increase of the cushioning material depends on its thermal properties.



3- Modeling: model description

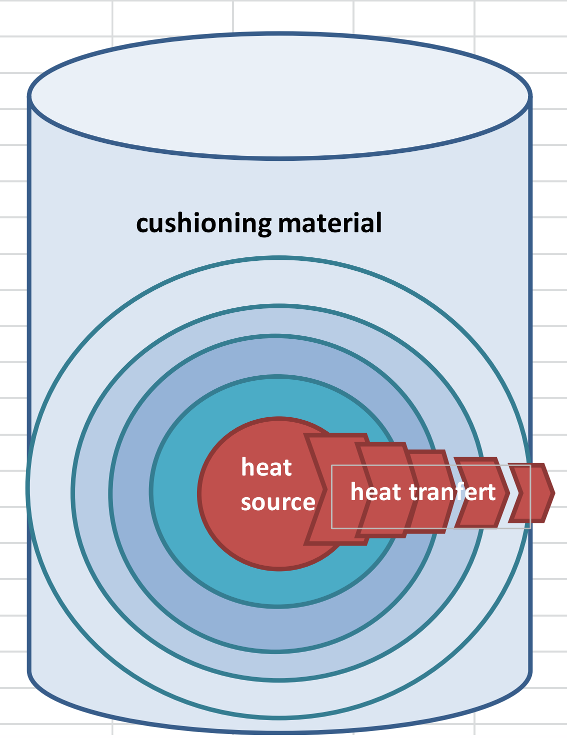
Objective:

- A simple static thermal model was not sufficient to analyze the results of the testing
- The testing was limited to one type and size of battery: there is a need of a model allowing a good prediction of the thermal behavior in case of different battery and packaging sizes or other cushioning materials.

Model description:

- A dynamic model has been created: simplified finite elements calculation under Excel, using heat propagation in isotropic spherical conditions through 4 layers of material.

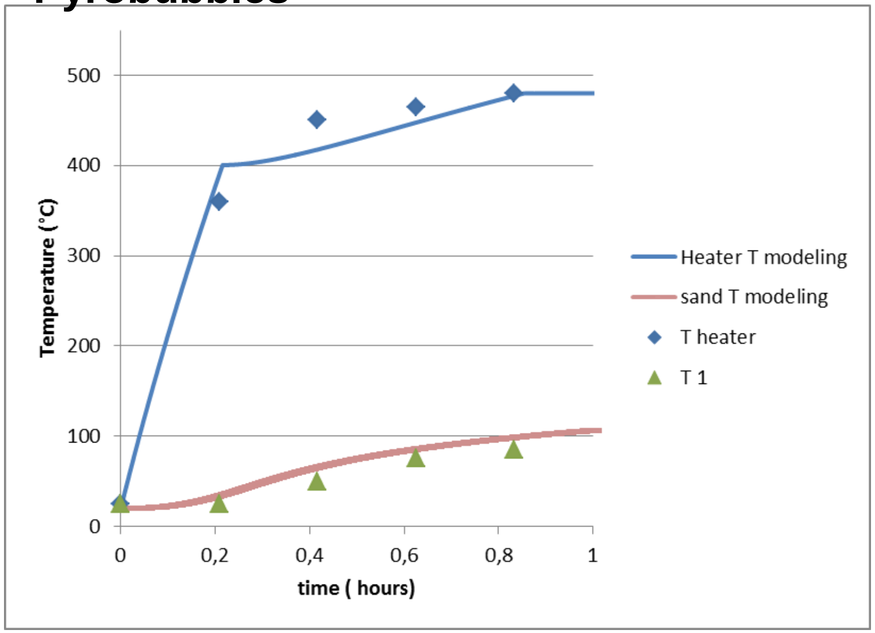
- Boundary conditions can be adjusted
- Heat source size and layer thickness can be adjusted



