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Lithium-ion batteries: safety issues

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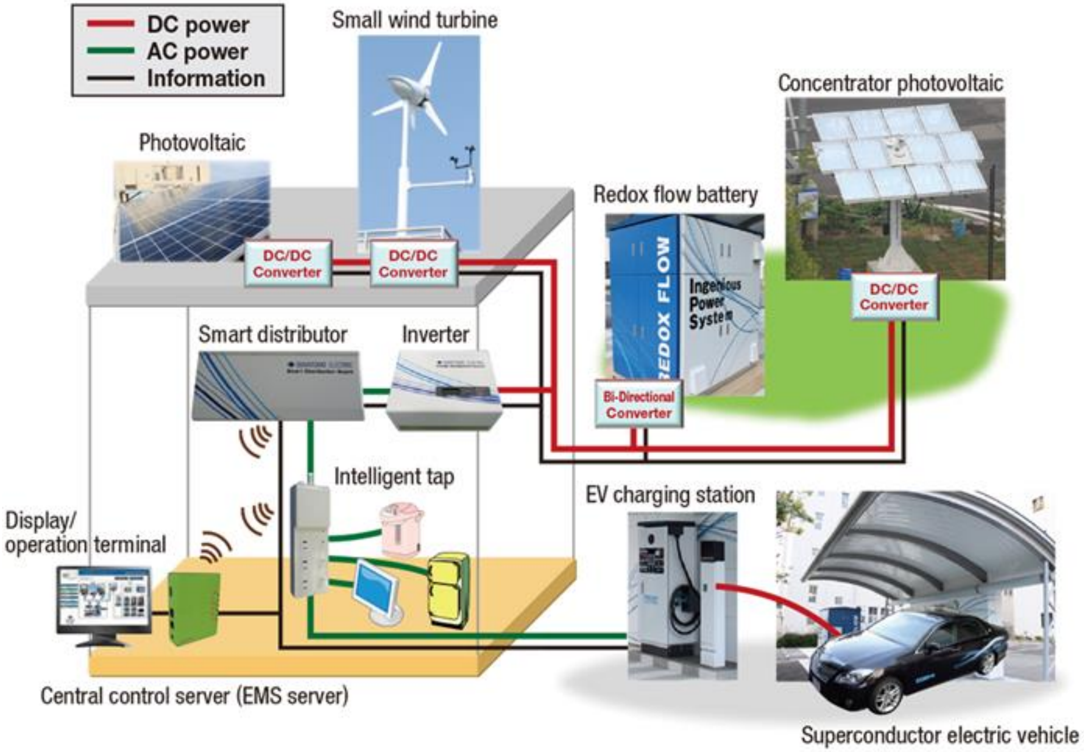
Summary

1. Introduction: cell types and safety problems
2. Cells characterization
3. Hazard Identification and accidents prevention
4. *Break ?*
5. Cooling systems evaluation
6. Extended modelling

Introduction



- Continuous effort to reduce the emissions of greenhouse gases and increase the amount of renewable energy sources
- There is a strong interest in the introduction of rechargeable energy storage systems in the main electric network (large stationary systems and off-grid solar PV power systems).

Introduction

Many industrial sectors, ranging from portable devices (laptops, cell phones, etc.) to automotive and power industry, strongly depend on the capability of storing <u>large quantities of energy at high density</u> (energy per unit mass or volume)

Electrochemical storage systems are one of the most attractive technologies:

- Secondary batteries are rechargeable
- Secondary batteries allow to solve the problem of intermittent availability of energy sources (e.g. wind energy);
- Secondary batteries allow to convert energy from renewable sources in a much wider range of application (e.g. automotive industry).

Introduction

Interest in low- or zero-emission vehicle:
Electric vehicle industry development

↓

Lithium-Ion batteries:
High specific power and specific energy density

↓

Ideally suited for high rate-of-discharge applications

Introduction

- **Lithium batteries** have in perspective the best technical characteristics compared to other electrochemical storage systems
  - rechargeable
  - high energy density (up to 230 Wh/kg),
  - high power density (up to 500 W/kg),
  - long cycle life (more than 1000 cycles)
  - lack of memory effect
  - low self-discharge rate

Lithium-ion batteries

Different Shapes of the cell

Pouch

Cylindrical

Prismatic

Different Cathode materials

- Cobalt Oxide (LCO)
- Nickel Cobalt Aluminum Oxide (NCA)
- Nickel Cobalt Manganese Oxide (NMC)
- Manganese Oxide (Spinel)
- Iron Phosphate (LFP)

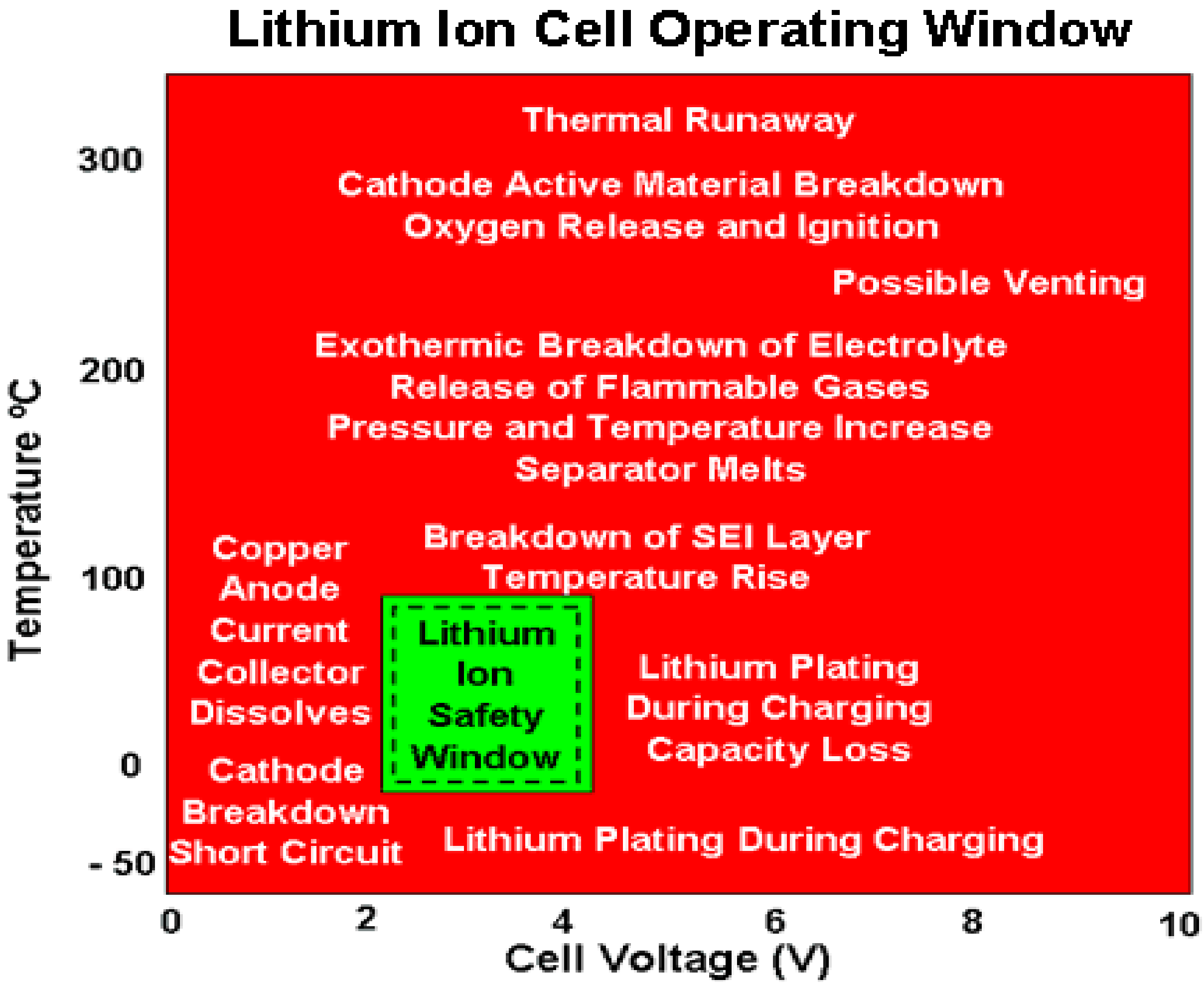
Introduction

PROBLEMS

•Efficiency and safety markedly depend on the temperature: Lithium secondary cells need careful temperature control.

•**High temperatures** can trigger a series of reactions causing:

- performance reduction
- permanent damage
- a complete failure or
- explosion of the cell

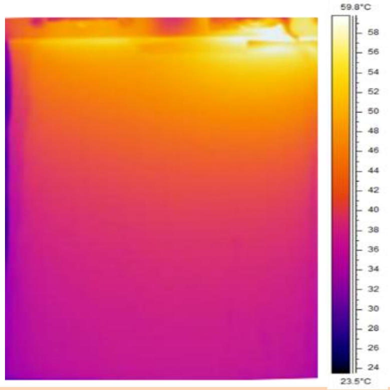


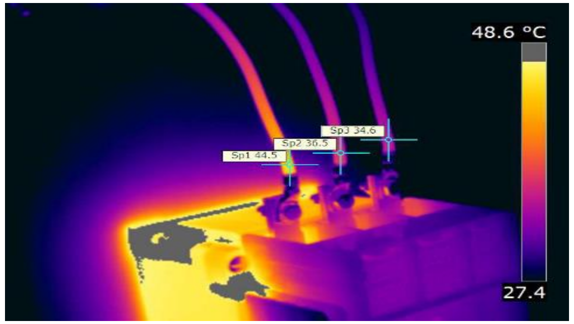
Introduction

Heat is a major battery killer for Li-ion cells

For optimal performance of a battery pack, the ***working temperature*** of the cells in the pack should be kept within a proper range (ideally 20 - 40 °C), and the ***temperature distribution*** in the cells should be as uniform as possible

Localized deterioration





Reduction of cycle life of cell, module, and pack

Thermal Runaway consequences

Cell

Module

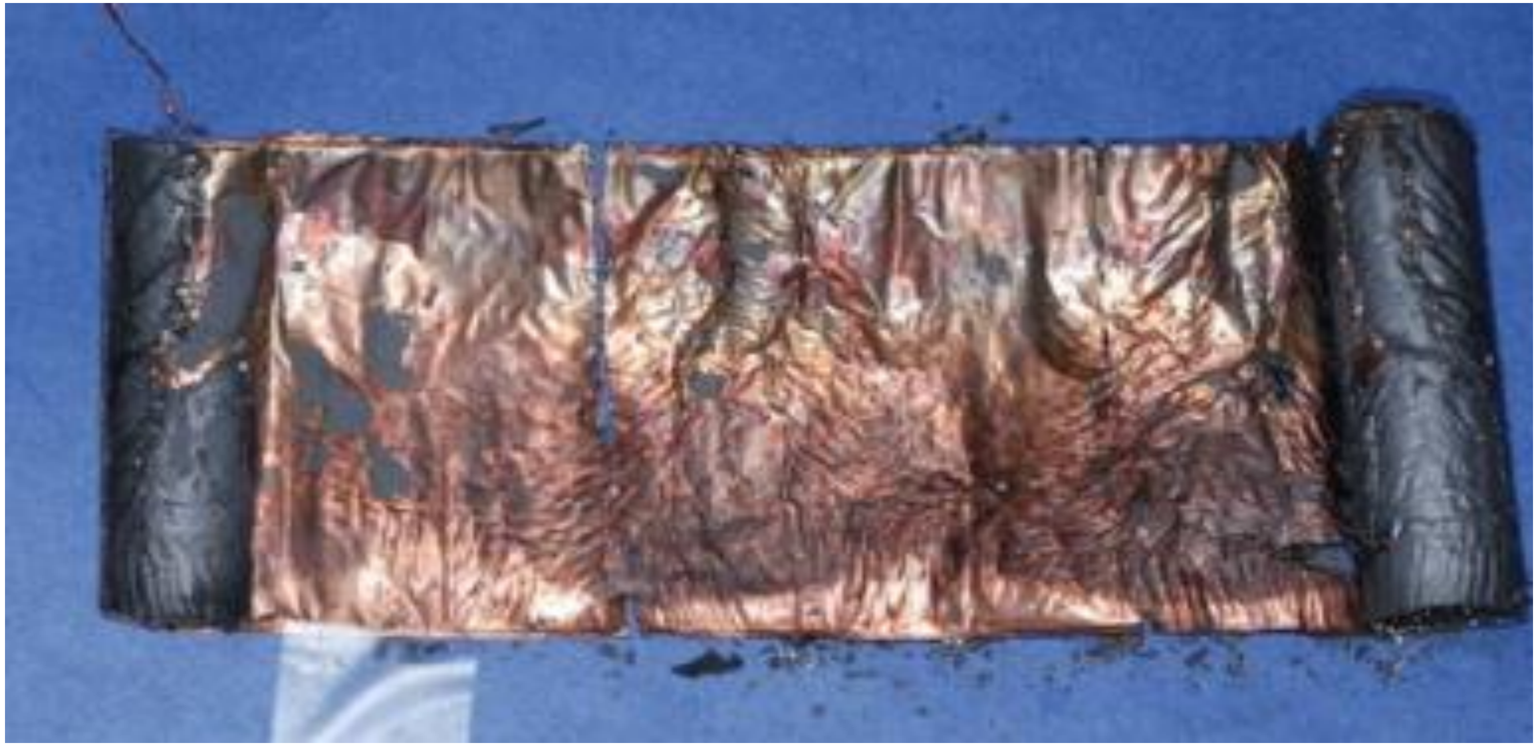
Computer

Electric Vehicle

Smart Phone

A number of past accidents have raised concern about Li-ion batteries reliability and safety

Thermal Runaway consequences

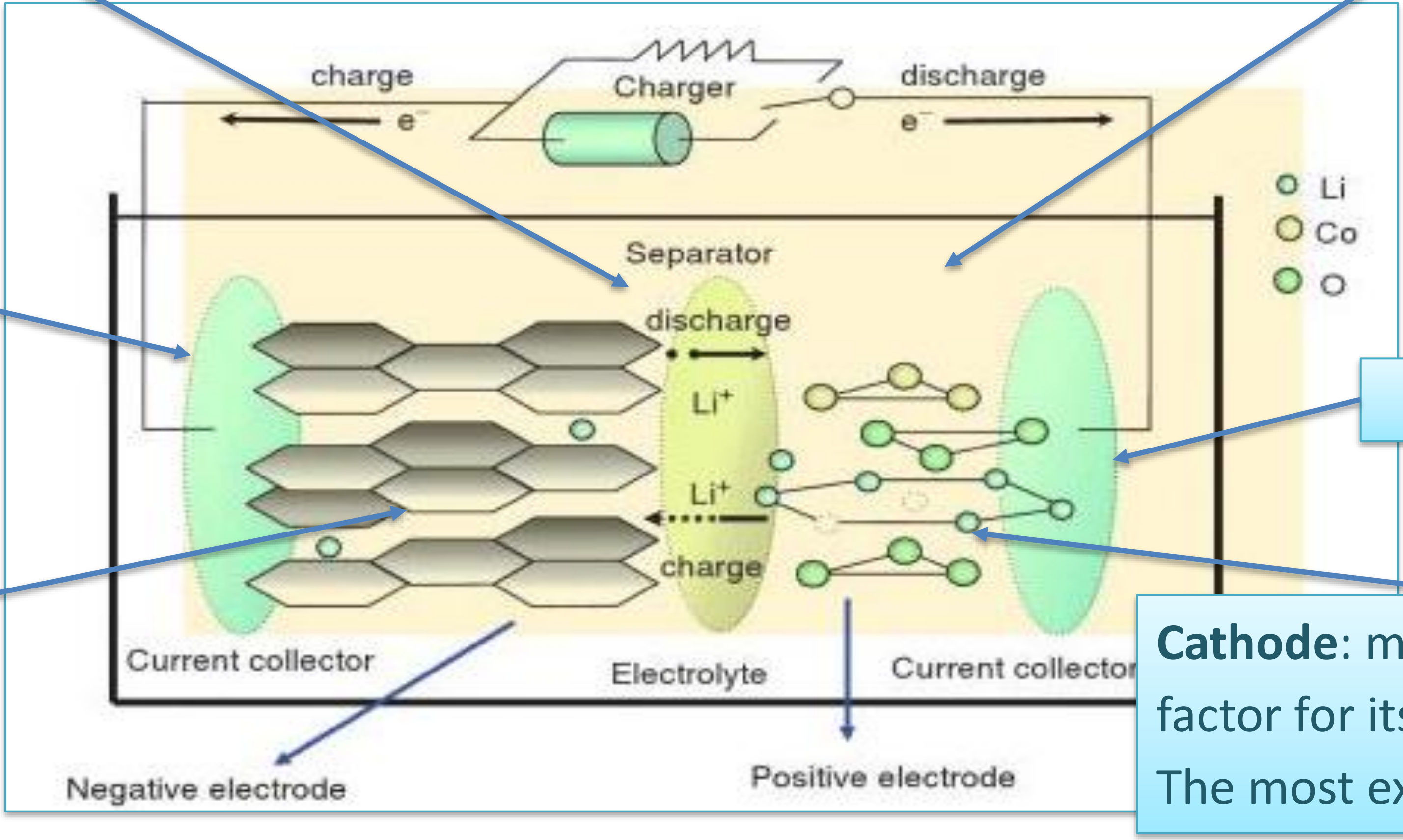


A Lithium ion battery after a thermal runaway:
The aluminium current collector is melted and the separator is consumed; only the copper current collector and a black friable material, mainly composed of cathodic material, still remain

Thermal Runaway consequences

Year	**Accident**	**Cause**
2006	Explosion in a laptop PC	Cell internal short-circuit
2006	Explosion in a cellular telephone	Cell internal short-circuit
2007	Explosion in a laptop PC	Cell internal short-circuit
2008	Fire on a hybrid electric vehicle (HEV)	Battery overheating (cathode)
2008	Fire in a laptop	Battery overheating
2009	Fire on a civil transportation flight	Battery fire
2010	Two electric buses fire (EV)	Battery overheating (cathode)
2010	Fire on a Boeing B747-400F	Battery overheating
2011	Fire on a electric vehicle (taxi)	Overcharge
2011	Fire on an electric vehicle (bus)	Battery overheating (cathode)
2012	Fire on an electric vehicle (taxi)	Cell internal short-circuit
2013	Fire on a Boeing 787 Dreamliner aircraft	Battery overheating
2013	Fire on a hybrid electric vehicle (HEV)	Mechanical impact of the battery with a metal object
2015	Fire in a bag containing a *quadcopter* drone connected to a Li-ion battery	Thermal runaway
2015	Electronic cigarette (E-cig) fire	Battery overheating
2015	Mobile phone fire	Battery overheating

Main components of a Li-ion cell



Separators: porous polyethylene, polypropylene, or composite polyethylene / polypropylene films.

Electrolyte: organic solvent and dissolved lithium salt

Copper

Aluminum

Anode: based on carbon (primarily graphite) and the oxide spinel $Li_4Ti_5O_{12}$

Cathode: metal oxide, limiting factor for its reduced capacity. The most expensive part.