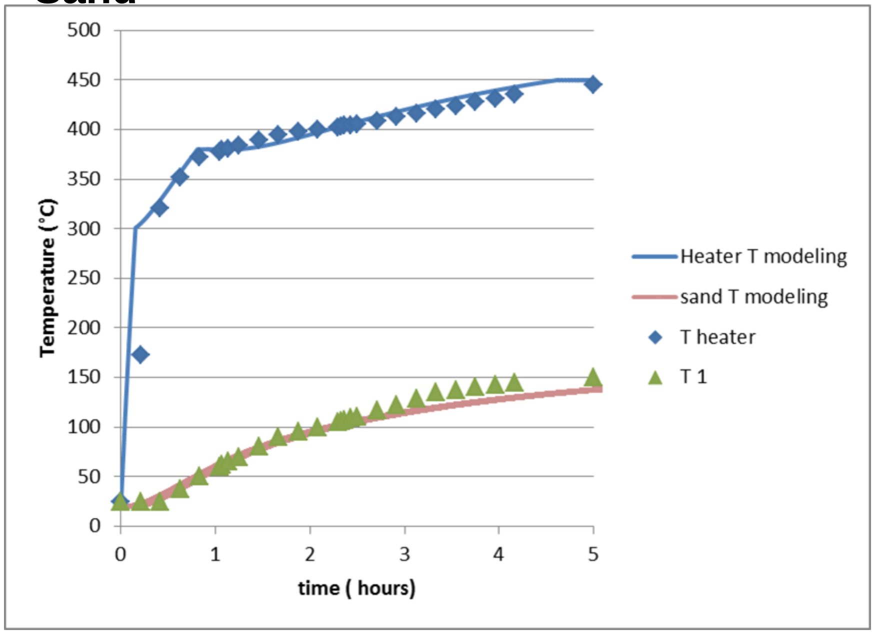
3- Modeling: calibration

- The heating phase (phase A) with stable parameters (heater at 150 W), was used for the calibration of the thermal parameters, based on the data for thermal properties of 5 cushioning materials.
- Comparison of experimental data with simulated data shows an acceptable fit: example for sand and pyrobubbles, temperature T1 of the material at 30 mm from the heater.

Pyrobubbles



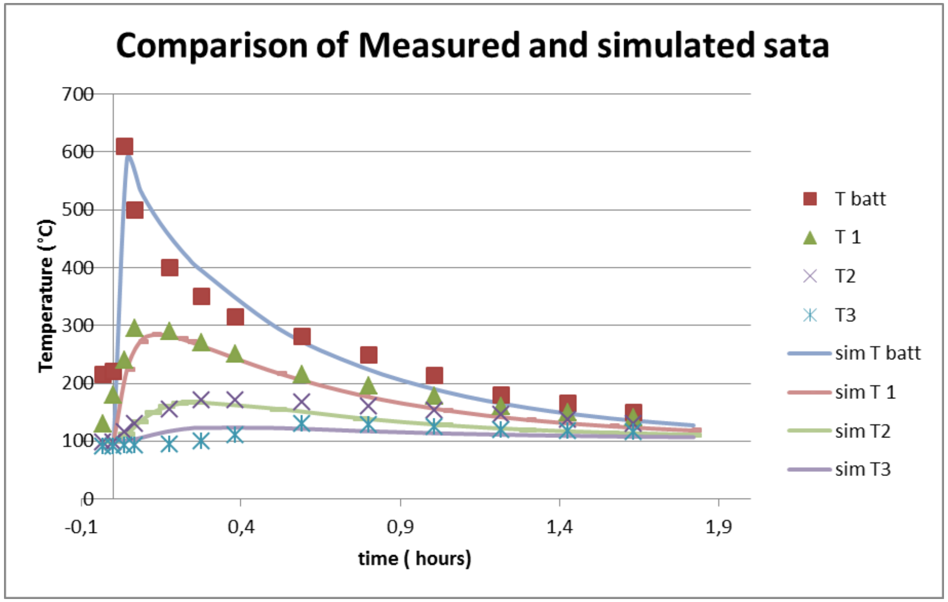
Sand



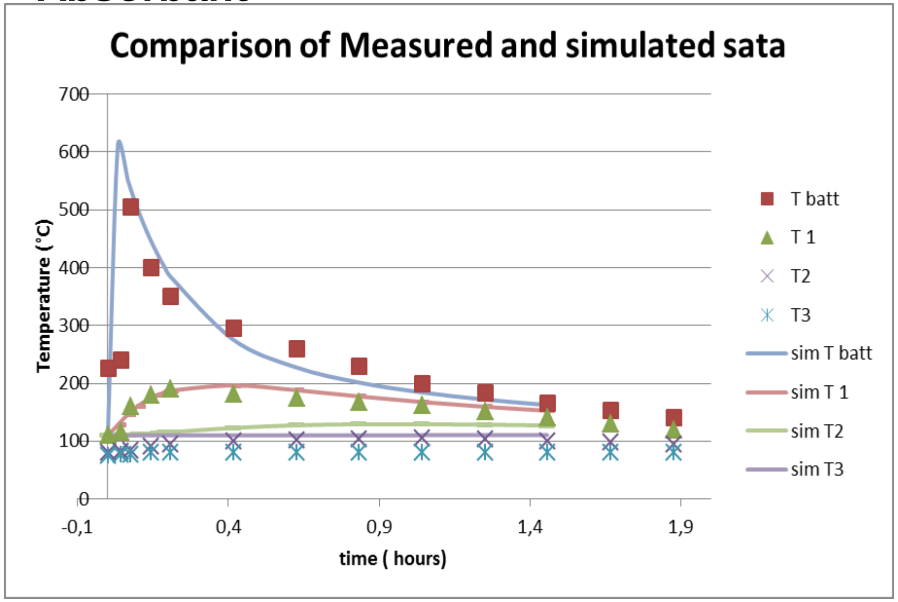
3- Modeling: cooling simulation

- Using the same parameters defined in the calibrating phase, the runaway phase and the cooling phase were calculated
- The initial temperature was set at the level of the material surrounding the cell at the runaway phase start.
- The simulation is showing acceptable results for the different layers of the cushioning materials during the cooling phase.