Thermal Runaway sequence

Unless heat is removed faster than it is generated, a ***Thermal Runaway*** may occur

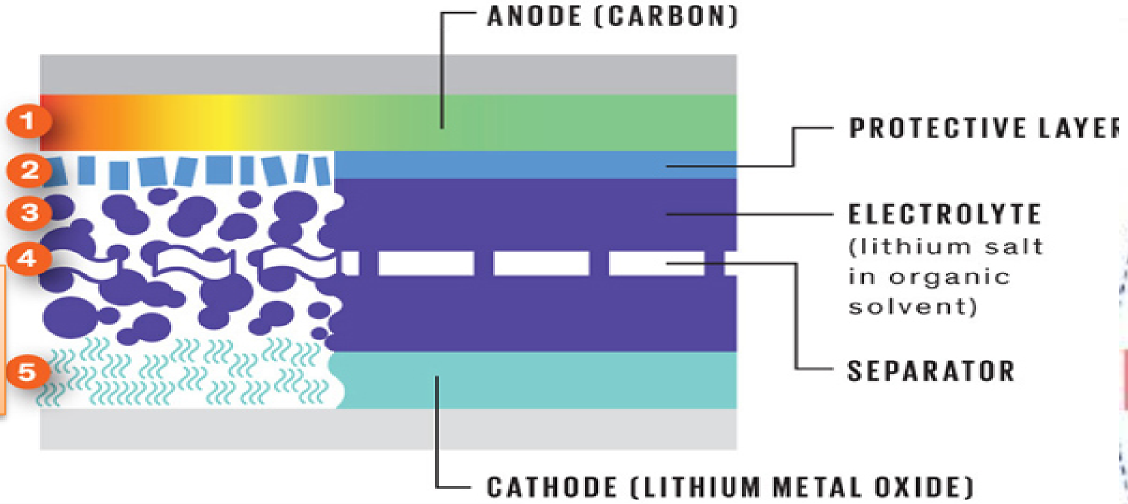
1. Heating starts

2. Protective layer breaks down (80°C)

3. Electrolyte breaks down into flammable gases (110°C)

4. Separator melts, possibly causing a short circuit (135°C)

5. Cathode breaks down, generating oxygen (200°C)



Fire or explosion

Introduction

Safety concerns because of the use of energy materials

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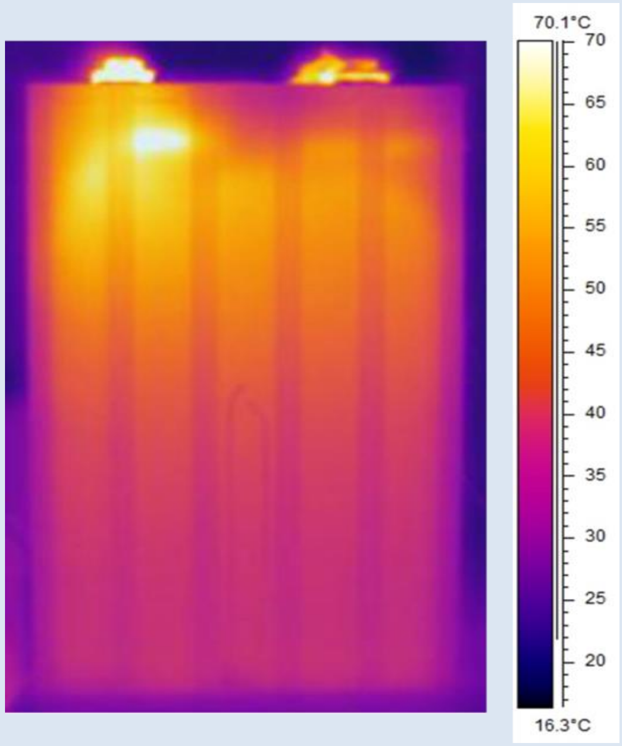
EXPERIMENTAL THERMAL ANALYSIS OF LITHIUM-ION BATTERIES



Introduction

A number of papers in the literature report numerical analyses of the battery thermal behavior

- in most of the cases they are purely theoretical or numerical models, with no experimental validation
- in other cases they provide conflicting results

Only few papers report *experimental* and *quantitative* investigations of real systems under various operating conditions

More detailed information are needed to assess

- the conditions requiring adequate attention
- the extent of the phenomenon

Experimental campaign

Different **chemistries** for the same geometry

Lithium Iron Phosphate (LFP): inexpensive, non-toxic, long life cycle, resistant to high temperatures

Lithium Nickel Manganese Cobalt Oxide (NMC):
- good stability with cycling
- high reversible capacity
- milder thermal stability at charged state

Cathode Chemistry	Capacity (Ah)	Geometry	No. of cells
LFP	100	Prismatic	1
	20	Pouch	1
	40	Prismatic	1
	4.5/4.3	Cylindrical	1
NMC	20	Pouch (different samples)	3

Different **geometries** for the same chemistry

Cylindrical

Prismatic

Pouch

Experimental Procedure

Cycler Eltra E-8094
Voltage 3.6 ÷ 6V
Current 0÷280A

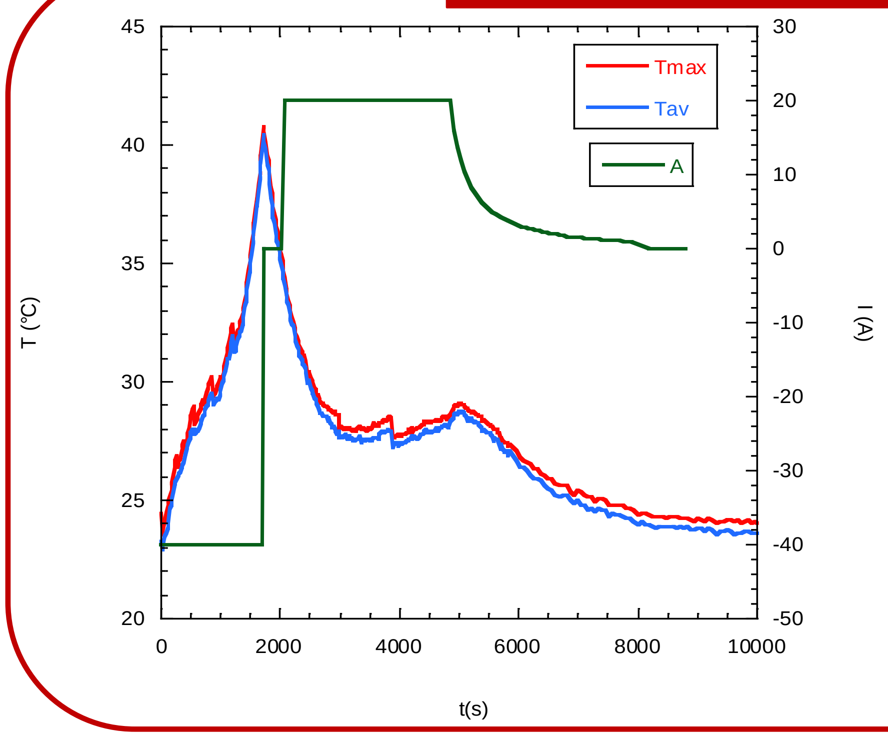
Charge and discharge cycles are performed on each cell, monitoring temperatures with an infrared camera.

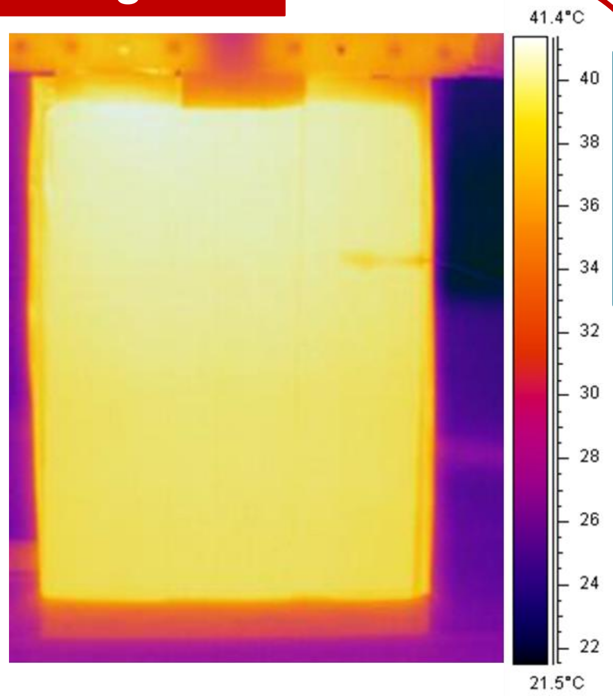
Portable cycler Eltra E-8325
Voltage: 0 ÷ 18V
Current: Charge 80Amax
Discharge 150Amax

Thermographic camera:
to measure the emitted infrared radiation

LFP Pouch-type

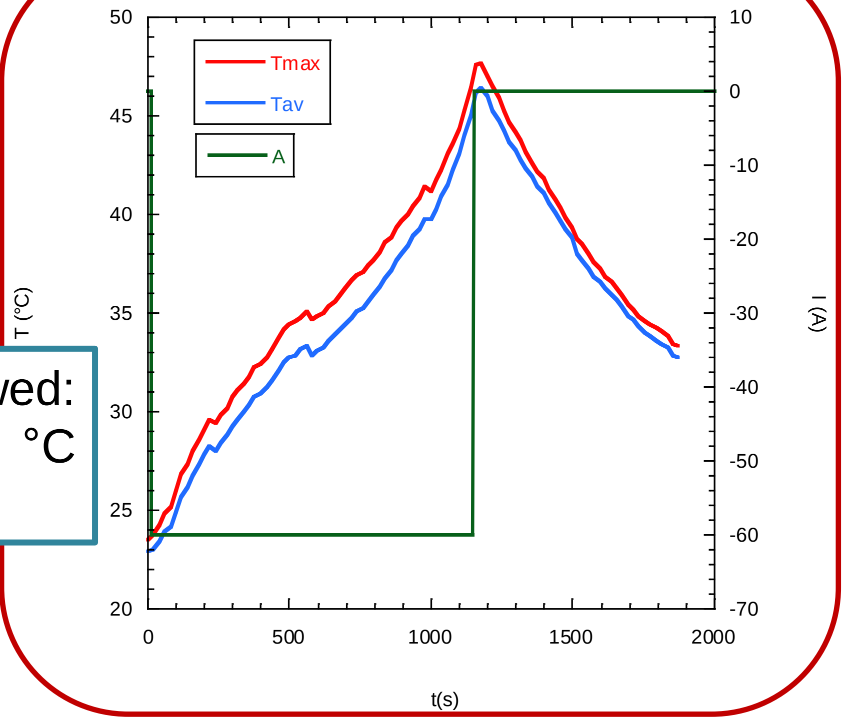
Discharge: 2C and Charge: 1C





- T_{max} at the end of the discharge: 41 °C, well within the safe range (65 °C)
- almost coincident T_{max} and T_{av}: uniform temperature distribution and no hot spots

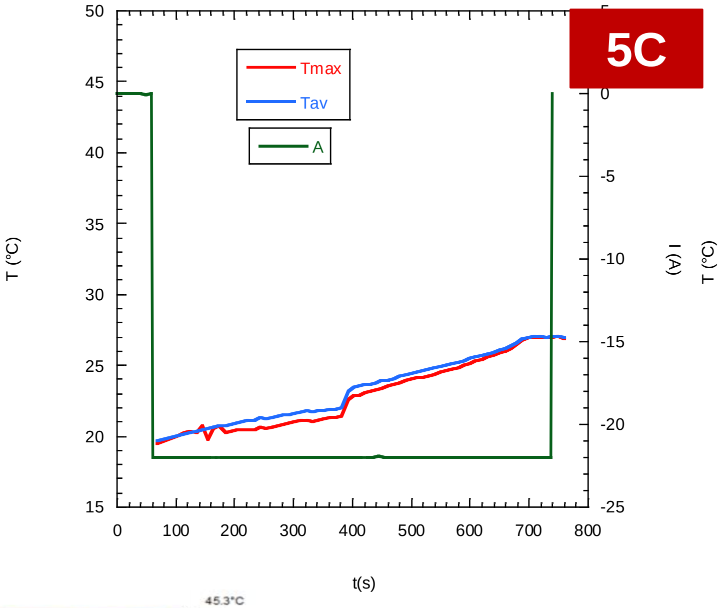
Discharge: 3C

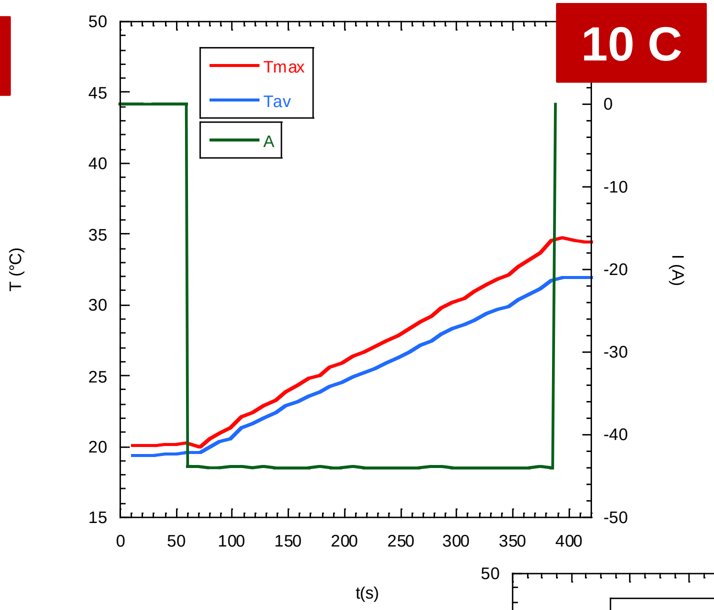


At a rate 50% higher than the maximum allowed: T_{max} reaches a maximum of approximately 48 °C at the end of the discharge.

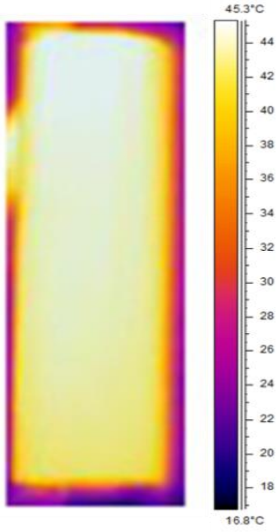
The cell remains well within the safety limits provided. The temperature is uniform over the entire surface of the cell and no hot spots were generated

LFP, Cylindrical-type

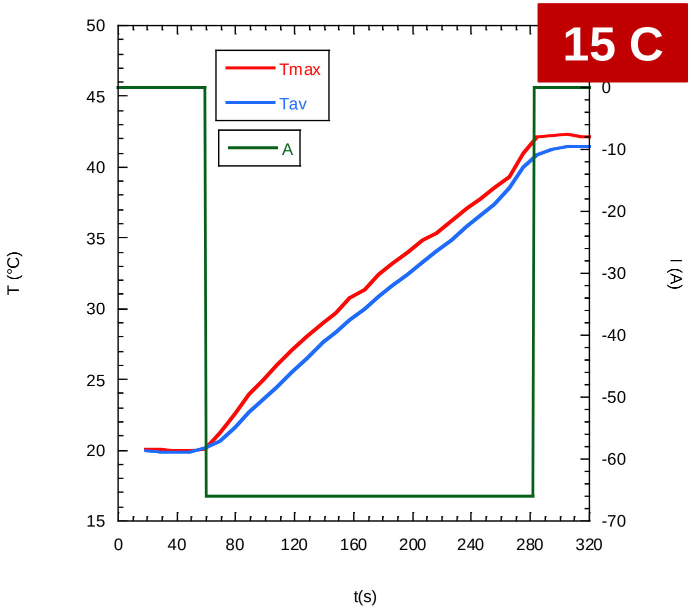


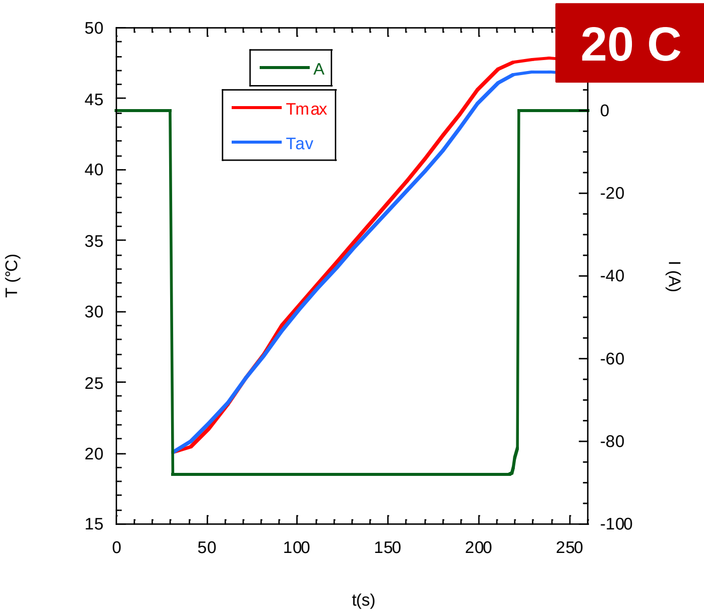


Very good performance: T_{max} at the end of the discharge phase (27, 35, 42 and 48 °C, for the four conditions tested) was always below 55 °C (maximum allowed)



- Usually, max discharge rate = 3÷5 C
- T_{max} and T_{av} are almost coincident over the whole test interval



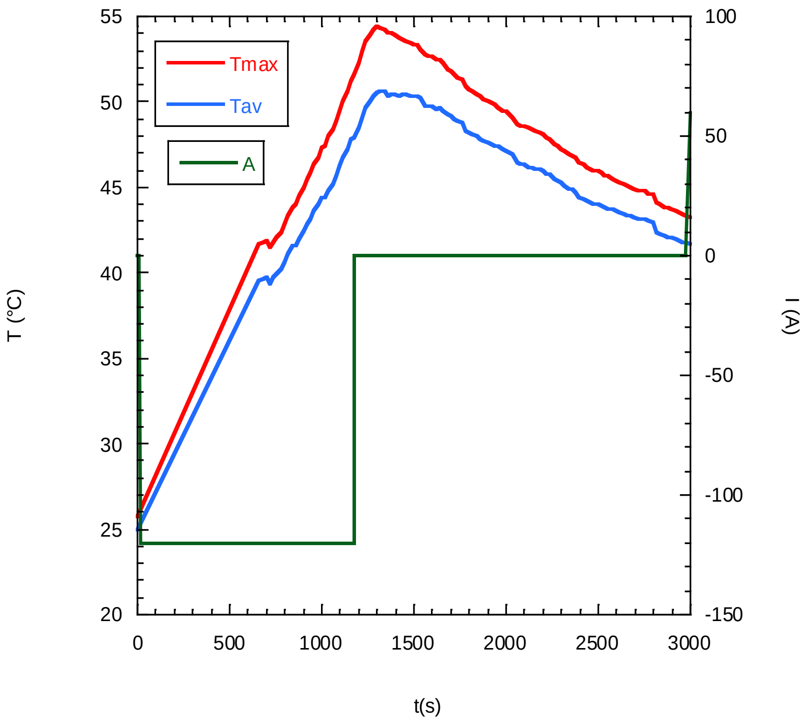


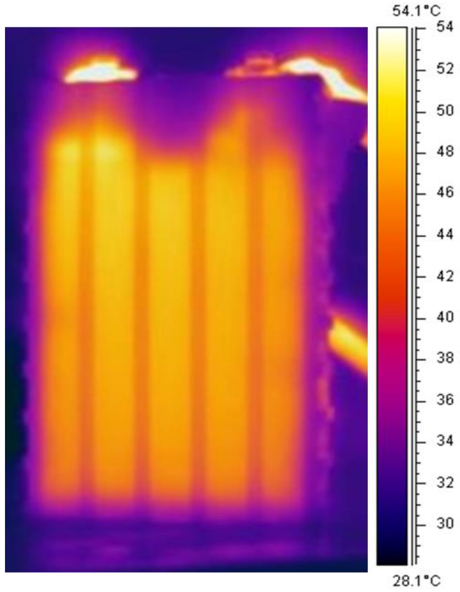
LFP Prismatic type

The cells were tested with the maximum continuous discharge rates indicated by the manufacturer

Winston Battery: 40 Ah

Discharge: 3C





- When operated at the worst conditions allowed, **the cell is capable of remaining below the maximum operating temperature (85 °C)**.
- A slight difference in the average and maximum temperature profiles, indicates some non-homogeneous distribution of the temperature on the cell surface.

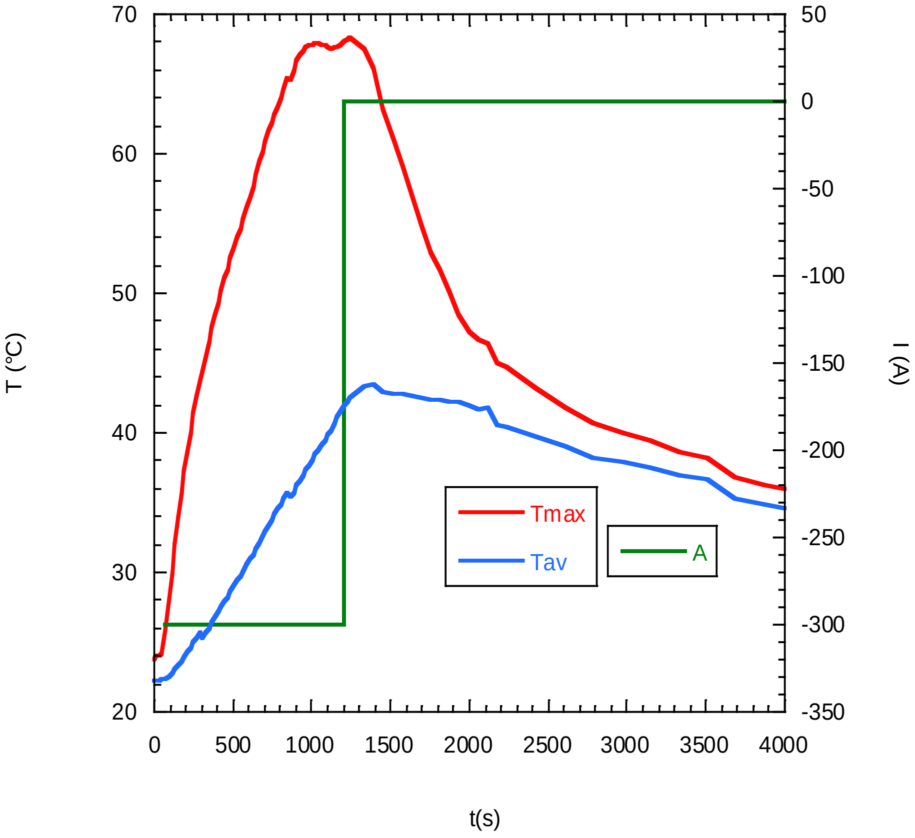
LFP Prismatic type

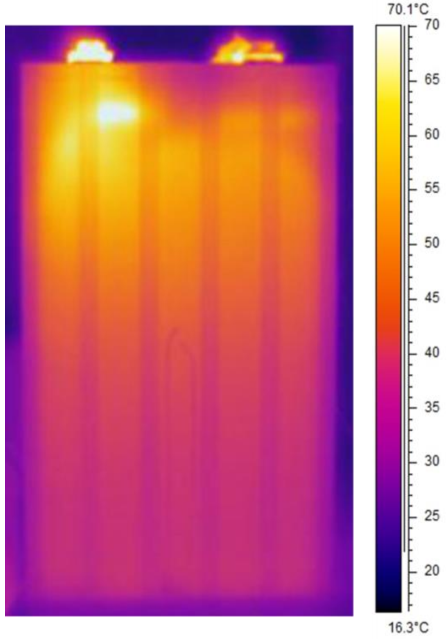
The cells were tested with the maximum continuous discharge rates indicated by the manufacturer

HiPower: 100 Ah

Discharge: 3C

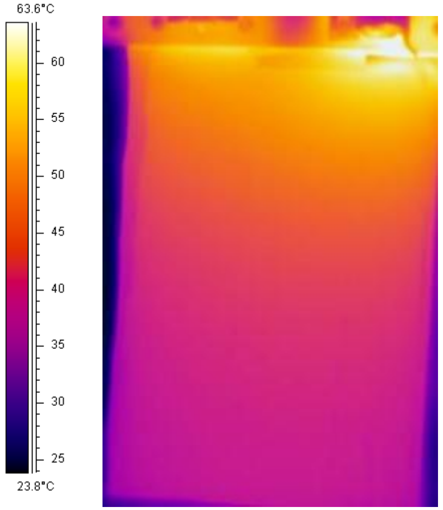
- This battery has proved to be **critical from the thermal safety point of view**, when used under conditions close to the extremes identified by the manufacturer (T_{max} < 65 °C)
- A remarkable difference is present between the anode area and the rest of the cell surface: about 25 °C at the end of the discharge (too high T_{max})
- *This cell had been previously stored away for a long time*

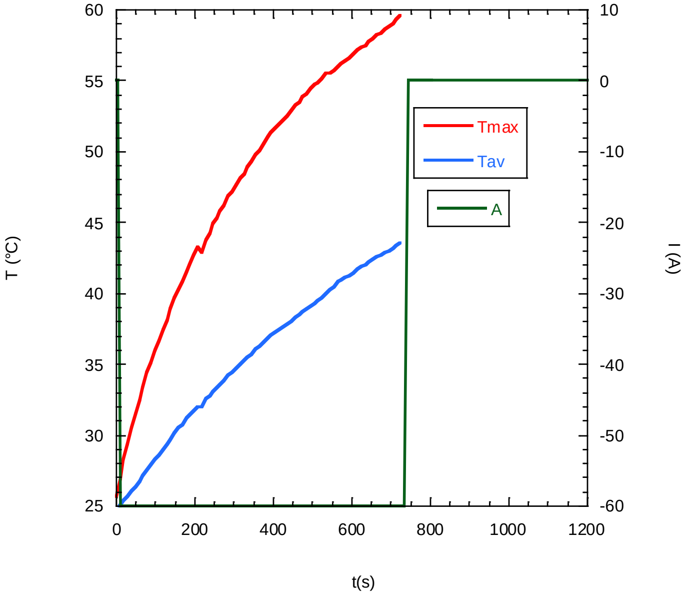




NMC, Pouch-type

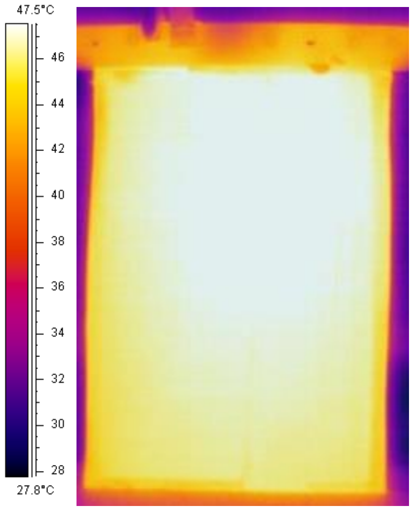
OLD CELL

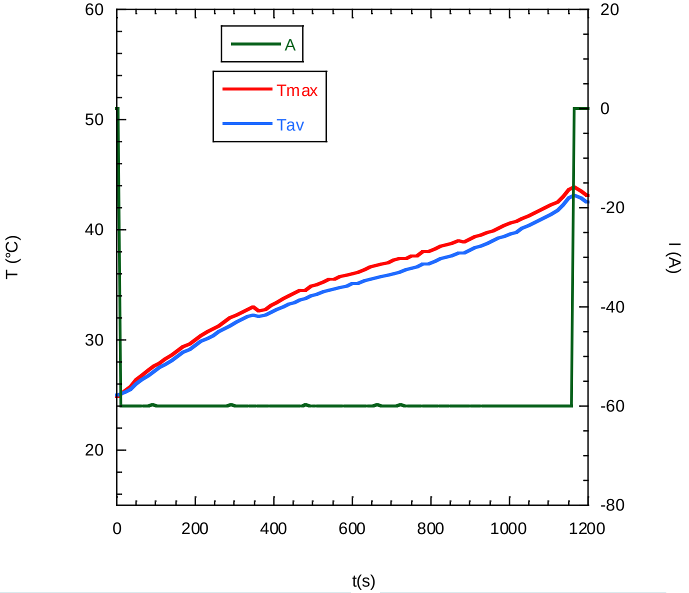




Hot point located at the cathode

NEW CELL





Uniform temperature distribution on the surface
A smaller than allowed discharge current was used

Significant **difference in the thermal behavior of new and old cells.** Aging seems to play a significant role: at the same discharge/charge conditions, both temperature increase and local heat generation, are much larger for old cells

Conclusions

NEW CELLS

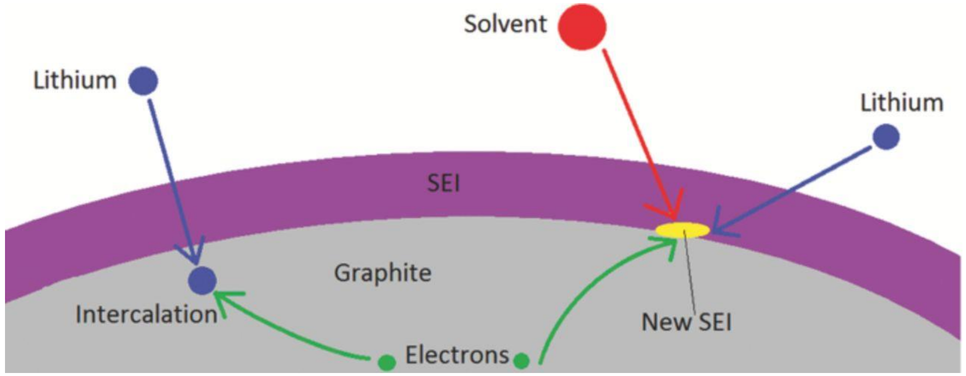
Different chemistries:

- **LFP cells do not** reach temperatures that **exceed** the safety limits; in some cases (pouch type) the cells proved to withstand even discharge/charge conditions more severe than those allowed by the manufacturer;
- **NMC cells**, tested at the maximum discharge and charge rates, **always** reached temperatures that **exceeded** the safety range.

In terms of **surface temperature distribution** for both chemistries a quite uniform temperature distribution was observed, with temperature peaks of less than 3÷4 °C higher than T_{av}. **This result was independent of the shape (pouch, cylindrical or prismatic) and the size of the battery.**

OLD CELLS

- Ageing, either during use (i.e., on cycling) <u>and on storage</u>, is the main responsible for the generation of hot spots
- Side reactions occur between electrolyte and electrodes, (though with different mechanisms at anodes and cathodes)
- The solid electrolyte interphase (SEI) thickness is a function of operating cycles. It initially protects the electrodes against solvent decomposition
- SEI thickening on the anode leads to a gradual capacity fade and increased internal resistivity (higher resistance to Lithium ions flow)
- Increased internal resistivity causes the increase of the battery temperature



Conclusions

A proper characterization of the thermal stability of Li-ion cells under different working conditions allows:

- to predict the cycle life of the batteries,
- to devise a proper thermal management system and avoid thermal runaway

LFP batteries:

- new LFP batteries were more reliable than NMC cells, with a very limited temperature increase, even under large loads, and independently from the geometrical configuration
- ageing can give rise to local overheating

NMC cells:

- new NMC cells always exceeded the temperature limits, even when used under conditions still within the nominal safety range; limited local overheating was observed
- ageing gives rise to strong local overheating

PREDICTING AND PREVENTING ACCIDENTS: TECHNIQUES FOR HAZARD IDENTIFICATION (HazId) AND HAZARD EVALUATION (HEP)

Hazard identification (HazId)

- Setting up a methodology to identify and prevent (as much as possible) the possible accident scenarios
- Hazard evaluation techniques available from Risk Analysis
- Accident scenarios depend either on the battery itself and on the surrounding environment

Hazard identification (HazId)

Different techniques available:

- Safety Reviews
- Checklist Analysis
- Relative Ranking
- Preliminary Hazard Analysis (PHA)
- What-If Analysis
- What-If/Checklist Analysis
- Hazard and Operability Analysis (HAZOP)
- ***Failure Modes and Effects Analysis (FMEA)***
- Event Tree Analysis
- Fault Tree Analysis
- Cause-Consequence Analysis
- Human Reliability Analysis
- *Others*

Selection of HazId techniques

- “Selecting an appropriate HE technique is more an art than a science”
- There may be no “best” method for a given application
- Each HE technique has its strengths and weaknesses

Selection of HE techniques

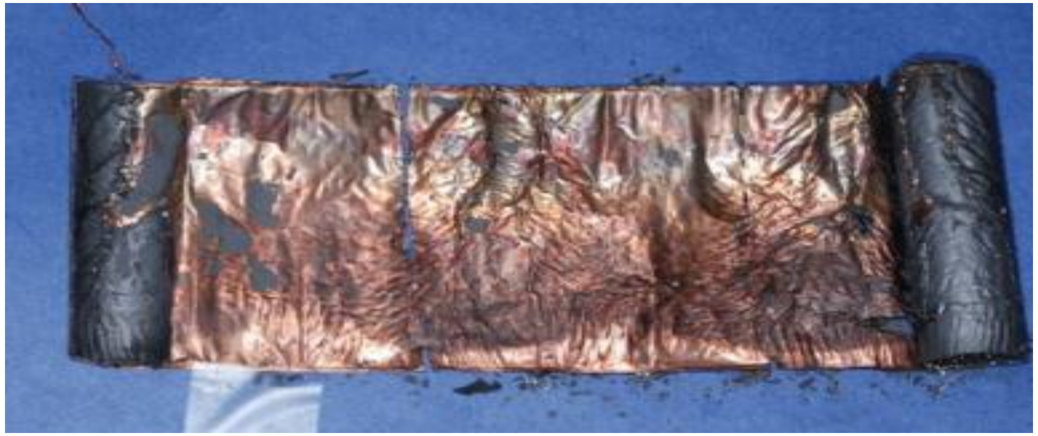
Many factors to consider (CCPS, 2008):

1. Motivation for the study
2. Type of results needed
3. Type of information available
4. Characteristics of the analysis problem
5. Perceived risk associated with the process/ activity
6. Resource availability and analyst/management preference

FMEA FOR LI-ION BATTERY SYSTEMS

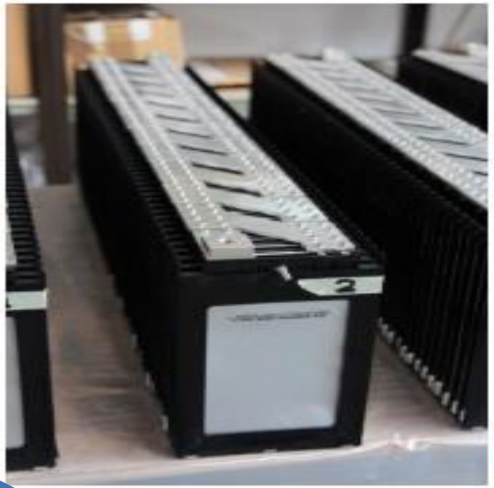
Typical failure modes

- **Electrical abuse**
  - Internal short-circuit
  - Overcharge
  - Excessive currents
  - Over-discharge
- **Thermal abuse**
  - High temperature
  - Low temperature
- **Mechanical abuse**
- **Internal defects**
- **Ageing**



System multiple levels

CELL:
- Anode
- Cathode
- Electrolite
- Separator
- Current collectors

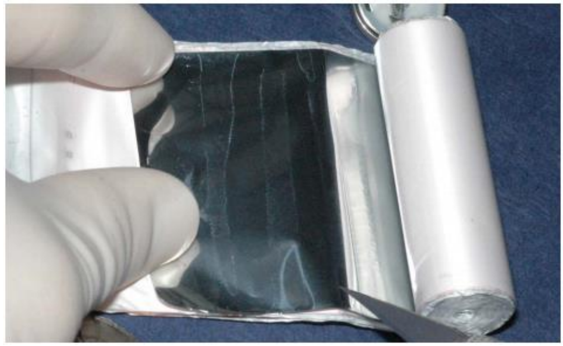


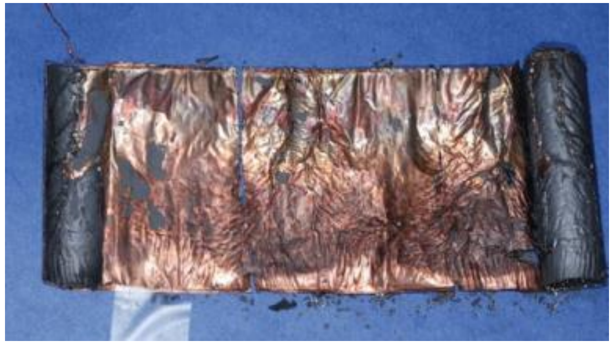
MODULE:
- Cells
- Cables
- BMS

PACK

Structure of a FMEA

Element	Failure Mode	Failure Cause	Consequences	Effects	Risk Mitigation Measures





FMEA of Lithium-ion batteries

FMEA application to a single Li-ion cell

Failure Mode	**Failure Cause**	**Consequences**	**Suggested actions**	**P**	**M**	**R**
Lithium plating and dendrites growth on anode surface	Charging the cell at high rates or high currents or low temperatures (below 25°C)	• Increase of the internal impedance of the cell and consumption of cyclable lithium • Dendrites can puncture the separator and finally cause an internal short-circuit of the cell, often the reason for a thermal runaway				
Thickening of solid electrolyte interphase layer (SEI)	Chemical side reactions between lithium, electrode and solvent	Increase in charge transfer resistance, reduction of capacity and power				
Decomposition of SEI	High internal cell temperature (> 60°C)	Gas release and thermal runaway				

FMEA of Lithium-ion batteries

Two different columns have been included in the table:

- the *"Effects"* column lists all the possible immediate and direct physical phenomena which can follow each failure mode;
- the *"Consequences"* column describes all the possible final consequences (which in some cases may be *delayed* consequences) of each of the immediate outcomes on a number of sensitive targets

FMEA of Lithium-ion batteries

FMEA application to a single Li-ion cell

Element	**Failure Mode**	**Failure Cause**	**Effects**	**Consequences**	**Risk reduction measures**
Anode (Active Material)	Lithium plating and dendrites growth on anode surface	Charging the cell at high rates or high currents or low temperatures (typically below 25°C) Over-Voltage operations	Increase of the internal impedance of the cell and consumption of cyclable lithium Dendrites can puncture the separator and finally cause an internal short-circuit of the cell, with chemicals release often leading to a thermal runaway Swelling of the cell	<u>Cell</u>: reduction in life span <u>Thermal runaway</u>: • Cell: fire or explosion • People: burns • Equipment: fire propagation <u>Chemicals release</u>: • People: toxic exposure and/or asphyxiation • Equipment: corrosion • Environment: pollution	Control the rate of charge Implement a heating system Control the cell temperature (e.g. using a BMS) and if too low activate the heating system Implement a thermal barrier against thermal runaway

Comprehensive methodology

- Items in the “Actions” column can also appear in the “Failure mode” one
- The role of the surrounding environment is crucial and markedly influences the FMEA tables

⬇

- Different analyses required for each level and for each phase

FMEA of Lithium-ion batteries

FMEA application to a Li-ion cells module

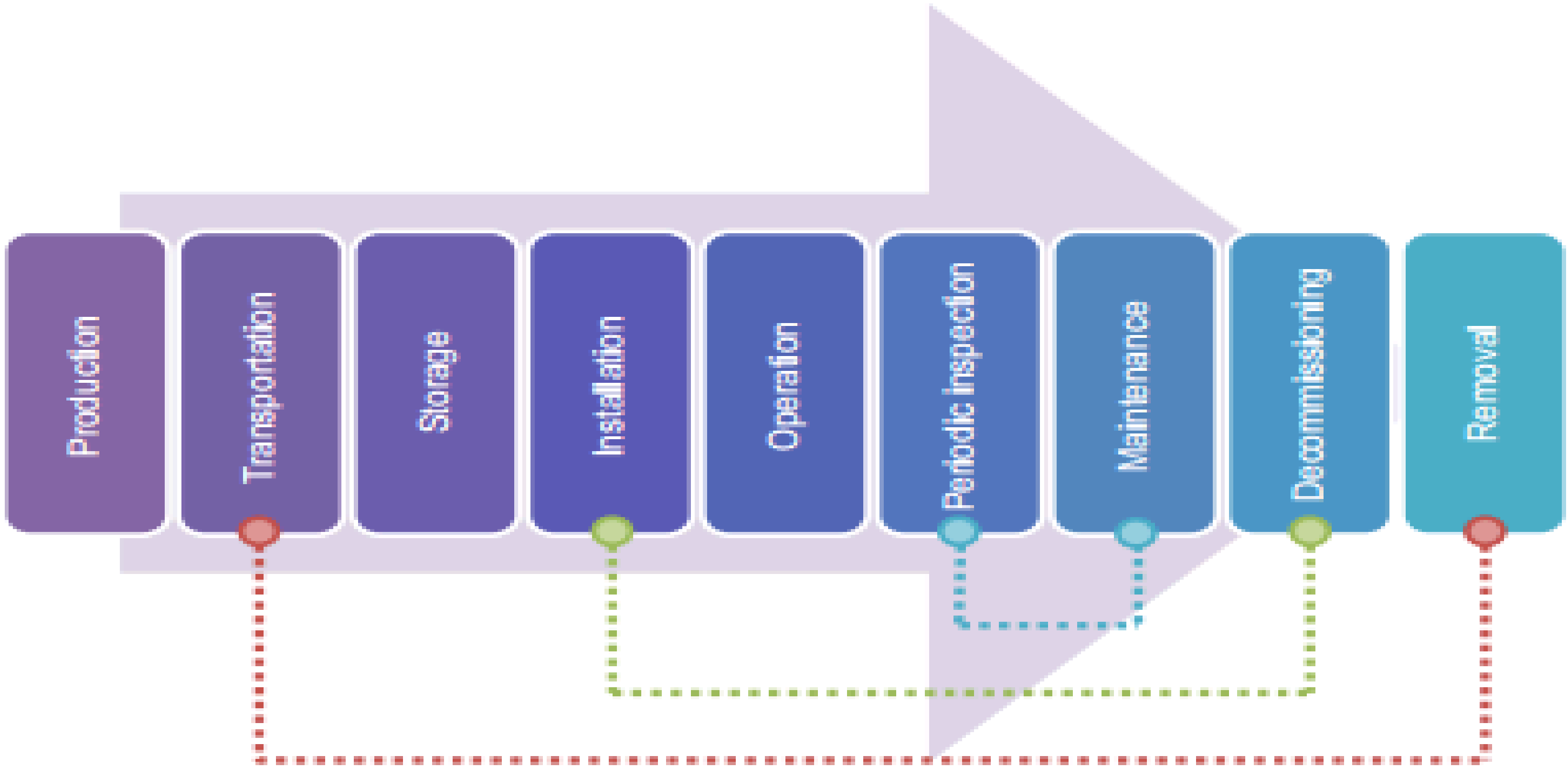
Element	**Failure Mode**	**Failure Cause**	**Effects**	**Consequences**	**Risk reduction measures**
Cell	High temperature	High ambient temperature Internal reactions Improper installation/connection of the cell Overcharge of a cell and BMS failure (typically > 4.15 V)	Electrolyte leakage or other hazardous chemicals release Thermal runaway (cell and module fire)	Hazardous chemicals release: People: toxic exposure and/or asphyxiation Equipment: corrosion and additional releases Environment: pollution Fire: People: burns Equipment: fire propagation	---------- →-> ->

FMEA of Lithium-ion batteries

FMEA application to a Li-ion cells module

Risk reduction measures
The battery installation area should have a restricted access
Operators must be qualified and wear personal protective equipment (PPE)
Use electronic boards specifically designed to avoid corrosion
Use electronic boards specifically designed to avoid corrosion and fire propagation
Protect each module metallic part against corrosion
Verify if each connection is correct during assembling phases of cells
Control ambient temperature
BMS must shut off the current and disable fans in order to avoid fire propagation
Implement a thermal barrier against thermal runaway propagation between cells inside the module
Implement a thermal barrier to avoid fire propagation outside the module
Implement an alarm for cell voltage. In case of BMS failure the operator must shut off the current once the alarm is on