Sorbix



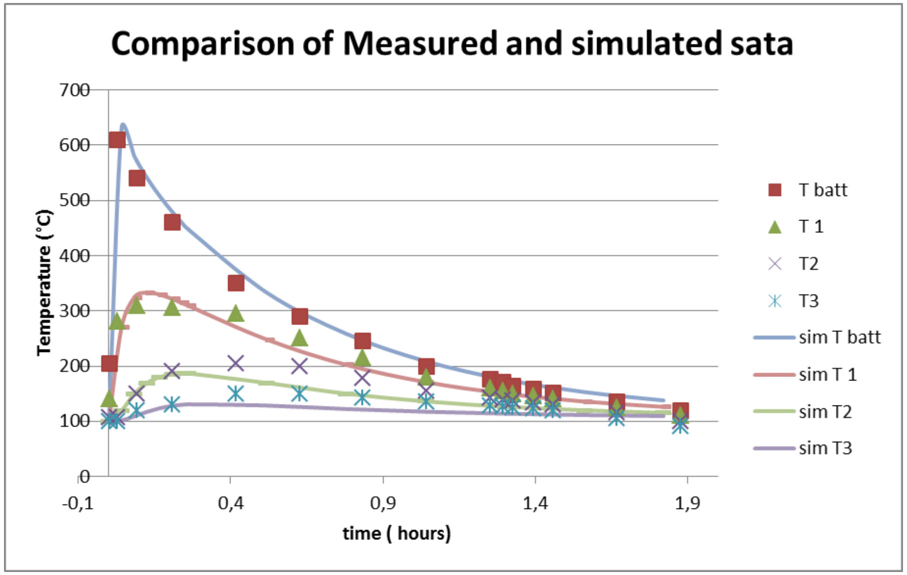
Absorbant



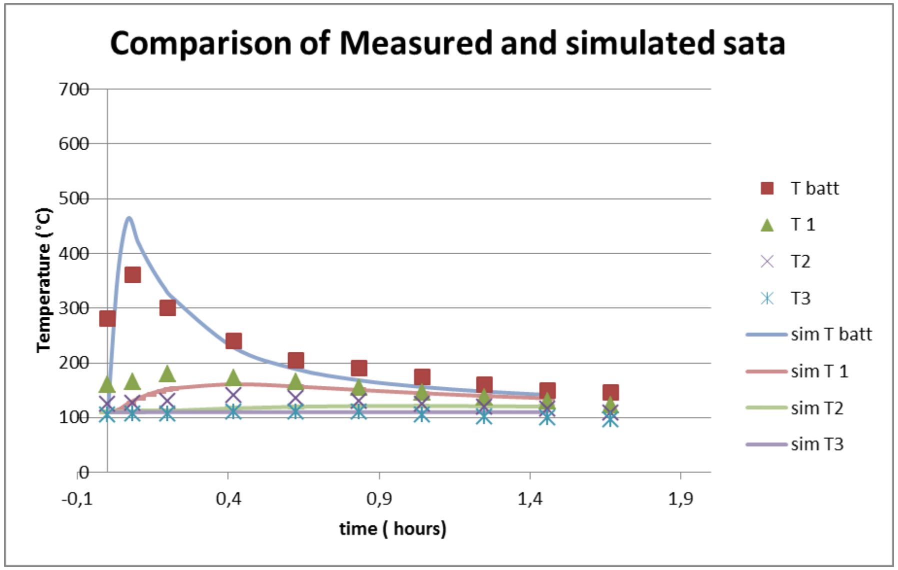
3- Modeling: thermal runaway simulation

- Due to the large difference observed in the max. runaway temperature, it is necessary to adjust the Li-ion battery energy release in order to fit the observed temperatures.
- Simulation of the vermiculite and sand is showing acceptable results, even in this case of large heat release difference.

Vermiculite



Sand



3- Modeling: thermal runaway energy calculation

- The simulation allows to recalculate the total heat emitted during the runaway: the results are reported in the table.
- They are compared to a reference energy release for Li-ion cell run away without flames of 870 kJ/cell kg (ref. 2)

	Calulated heat release (kJ/cell kg)	% theoritical heat release
sand	500	58%
absorbent	700	81%
Pyrobubbles	800	93%
sorbix	800	93%
Vermiculite	800	93%

- it is clear that the heat absorbing properties of the sand contributes in reducing the total energy release (this effect of slowing the runaway reaction by external cooling was already identified, particularly for small cells).

Ref 2: RECHARGE, Li-ion safety, July 2013, http://www.rechargebatteries.org/communication/recharge-positions/

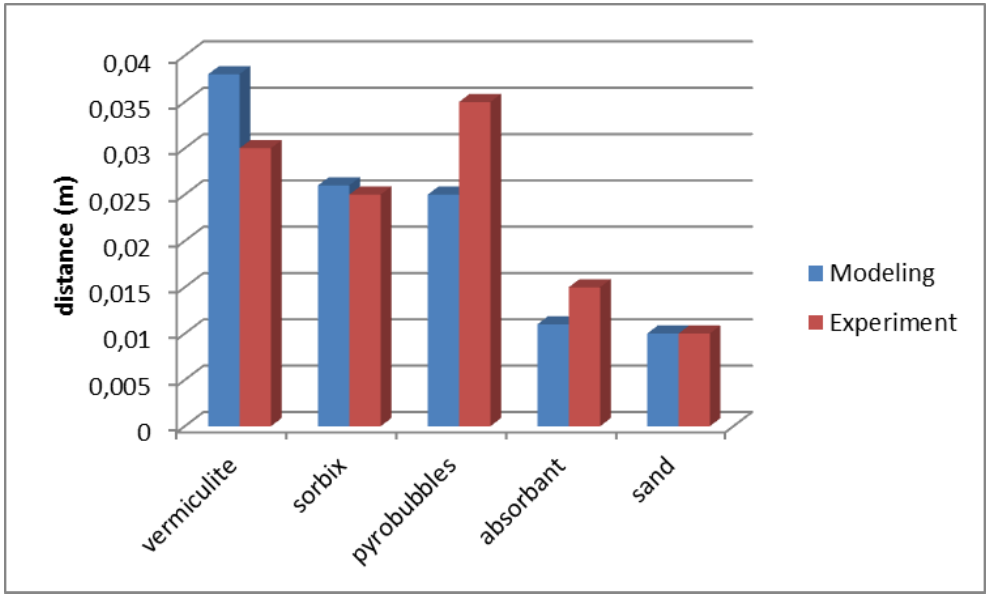
4- Cushioning calculation: Minimum Safe Distance (MSD)