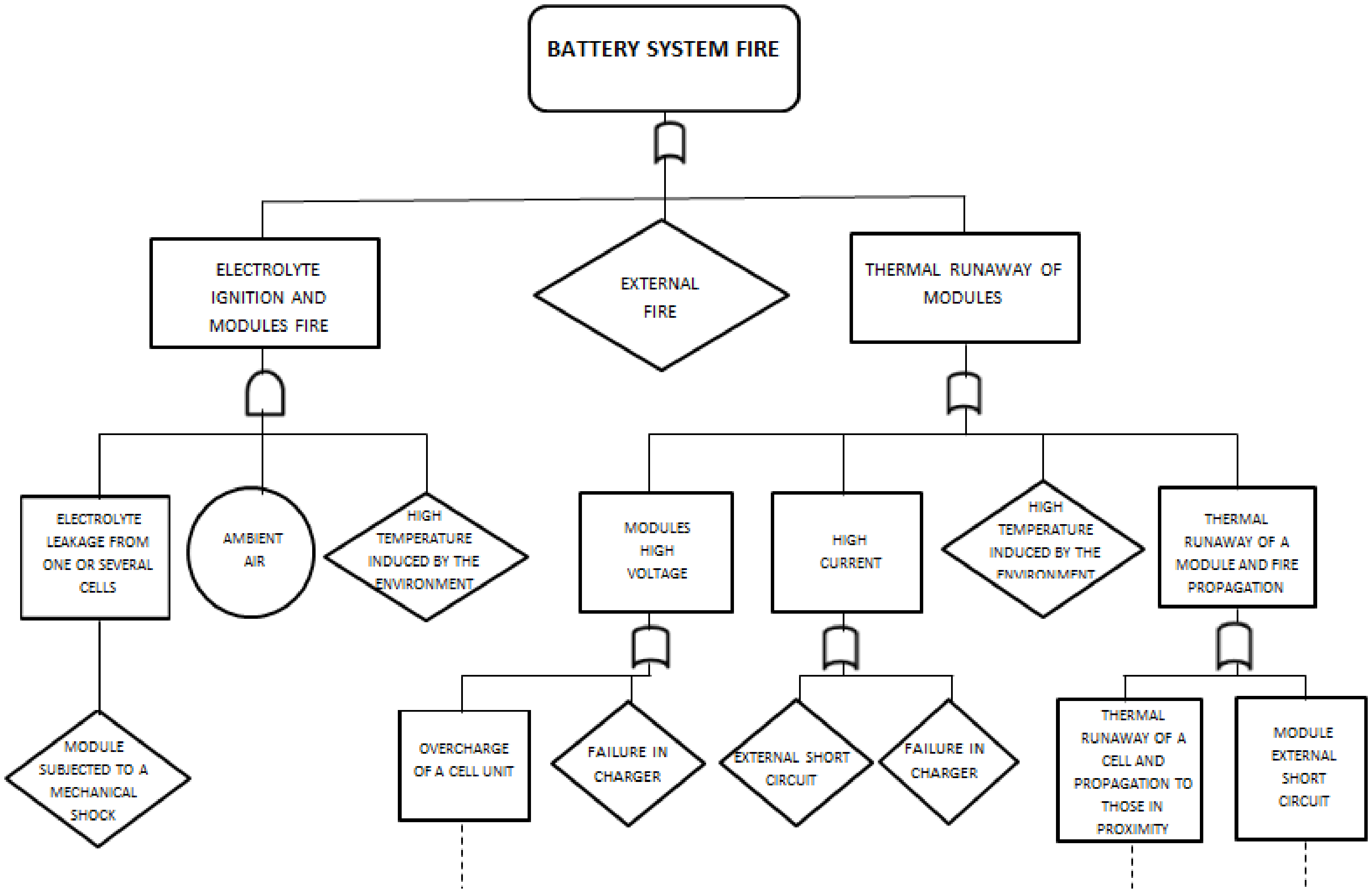
Multiple phases



STABALID project*

*F.J. Soares, L. Carvalho, I.C. Costa, J.P. Iria, J.-M. Bodet, G. Jacinto, A. Lecocq, J. Roessner, B.Caillard, O.Salvi, “The STABALID project :Risk analysis of stationary Li-ion batteries for power system applications”, Reliability Engineering and System Safety, 140 (2015), pp. 142–175

Fault Tree Analysis



- BATTERY SYSTEM FIRE
  - ELECTROLYTE IGNITION AND MODULES FIRE
    - ELECTROLYTE LEAKAGE FROM ONE OR SEVERAL CELLS
      - MODULE SUBJECTED TO A MECHANICAL SHOCK
    - AMBIENT AIR
    - HIGH TEMPERATURE INDUCED BY THE ENVIRONMENT
  - EXTERNAL FIRE
  - THERMAL RUNAWAY OF MODULES
    - MODULES HIGH VOLTAGE
      - OVERCHARGE OF A CELL UNIT
      - FAILURE IN CHARGER
    - HIGH CURRENT
      - EXTERNAL SHORT CIRCUIT
      - FAILURE IN CHARGER
    - HIGH TEMPERATURE INDUCED BY THE ENVIRONMENT
    - THERMAL RUNAWAY OF A MODULE AND FIRE PROPAGATION
      - THERMAL RUNAWAY OF A CELL AND PROPAGATION TO THOSE IN PROXIMITY
      - MODULE EXTERNAL SHORT CIRCUIT

Integrated analysis

FMEA

+ Check-list Analysis

to include every phase of the battery cycle life

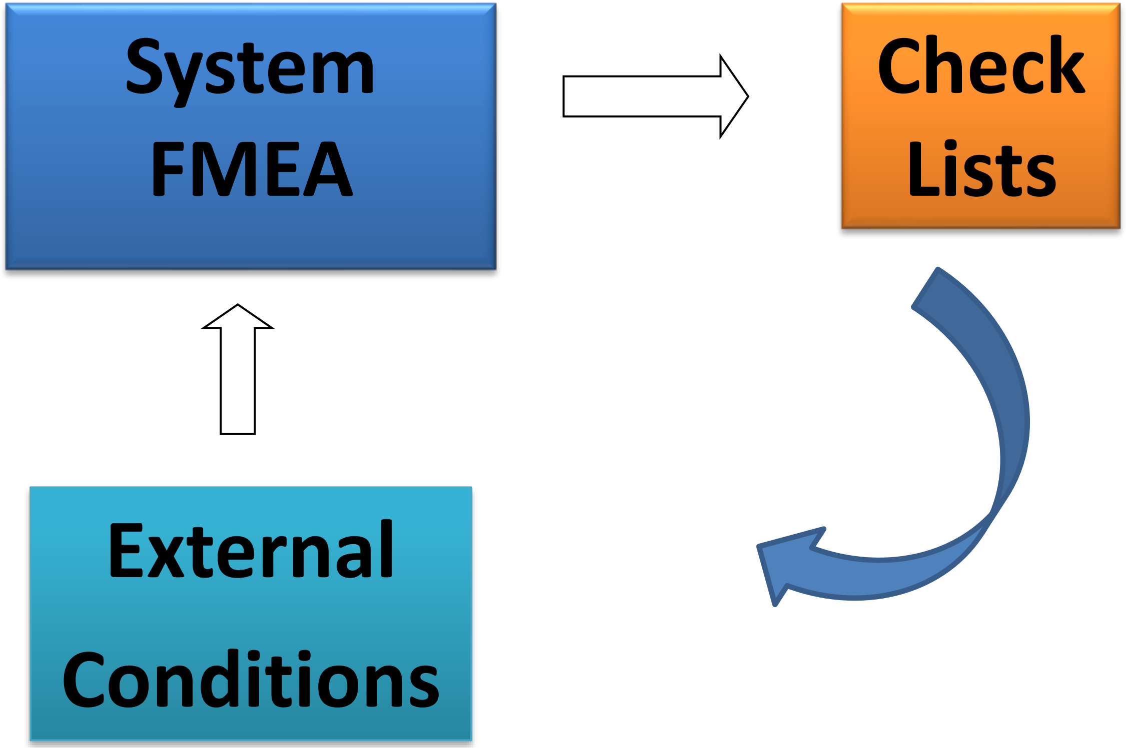
+ FTA

to consider the combination of multiple failures in a complex system


Produzione
Trasporto
Stoccaggio
Installazione
Attività Operativa
Ispezione periodica
Manutenzione

Comprehensive methodology

Other techniques are better suited for managing the external interactions



System FMEA

Check Lists

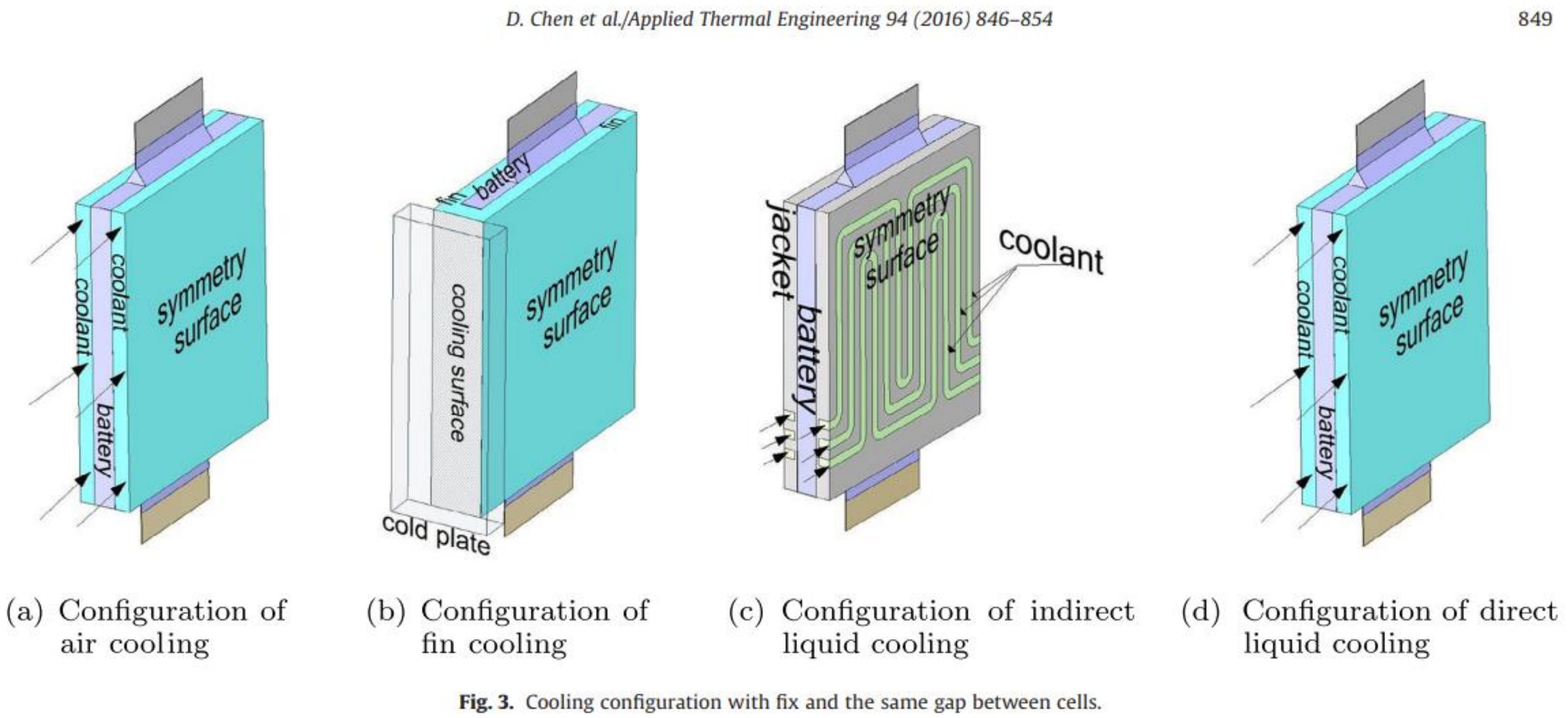
External Conditions

Conclusions

- An efficient hazard analysis methodology is required to identify all the possible accidental scenarios
- All the system components and cycle phases must be taken into account
- Clearer understanding of the interdependency between the battery and the surrounding environment is important
- The adoption of this methodology in practical applications, can lead to
  - higher energetic efficiency
  - reduced risk to people and environment

COOLING OF LI-ION BATTERIES

Introduction



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(a) Configuration of air cooling

(b) Configuration of fin cooling

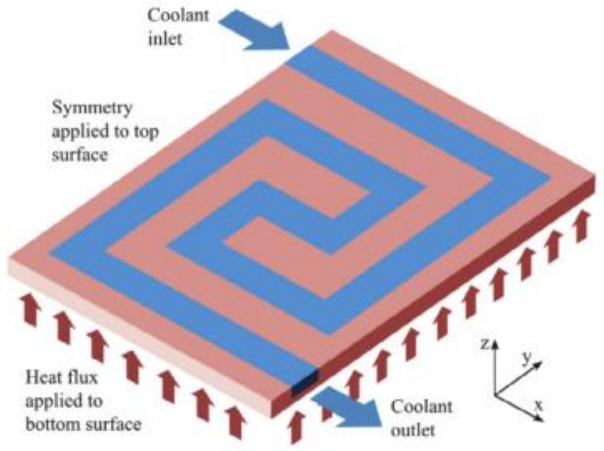
(c) Configuration of indirect liquid cooling

(d) Configuration of direct liquid cooling

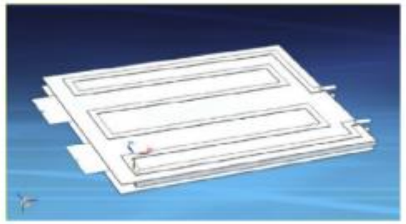
Fig. 3. Cooling configuration with fix and the same gap between cells.

Introduction

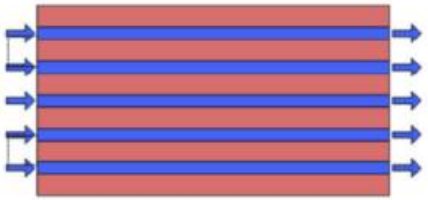
Y. Deng et al.



(a)Serpentine type[130]

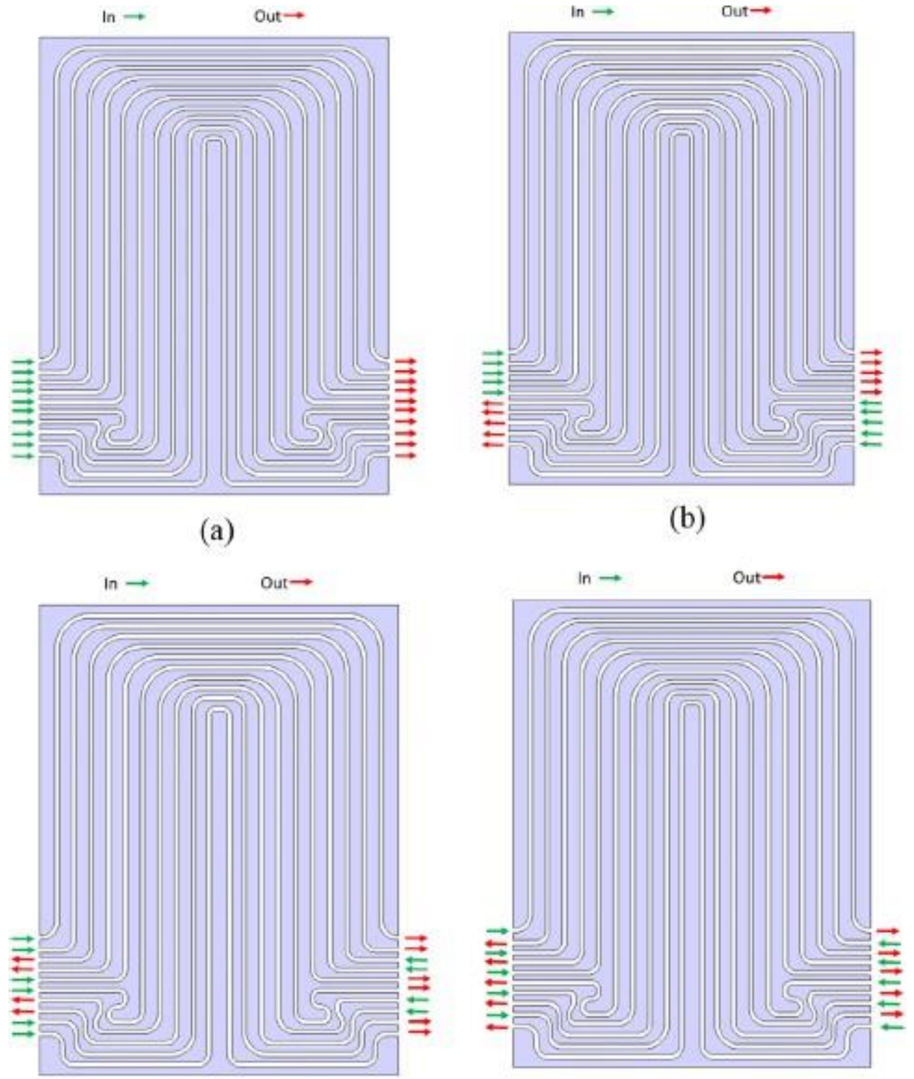


(b)U-turn type[132]



(c)Multi-channel type[137]

Fig. 14. Different types of cooling plate flow path.



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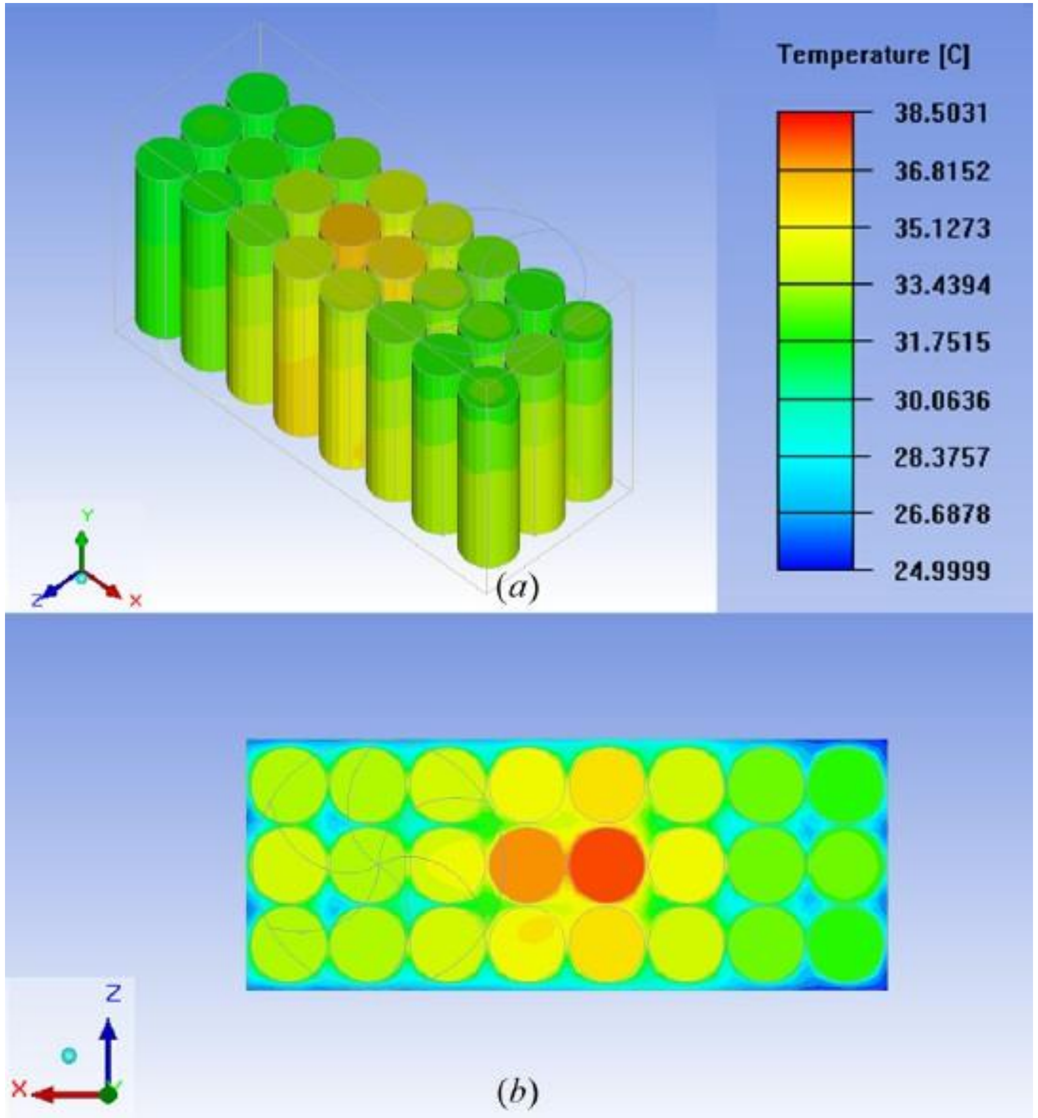
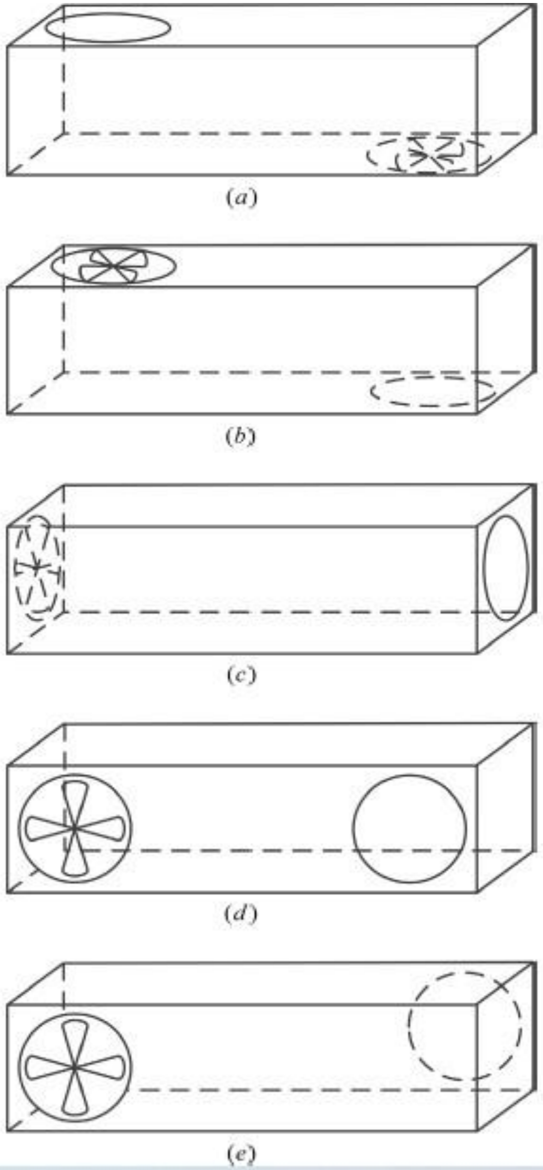
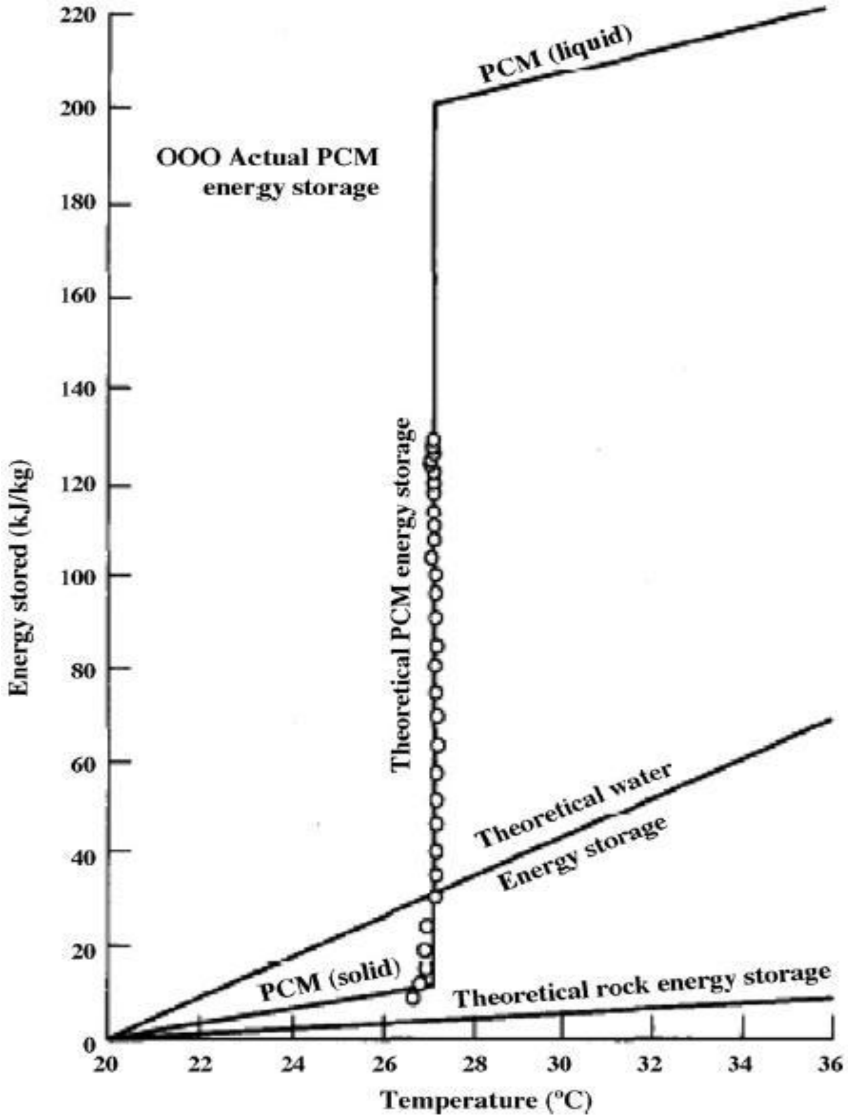
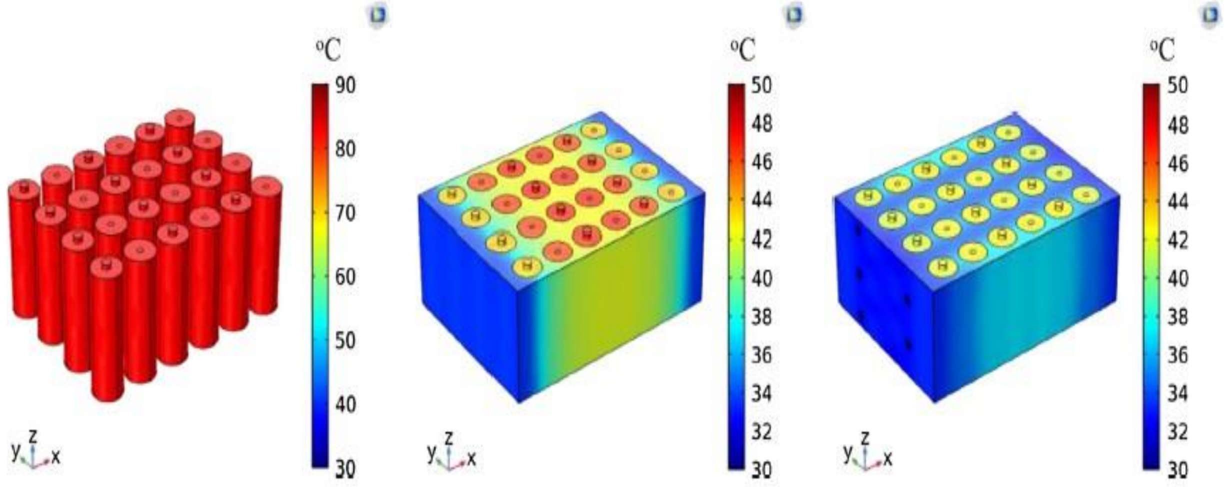




Introduction





(a) Natural convection

(b) PCM

(c) CPLS

Introduction

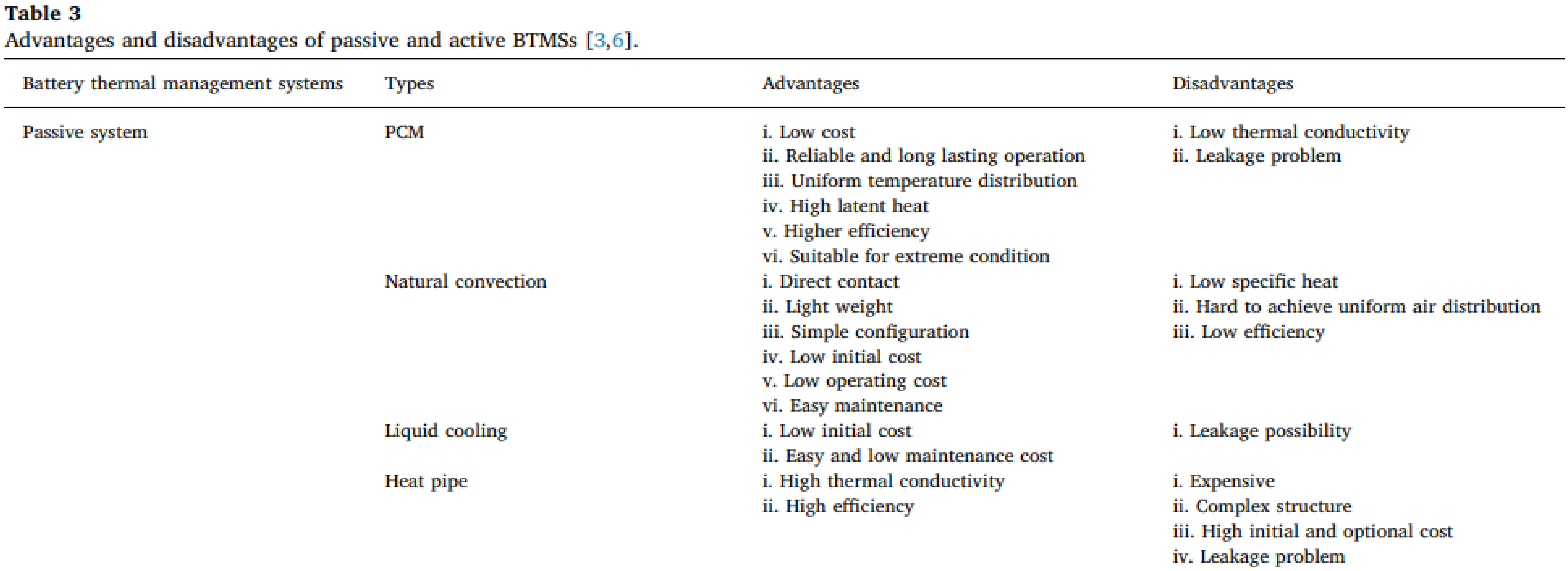
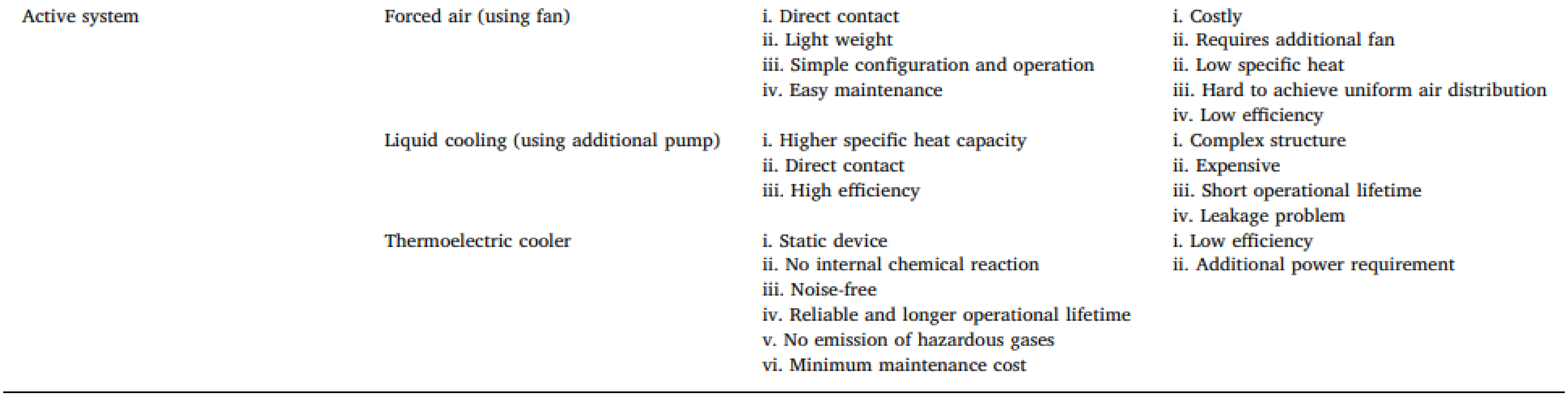


Table 3
Advantages and disadvantages of passive and active BTMSs [3,6].

Battery thermal management systems	Types	Advantages	Disadvantages
Passive system	PCM	i. Low cost ii. Reliable and long lasting operation iii. Uniform temperature distribution iv. High latent heat v. Higher efficiency vi. Suitable for extreme condition	i. Low thermal conductivity ii. Leakage problem
	Natural convection	i. Direct contact ii. Light weight iii. Simple configuration iv. Low initial cost v. Low operating cost vi. Easy maintenance	i. Low specific heat ii. Hard to achieve uniform air distribution iii. Low efficiency
	Liquid cooling	i. Low initial cost ii. Easy and low maintenance cost	i. Leakage possibility
	Heat pipe	i. High thermal conductivity ii. High efficiency	i. Expensive ii. Complex structure iii. High initial and optional cost iv. Leakage problem

Introduction



Active system	Forced air (using fan)	i. Direct contact ii. Light weight iii. Simple configuration and operation iv. Easy maintenance	i. Costly ii. Requires additional fan ii. Low specific heat iii. Hard to achieve uniform air distribution iv. Low efficiency
	Liquid cooling (using additional pump)	i. Higher specific heat capacity ii. Direct contact iii. High efficiency	i. Complex structure ii. Expensive iii. Short operational lifetime iv. Leakage problem
	Thermoelectric cooler	i. Static device ii. No internal chemical reaction iii. Noise-free iv. Reliable and longer operational lifetime v. No emission of hazardous gases vi. Minimum maintenance cost	i. Low efficiency ii. Additional power requirement

Introduction

A number of numerical studies analyzed the battery thermal behavior using air cooling systems

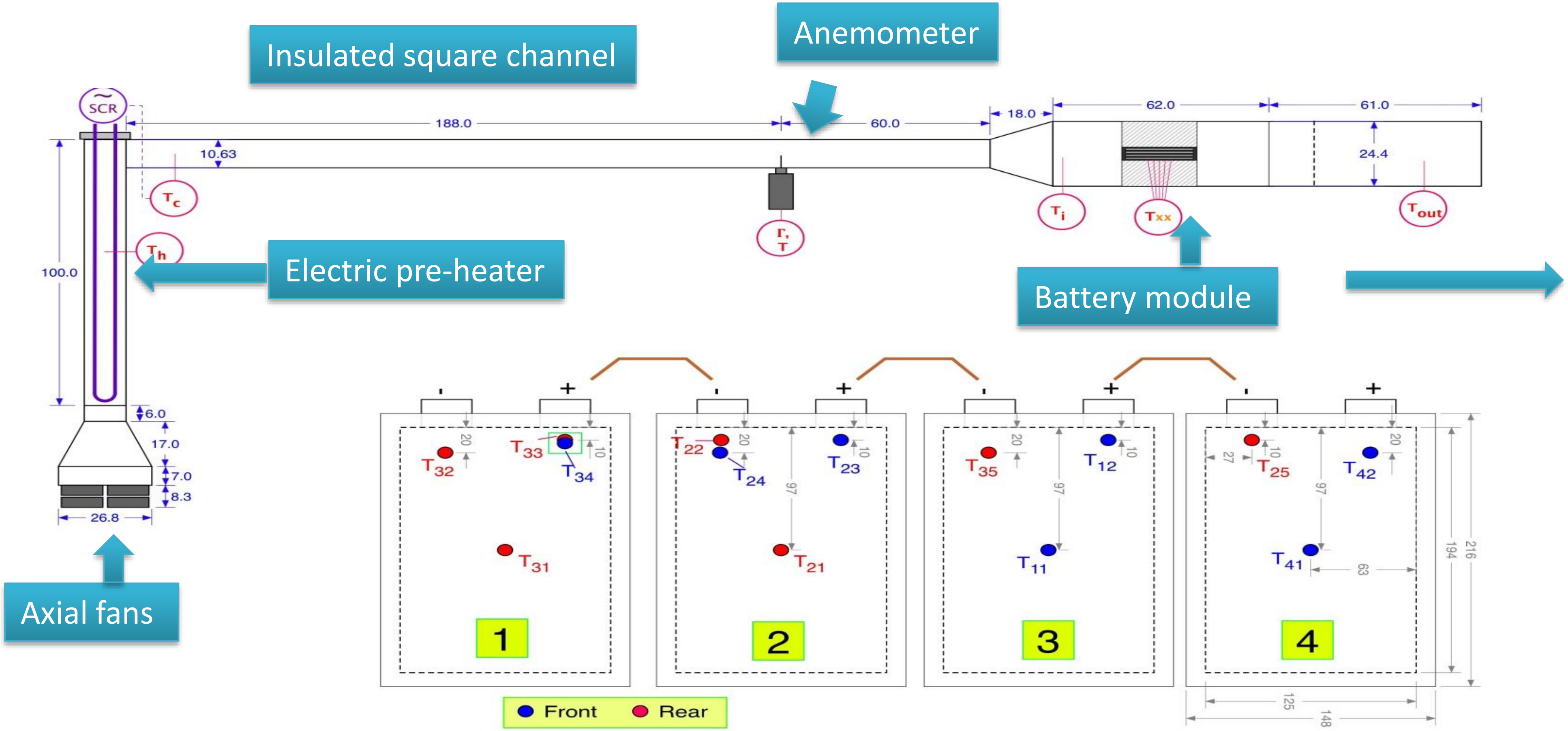
Few papers report *experimental quantitative* investigations of a system under various operating conditions (different air velocities and temperatures)

Experimental set-up:

- a battery pack, provided with air cooling, was locally monitored with thermocouples during intense discharge cycles (e.g. high acceleration of a car)
- the tests were performed on a module with four pouch cells connected in series
- the temperature uniformity within a cell and from cell to cell were analyzed under various operating conditions

Experimental apparatus

Set up for tests with cooling air at different flow rates and inlet temperatures



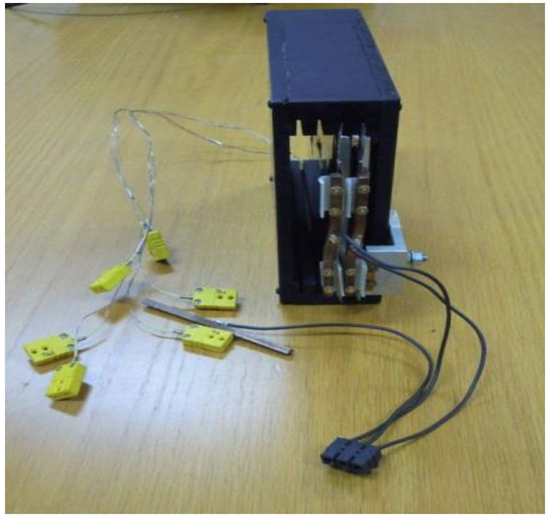
Insulated square channel

Anemometer

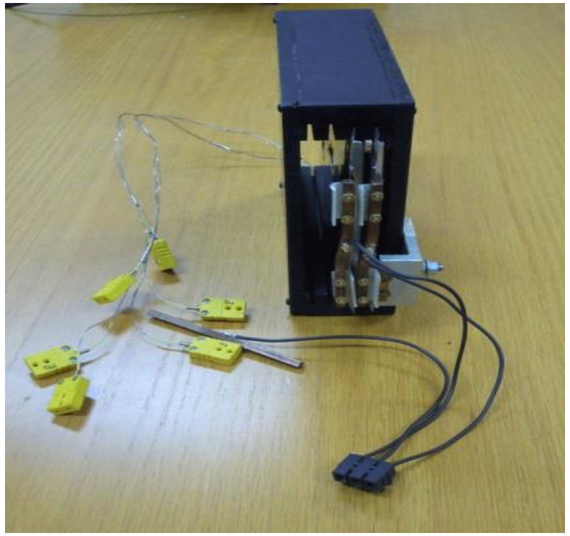
Electric pre-heater

Battery module

Axial fans



Experimental apparatus



- Pouch cells connected in series
- NMC based batteries
- Cells spaced 3 mm apart
- Nominal Capacity 20 Ah
- Maximum continuous discharge current 100 A (5C)
- Tmax=50°C

Old NMC pouch cells were adopted to run the cooling tests under the worst thermal conditions

Experimental apparatus

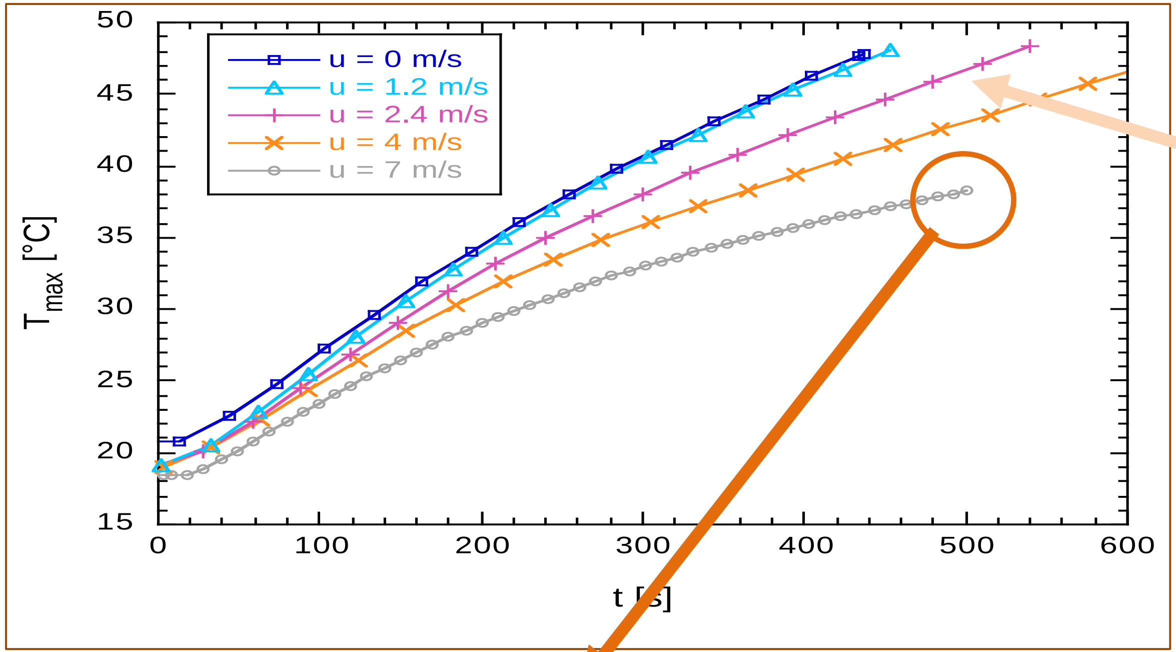
Air Velocity (m/s)	Re	T_0 (°C)	Regime flow
0	0	20	Natural Convection
0	0	30	
0	0	40	
1.2	473	19	Laminar Flow
2.4	949	18.6	
4	1580	18.6	
4	1478	30	
4	1396	40	
7	2757	19.2	Transitional Flow