- The « Minimum safe distance » MSD, is the thickness of the cushioning material layer allowing to stop the propagation to the next battery in case of one battery runaway
- It has been shown that Li-ion batteries do not release significant amounts of heat up to 100°C (ref 1). It is then considered that the distance where the cushioning material is heated at 100°C maximum is the MSD.

- ACCUREC has conducted experiments (ref 1) to measure this MSD with different cushioning materials.

- Results obtained with the model are quite comparable to the experiments, except for pyrobubbles: the test result is not in relation to the thermal properties measured in this case.

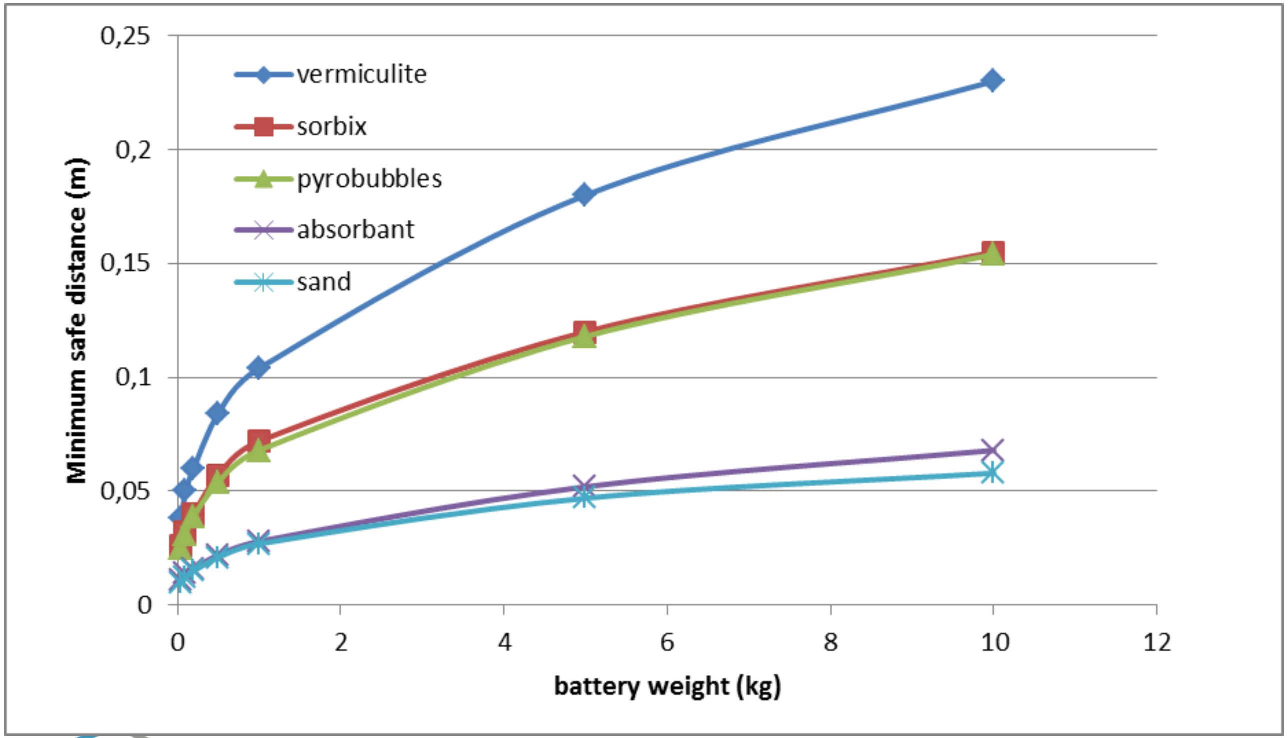
MSD for a Li-ion 18650 layer



4- cushioning calculation: MSD versus battery size

- Using the same model, the Minimum Safe Distance has been calculated according the battery size and weight.
- For this study, a maximum runaway energy has been used, whatever the cushioning material type, the type of li-ion chemistry or the battery size: 870 kJ/kg.