The experimental tests were carried out with an air velocity ranging from 0 to 7 m/s in the gaps between the batteries

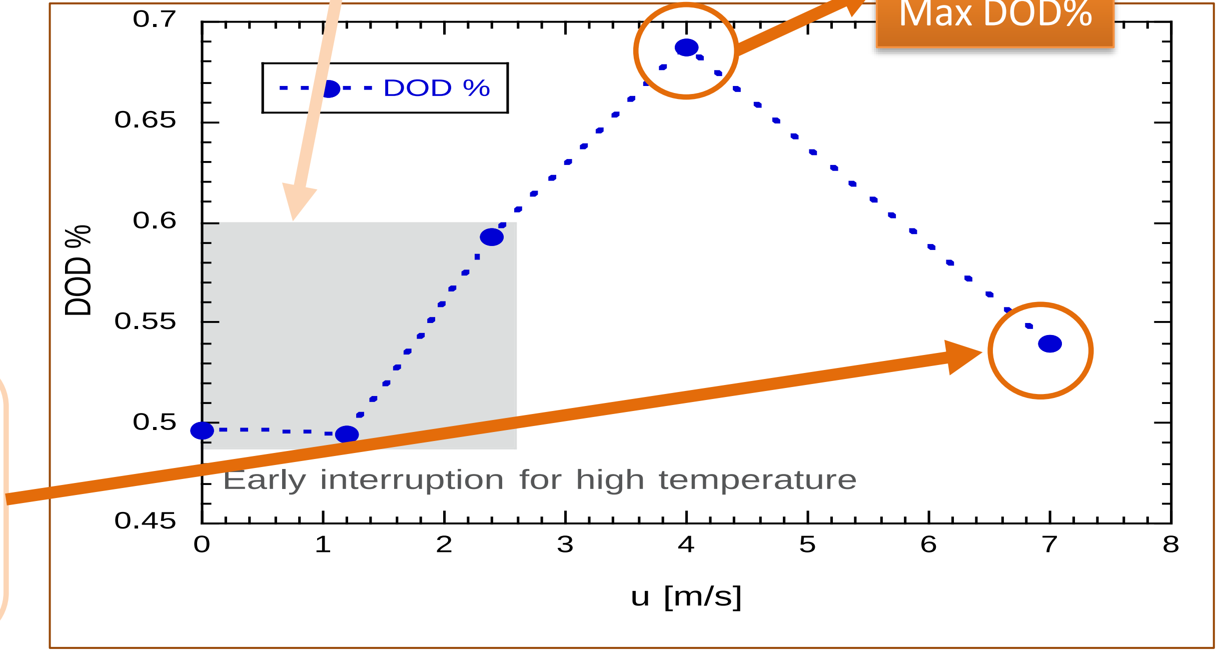
The higher temperatures are reached discharging the batteries at high current: a **4C discharge rate** was used for the tests.

The tests have been interrupted when the temperature of 48 °C was reached on the battery surface to work in safe conditions (i.e. at 0, 1.2 and 2.4 m/s).

Experimental results



At low air velocity (1.2 and 2.4 m/s) the tests were stopped earlier for safety reasons



4 m/s
Max DOD%

At the highest tested velocity, the T_{max} reached at the end of the discharge is well below the safety limit, but the **DOD% is very low**

Lithium-ion performs better when warm, since heat lowers the internal resistance, but this stresses the battery

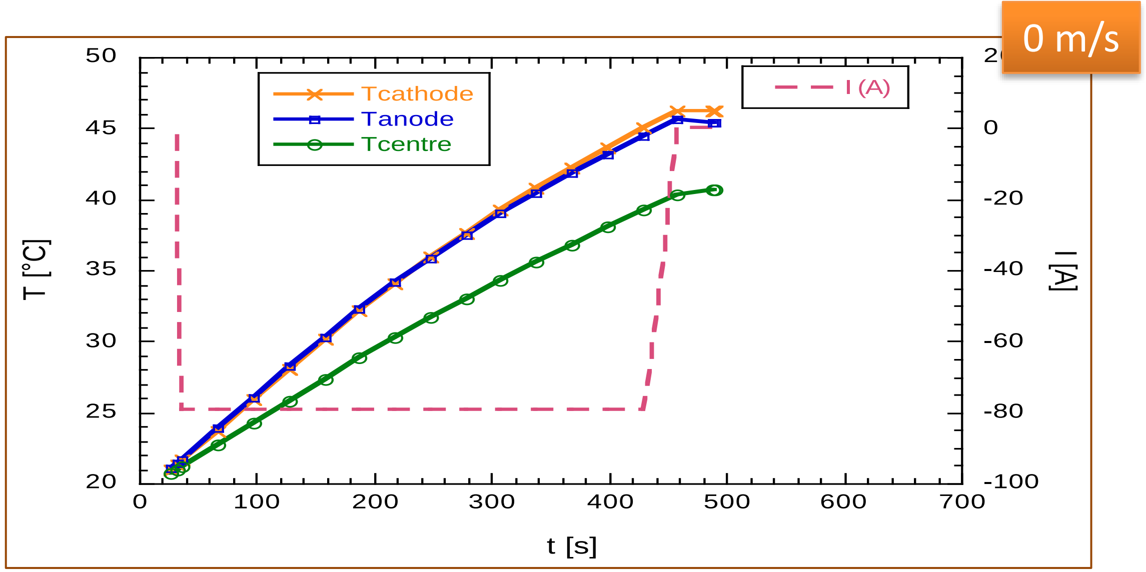
DOD% = Amount of energy that can be extracted from the battery (Depth Of Discharge)

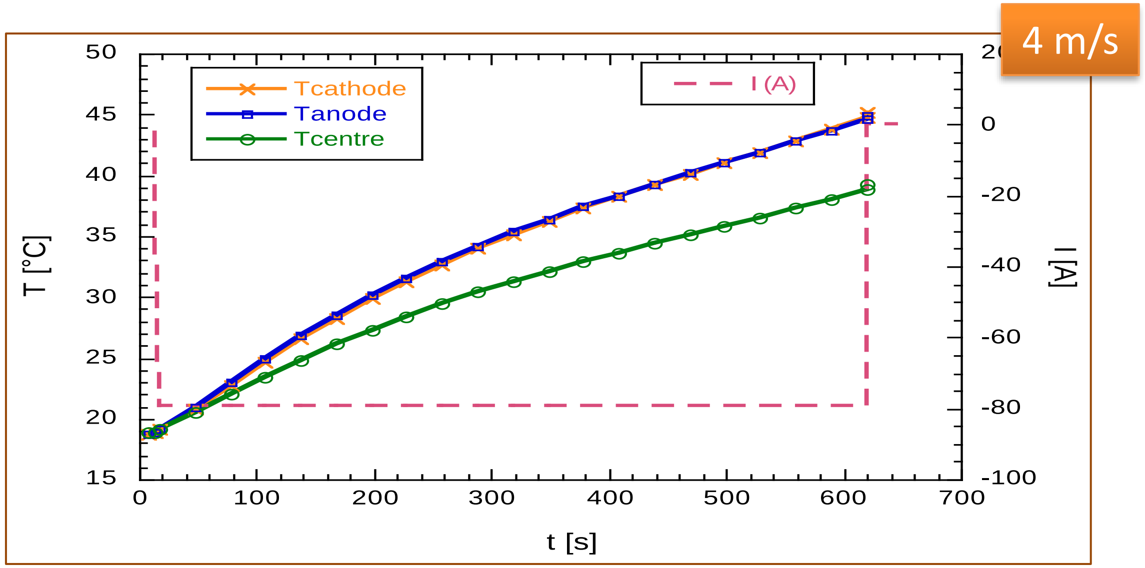
Experimental results

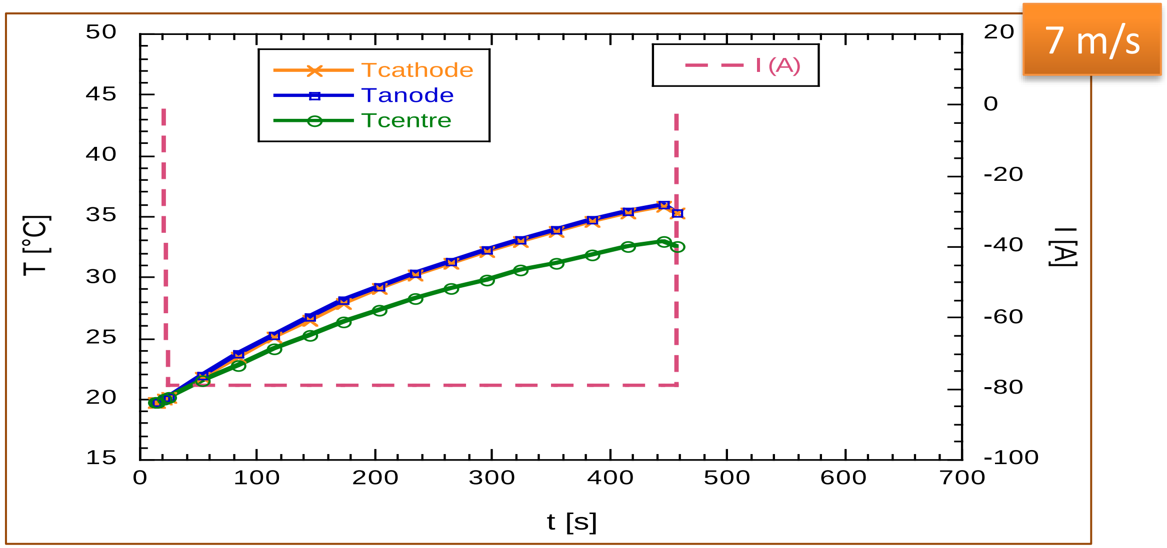
- Maintaining temperature uniformity, within a cell and from cell to cell, is important to achieve the maximum cycle life of cell, module, and pack
- uneven temperature distribution in the battery pack will lead to a localized deterioration and so to a capacity loss of the entire module
- the average temperatures at the anode, the cathode and the centre of cells were calculated as average values of all the thermocouples located on each of the three different areas of the four cells connected in series

Experimental results

Temperature distribution within a cell



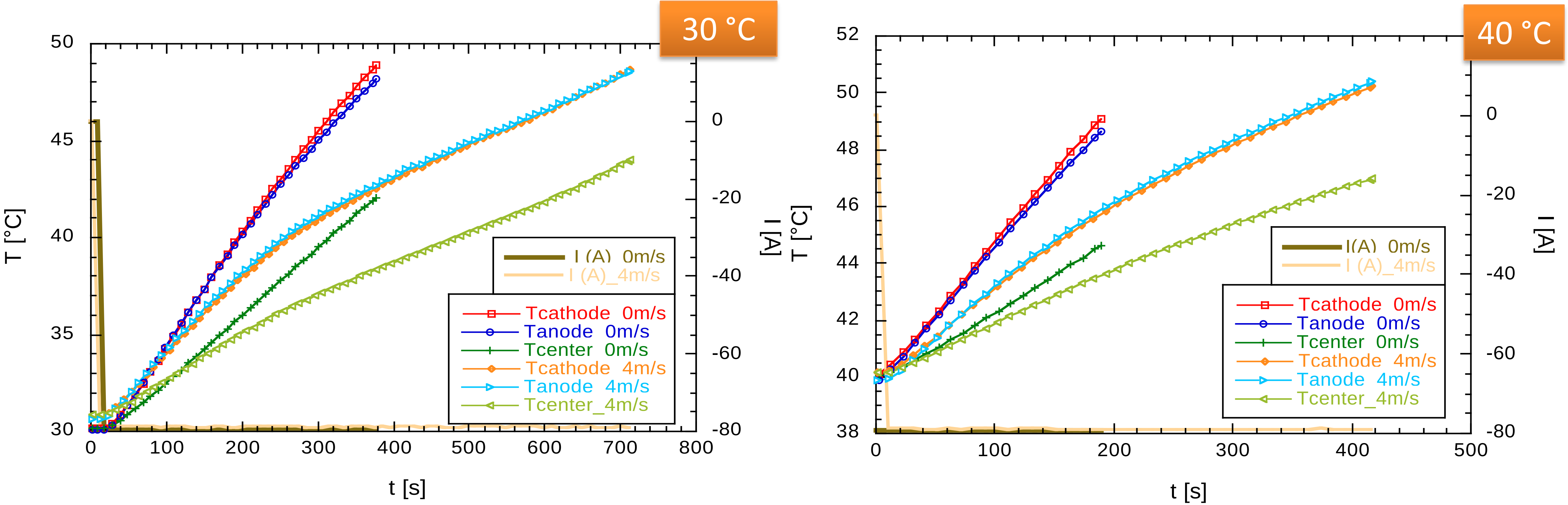




- Increasing air velocity, decreases the temperature difference between the centre of the cell and the electrodes.
- At 7 m/s **the difference decreases by 3 degrees** compared with the case of natural convection

Experimental results

Temperature distribution within a cell



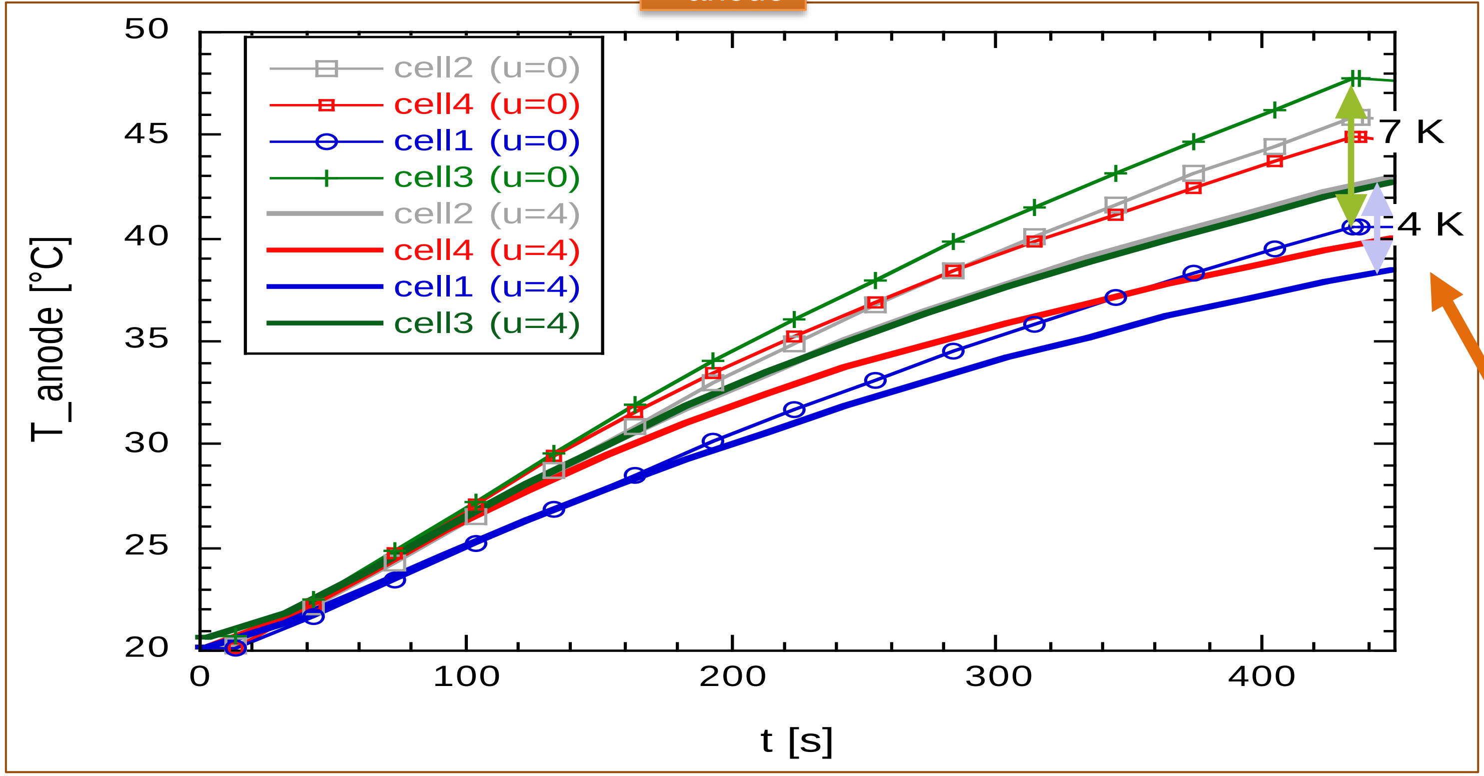
- As might be expected, at higher initial temperature, it becomes harder to keep the temperature below safe conditions

Experimental results

Temperature distribution inside the battery pack

A comparison was made between the temperatures of each battery in the module at the anode, the cathode and the centre with an air velocity equal to 0 and 4 m/s

T_{anode}



Increasing air velocity, the temperature at the anode is:

- more uniform in the module
- lower on each cell

ΔT_{max} :

- 7 K for natural convection
- 4 K at 4 m/s

Experimental results

It is actually possible to completely discharge the batteries, without exceeding the maximum allowable temperature for the cells, provided that a **minimum air velocity of 4 m/s is adopted**

Using **lower air velocities does not allow to keep the maximum temperature within the safety limits**. In particular, this is feasible under laminar flow regime, which is the only practical condition for vehicular applications

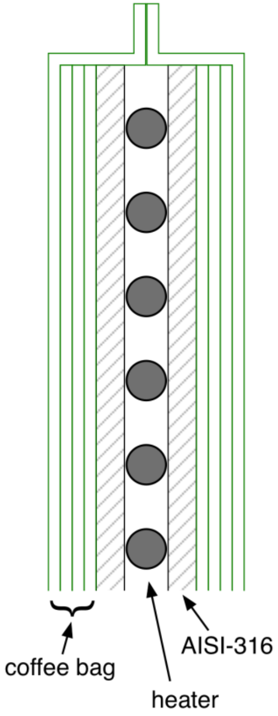
As far as the temperature distribution is concerned, as might be expected, **at increasing air velocities, a smaller temperature gradient is obtained**, both within a single cell, and among the different cells of the pack

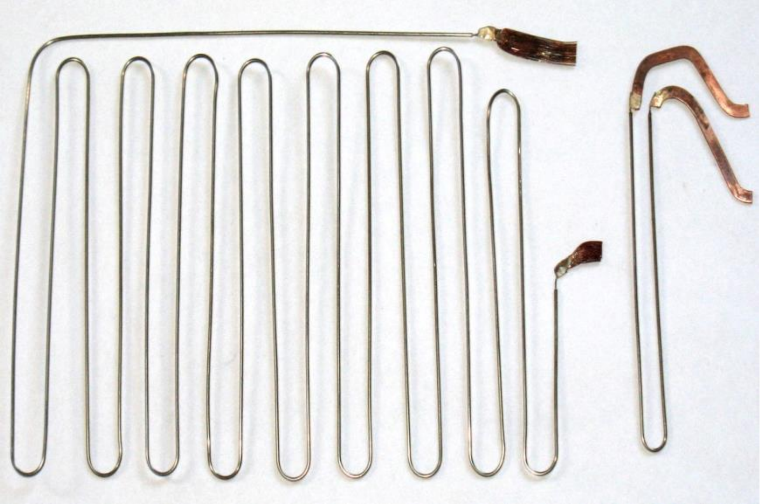
Nonetheless, under **no conditions** it is possible **to establish a sufficient temperature uniformity** within a cell and from cell to cell only using air as cooling fluid

Experimental results

A specifically devoted experimental facility was set up (standard power input, 60 W max) to check the cooling efficiency under more demanding conditions:

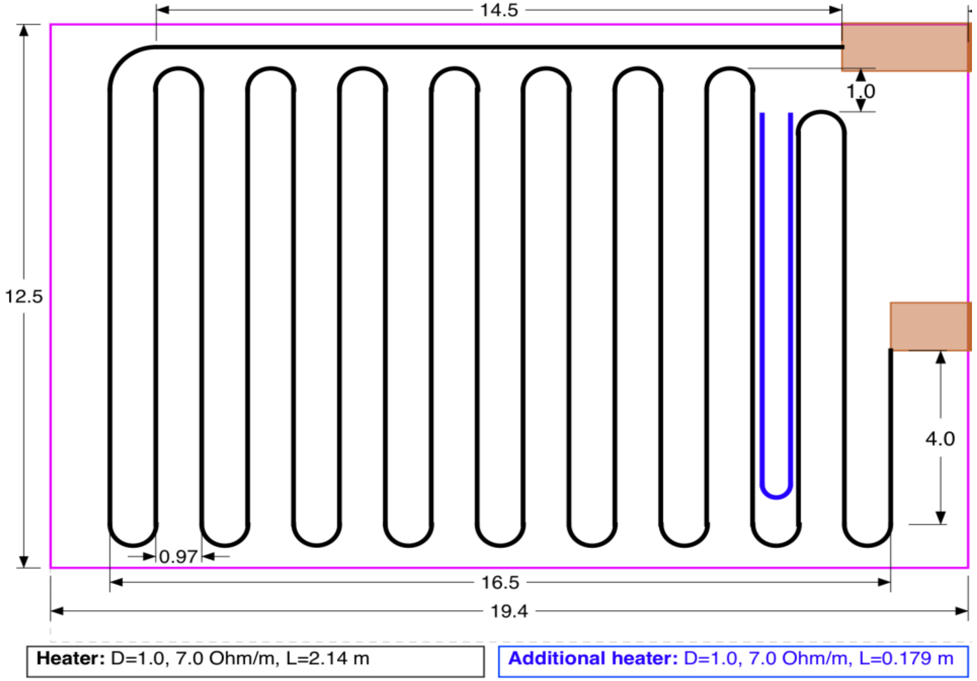
a) hot spots (max 27 W)

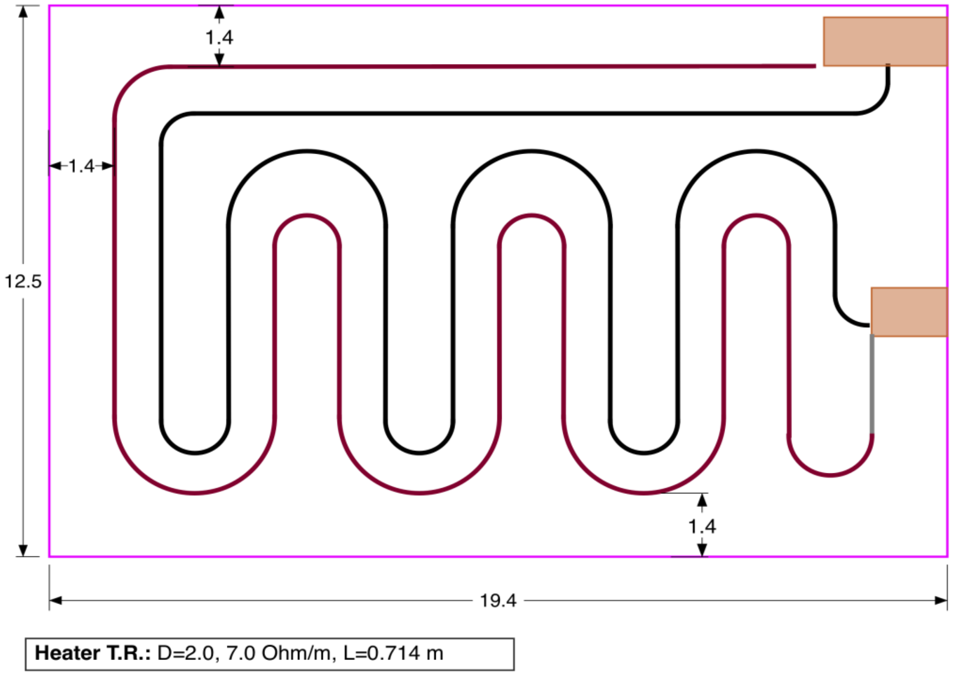




Experimental results

b) near thermal runaway conditions (500 W)



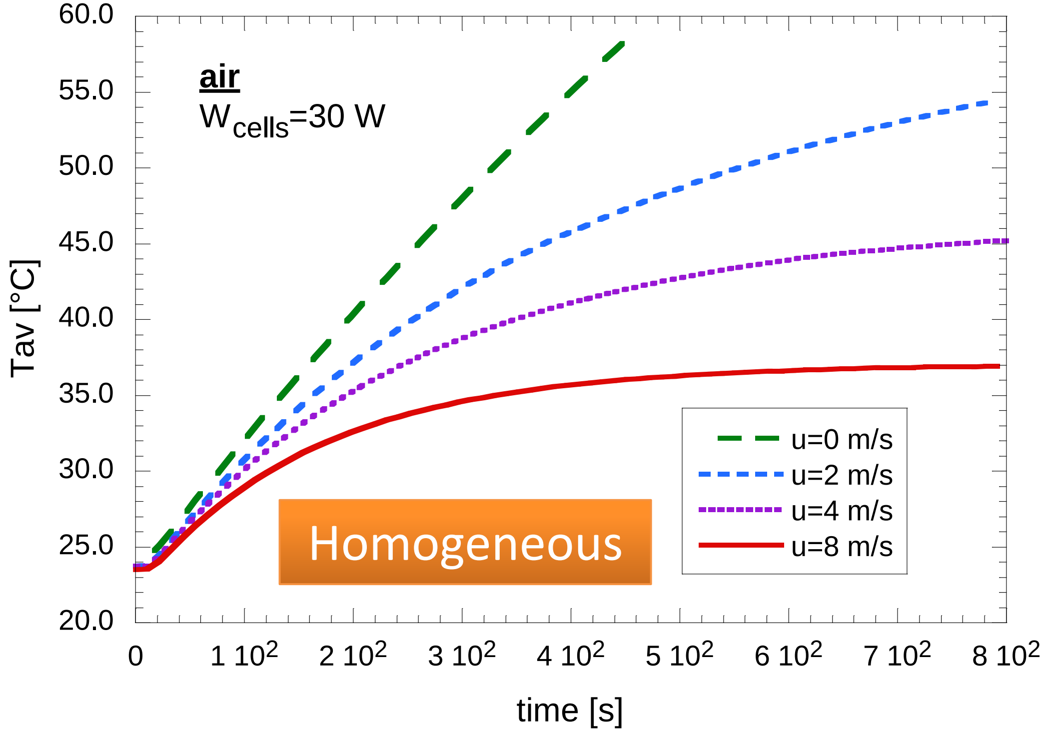


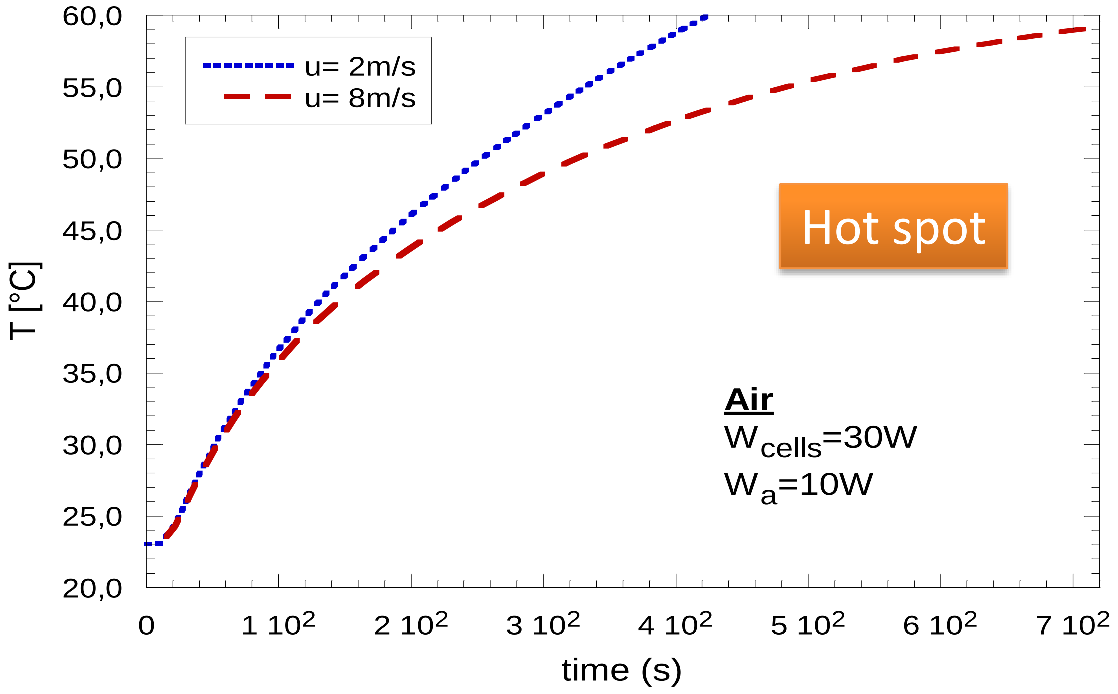
Distributed and localized heaters

The "Thermal Runaway" cell

Experimental results

Temperature distribution within a cell at 5C (30 W)





- 5C homogeneous heating: u>4 m/s is required
- Hot spots: <u>it is not possible to keep the temperature low with air</u>

Experimental results

Selection Criteria

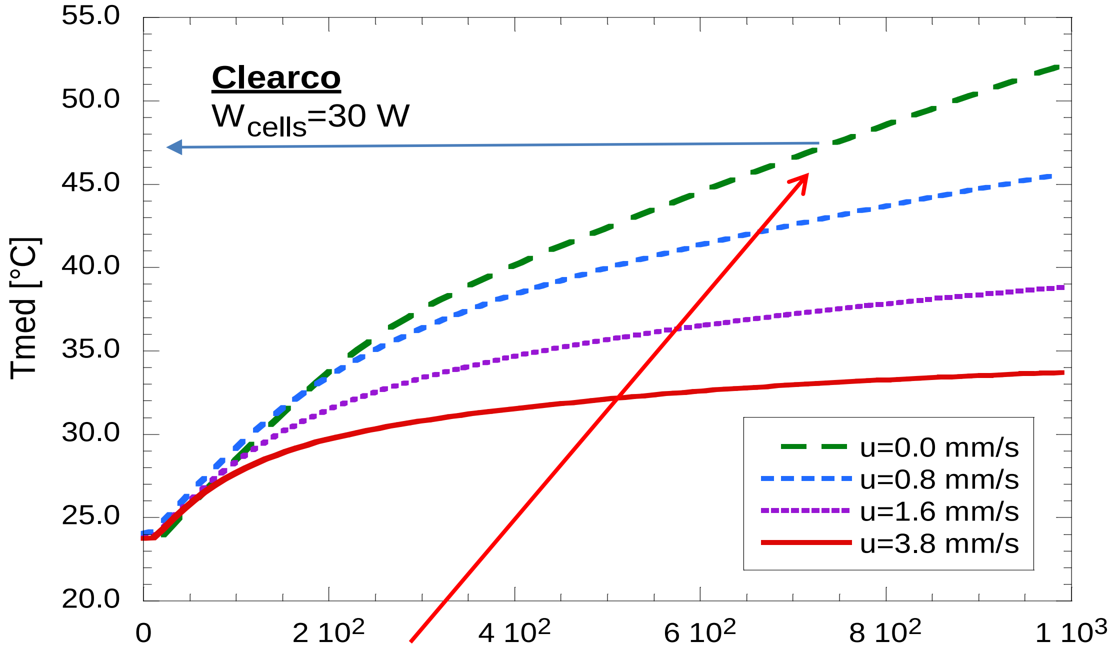
High Flash Point temperature
High boiling temperature
High degradation temperature
Low Pour point
Low coefficient of thermal expansion
High efficiency in removing the surplus heat

Two dielectric liquids have been tested:

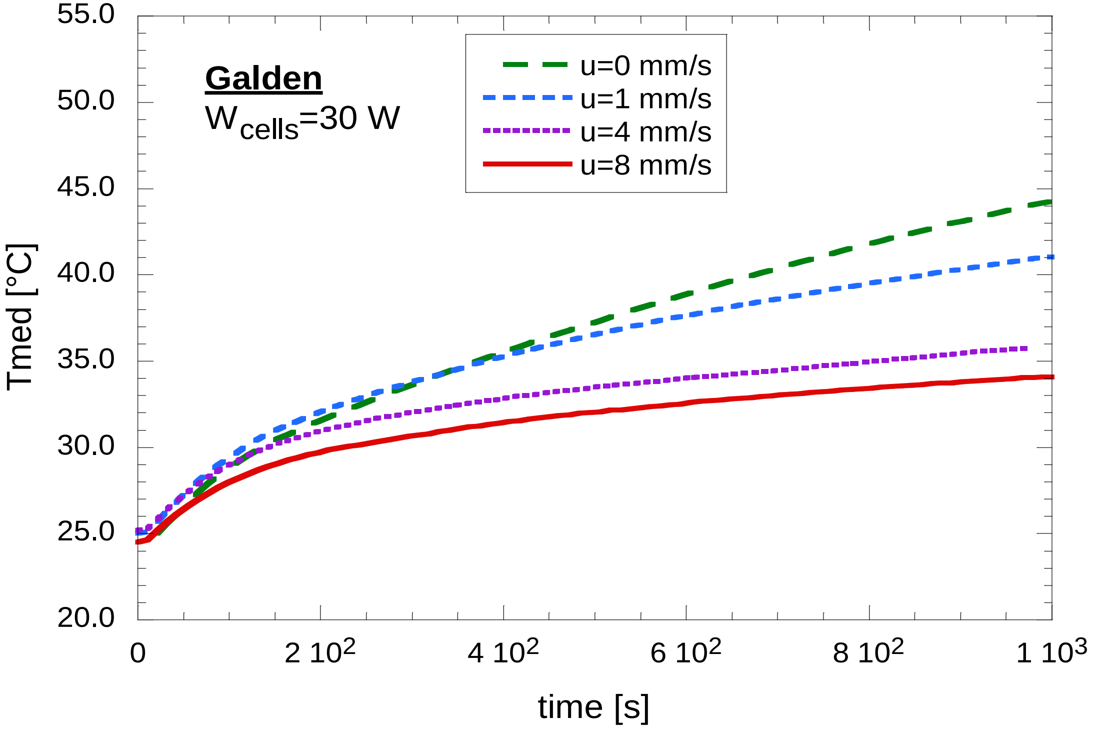
Fluid	Cp (J/kg K)	k (W/m K)	ρ (kg/m^3)	μ (kg/m s)	Type
Galden HT135	962.68	0,065	1720	$1.72 \cdot 10^{-3}$	Perfluorinated polyether
Clearco-50 cSt	1500	0,15	960	$4.8 \cdot 10^{-2}$	Silicone oil
Air	1004.1	0,026	1.17	$1.83 \cdot 10^{-5}$	

Experimental results

Temperature distribution within a cell at 5C (30 W)



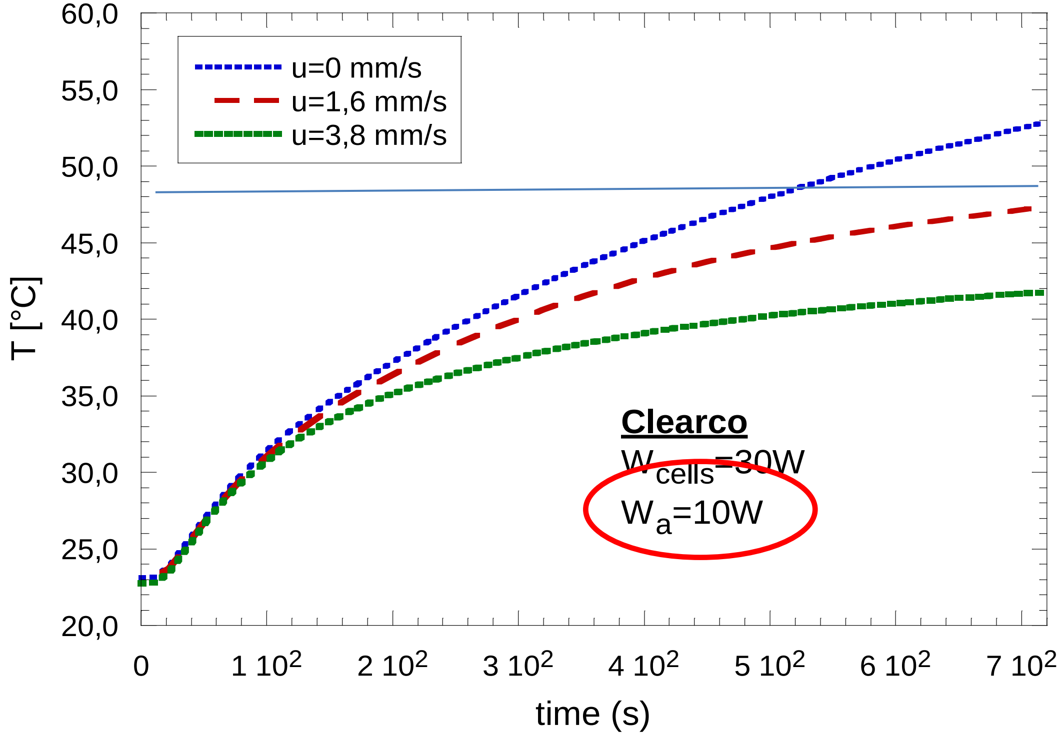
T= 47°C at the end of the discharge phase (720 s)

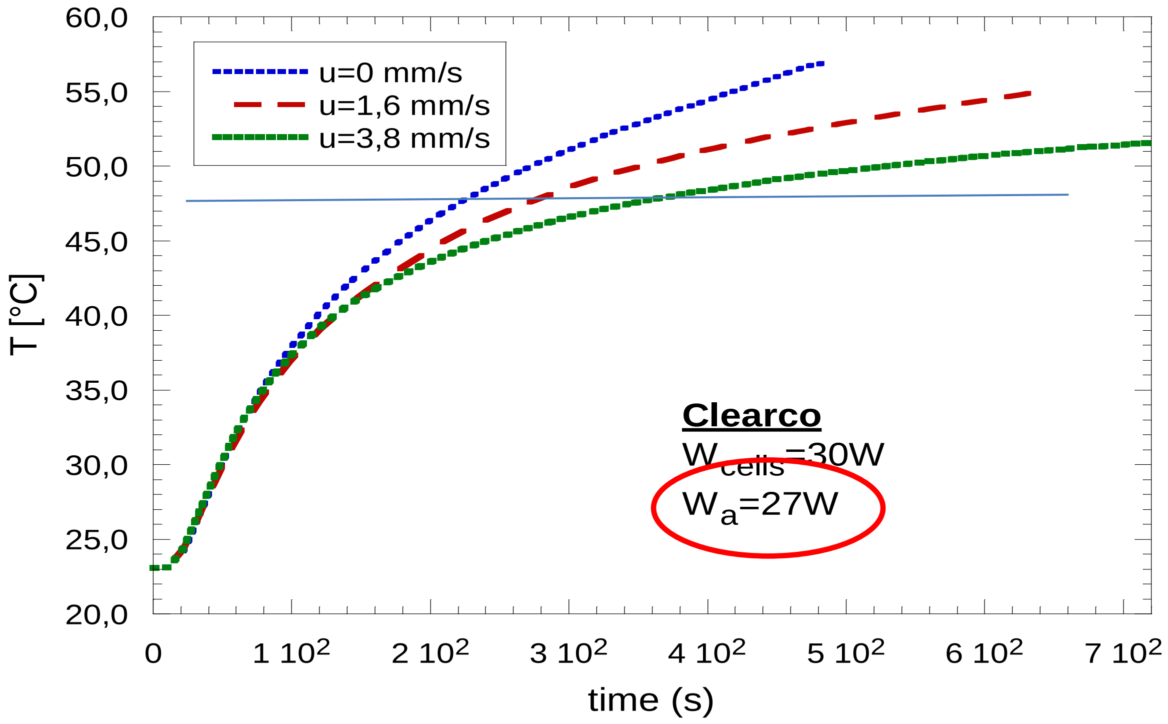


- It is possible to safely discharge, even with u=0 m/s (natural convection)
- The pumping power is very low at any u (u=mm/s)

Experimental results

Clearco with hot spots

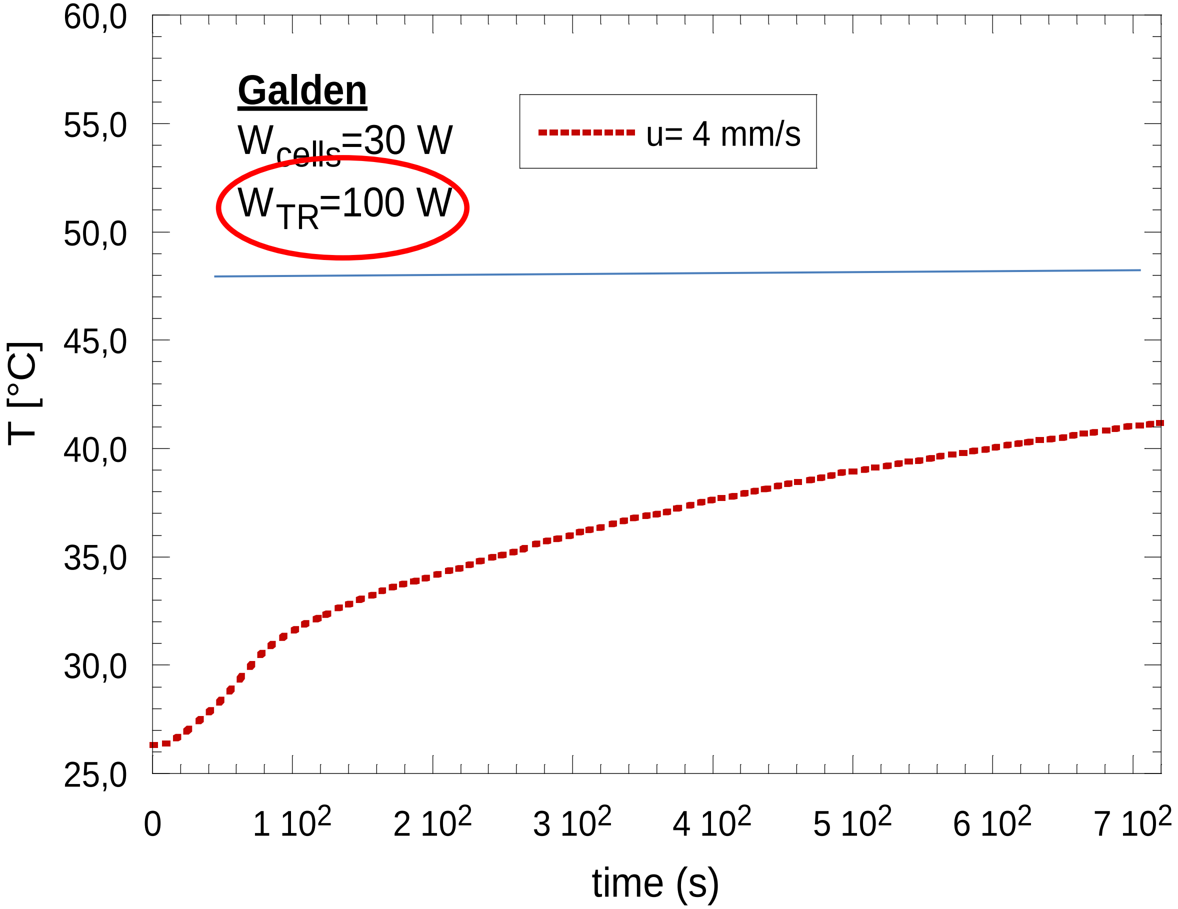




- It is never possible to safely discharge, at the highest heat input
- Better behaviour at W_{local}=10 W

Experimental results

Galden under thermal runaway



- The final surface temperature was only **41 °C**, after 12 minutes of operation (end of discharge)
- liquid velocity of 4 mm/s, corresponding to a pumping power of only **0.01 mW**.