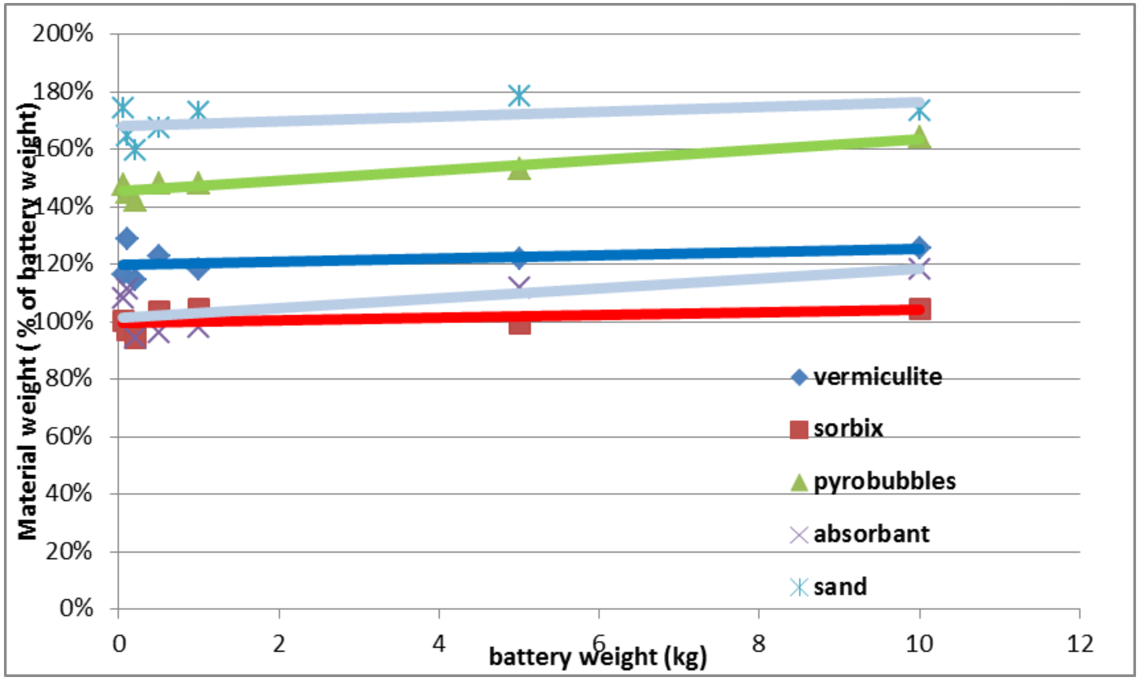
MSD according battery weight



Materials with high volumetric heat capacity requires less thickness for the MSD

4- Cushioning calculation: material weight vs battery weight

- The weight of a layer of MSD thickness, surrounding the battery has been calculated, and compared to the battery weight



- the % in weight of cushioning material is about constant over the batteries size range, for all cushioning materials.
- For this reason, an homogenous mix of batteries and cushioning material can be safe in case of one battery runaway, what ever the size of the battery, if the total ratio of cushioning material is respected

4- cushioning calculation: simple rules

- **Proposed quantities: based on the model MSD calculation, a simple geometrical calculation allows to propose the following quantities of cushioning material, respecting the MSD between batteries in an homogeneous mix of batteries and cushioning material:**

	vermiculite	sorbix	Pyrobub.	Absorbant	sand
weight ratio vs battery	0,4	0,4	0,6	0,2	1
volume ratio vs battery	10	5,5	5	1,7	1,6

- Many other materials are available. Some have specific properties (i.e. phase transition materials) and may not have the behavior described in this model.
- Decision on the best material can be made based on the product cost, the transport cost, or other constraints (max weight, max volume, process constraints, etc..).

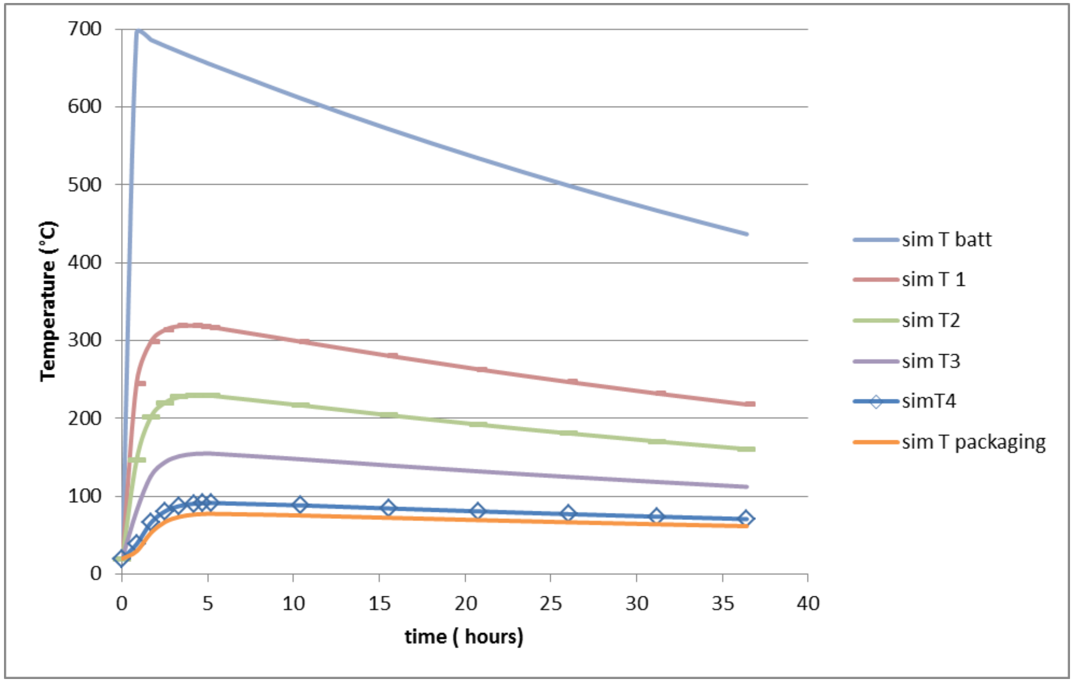
4- cushioning calculation: other cases

- **Case of Li metal battery:**
  - the model can calculate a minimum value: based on a typical runaway energy of 1300 kJ/kg, the required weight of cushioning material is about the double, compared to the Li-ion.

  - Nevertheles, this would require some test for validation, particularly for small cells, where the cooling effect of the cushioning material can reduce significantly the thermal runaway energy.

4- cushioning calculation: other cases

- **Case of large batteries in packaging with limited cushioning:**
  - boundaries conditions of the model adapted:the key parameter is the cooling efficiency of the packaging.
  - Example of a 100 kg battery surrounded by 7 cm vermiculite thickness in a metallic drum, in conditions allowing the natural convection cooling (i.e. single drum on a pallet).



  - the max. external temperature is 100°C, and decreases after 5h.

Conclusion

- the UN regulation on the transport of dangerous goods requires cushioning materials usage to protect for dangerous evolution of heat in case of battery runaway during transport.

- The thermal behavior of different cushioning has been modeled, and compared with the experimental results, showing an acceptable representation.

- It is shown that the key criteria to control the temperature increase in case of runaway of the battery is the % by weight of cushioning material versus the battery weight.

- Several ratios of cushioning materials versus battery are proposed as a result of this study.

- The amount of material is significant, involving some packaging costs. Nevertheless, a cost optimization is possible, based on the presented results.

Keep Li batteries transport safe !