Conclusions

In conclusion, it is very important:

- identifying the dangerous conditions of operation
- quantitatively characterizing the heat generation rate
- assessing the cooling capability of a given system under all possible conditions

Conclusions

In conclusion, it is very important:

- Dielectric liquids are generally much more efficient than air
- However, as shown before, the real cooling efficiency in all predictable scenarios has to be preliminarily assessed on a case-by-case analysis

A Simplified Model for Thermal Characterization of Lithium ion cells

Introduction

A simplified model allows to predict the thermal behaviour of a battery cell/pack refrigerated with any given cooling fluid.

It allows to quickly estimate the efficiency of a given cooling system under a range of working conditions, and thus identify the range of operation within which a given energy storage system can safely operate

- CFD modelling is a very powerful tool to get detailed results, but it is still too time consuming in terms of setup and calculation time;
- simplified one-dimensional models can provide good enough results more quickly, so that many different configurations can be preliminarily assessed

Thermal Characterization of Lithium ion cells

$$\dot{Q} = \boxed{I(V - E_0)} - \boxed{IT\frac{\partial E_0}{\partial T}} - \boxed{\sum_i \Delta H_i^{avg} r_i} - \boxed{\int \sum_j \left(\bar{H}_j - \bar{H}_j^{avg}\right) \frac{\partial c_j}{\partial t}\, du}$$

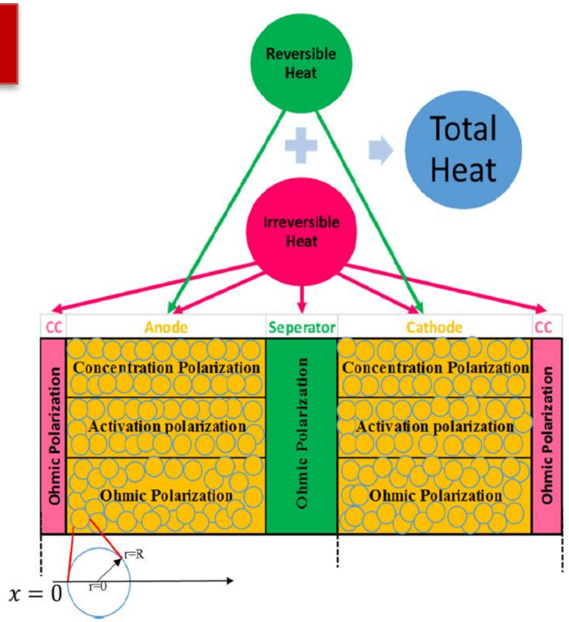
Heat of mixing

Irreversible heat

Current collectors: ohmic resistance due to the transport of electrons
Separator: ohmic resistance due to the transport of Lithium ion across the electrolyte.
Electrodes: ohmic resistance due to: the transport of electrons to the electrically conductive materials, the transport of Lithium ion across the electrolyte and the activation/concentration polarizations that occur at the **active sites**.

Electrodes: the reversible heat is due to the entropy changes related to specific reactions at the **active sites**.

Reversible heat



Heat due to the side reactions accounting for aging

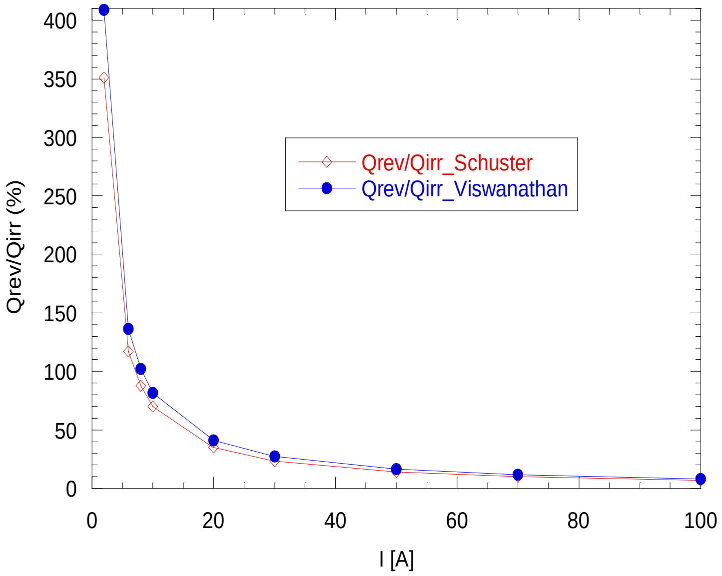
E_0 is the Open Circuit Voltage (OCV), T the cell temperature, ΔH_i^{avg} the enthalpy variation associated with the i-th chemical reaction, r_i its reaction rate, H_j the partial enthalpy of species j, H_j^{avg} the average enthalpy of species j, c_j its concentration, u is the battery volume

Reversible Heat

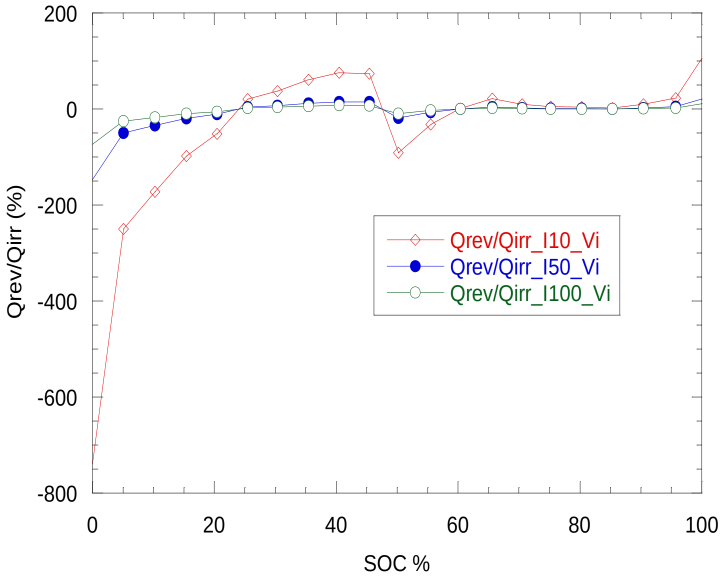
$$Q_{rev} = IT\frac{\partial E_0}{\partial T}$$

The reversible heat is due to the entropy changes related to specific reactions at the active sides
it can be either endothermic or exothermic depending on the current and the state of charge (SOC)

Reversible heat of the cell with a cathode chemistry NMC, from literature data



Qrev/Qirr varying the charge/discharge current for a SOC=50%
Increasing the current rate the influence of the reversible heat decrease



Qrev/Qirr varying the SOC%, for I=10 A, 50 A e 100 A.
The higest influence of the Qrev there is for low SOC%

Battery Thermal Model

The model is useful to evaluate the efficiency in removing the surplus heat, using monophase dielectric fluids

$$MC_p\frac{dT}{dt} + hS(T - T_a) + \varepsilon S\sigma(T^4 - T_a^4) - \dot{Q} = 0$$

$$T(t) = \left[T_i - \frac{\beta}{\alpha}\right]e^{-\alpha t} + \frac{\beta}{\alpha} \quad \left\{\begin{array}{l} \alpha = \dfrac{2hSF_a c_{pa}}{(2F_a c_{pa} + hS)Mc_p} \\[2ex] \beta = \dfrac{\dot{Q}}{Mc_p} + \dfrac{2hSF_a c_{pa}}{(2F_a c_{pa} + hS)Mc_p}T_{ai} \end{array}\right.$$

A simplified approach was used considering that the temperature of a battery varies with time but remains uniform throughout the system at any time

h=(Nu*k)/D

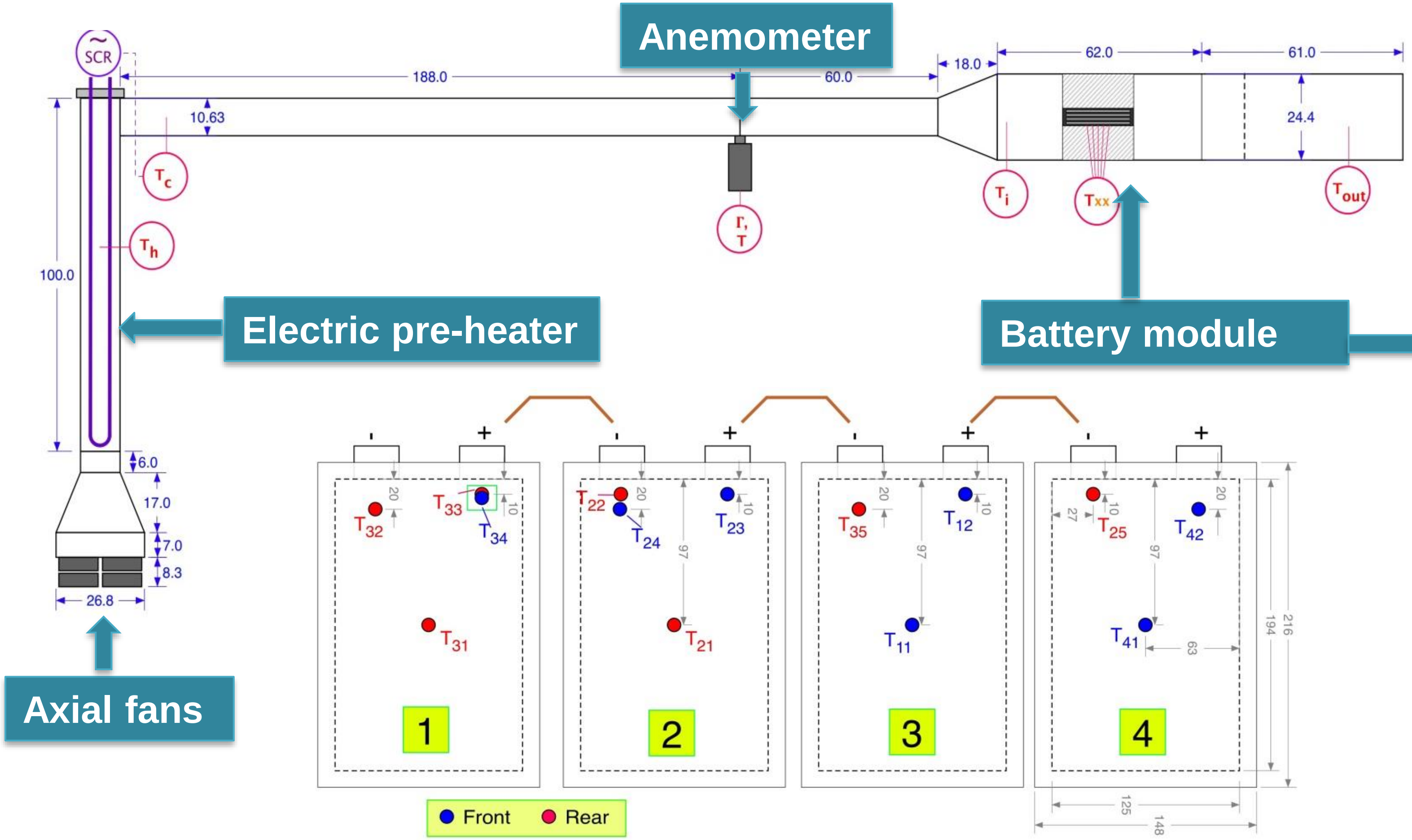
Correlations used to calculate the ***Nusselt number***:

- *Natural Convention*: Churchill
- *Laminar Flux*: Shah, Baehr-Stephan (St), Stephan-Preuber (Ste), Hausen (Haus)
- *Transitional/Turbolent Flux*: Colburn (DB) , Gnielinski (Gn)

Experimental set up for model validation

Set up to run the tests using cooling air at different flow rates and inlet temperatures

- Pouch cells connected in series
- NMC based batteries
- Cells spaced 3 mm apart

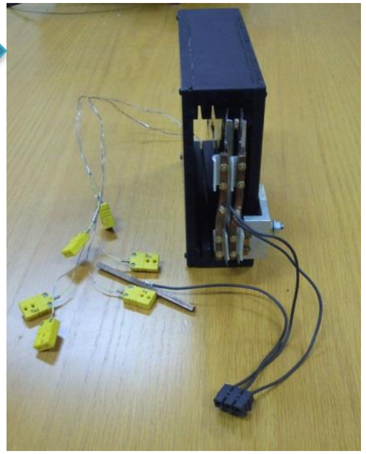


Anemometer

Electric pre-heater

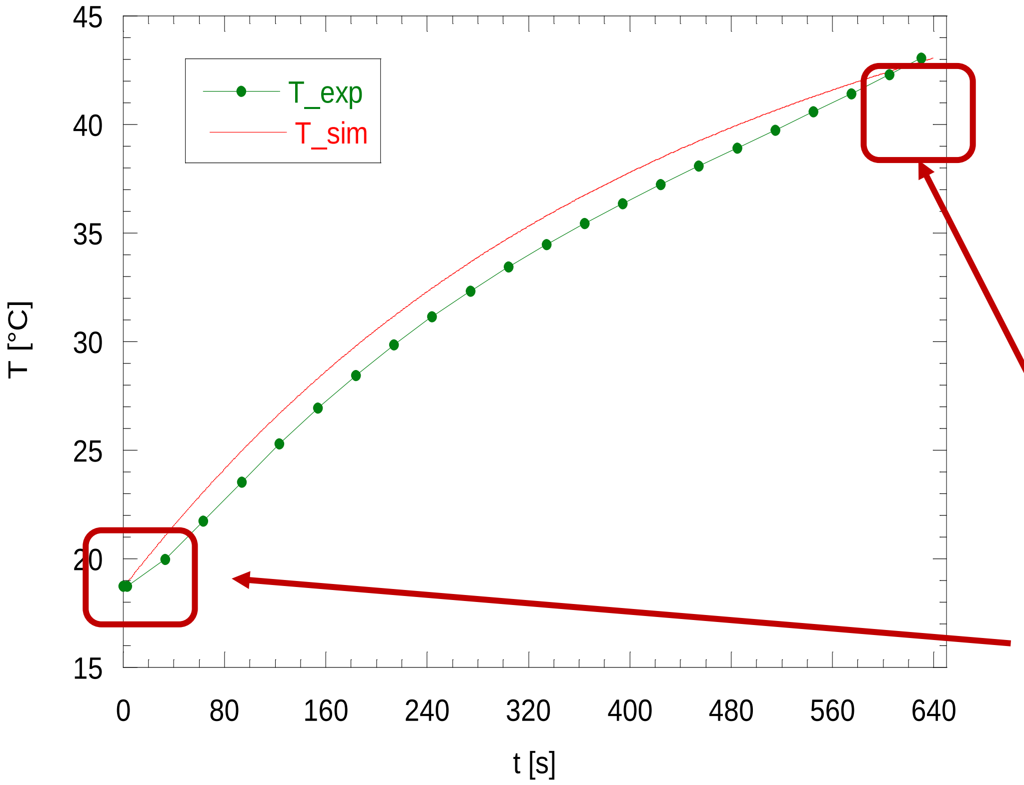
Battery module

Axial fans



Model Validation

Comparison for a 4C discharge and air velocity of 4 m/s (1.5 10^{-3} m^3/s)



A very good accuracy is obtained.
The difference in the two curves can be explained by considering the following issues:

- at the end of the discharge, the experimental temperature rises more rapidly than predicted, probably due to the **higher resistance characterizing an aged cell at low SOC (%)**. This issue has been neglected in the simulation (constant resistance adopted);
- **a small delay is required for the cycler to generate the full regime current.**

Cooling fluids: dielectric oils

Dielectric oil selection

Dielectric oils can drastically reduce the temperature in a battery pack

Selection Criteria

High Flash Point temperature
High boiling temperature
High degradation temperature
Low Pour point
Low coefficient of thermal expansion
High efficiency in removing the surplus heat

SILICONE OIL (Clearco)

No significant effects on health for users
High flash point temperature (it is possible to operate close to Thermal Runaway conditions)

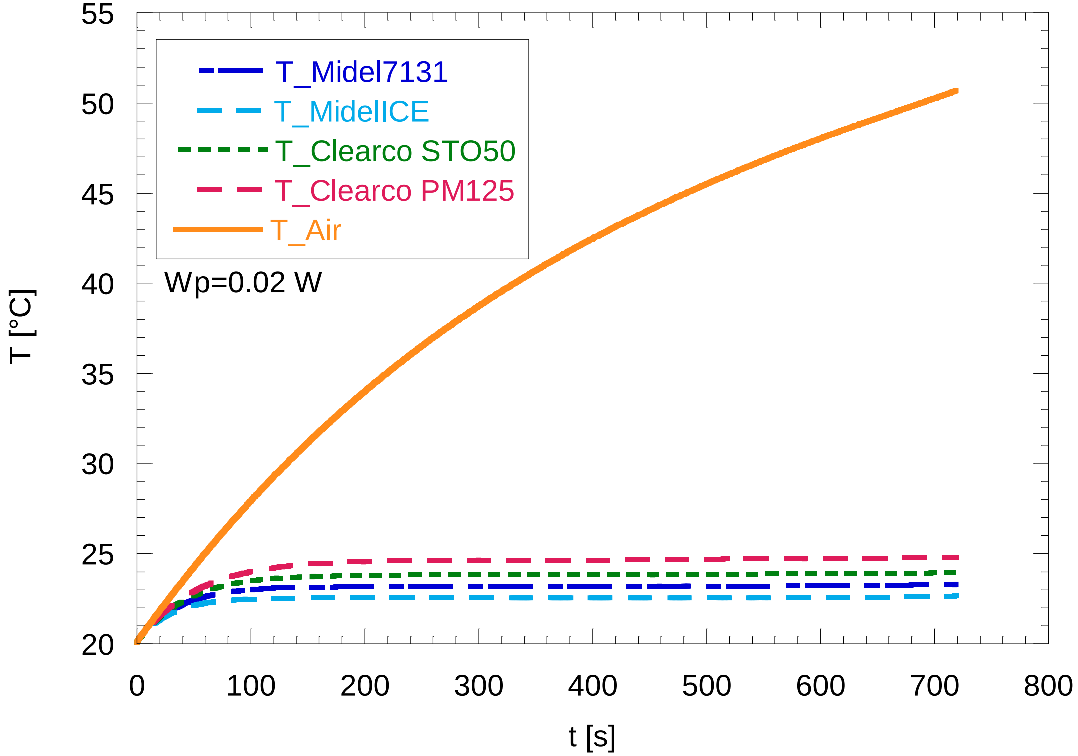
OIL OF NATURAL ORIGIN (Midel)

No significant effects on health for users
Low viscosity (higher efficiency)

Comparison between air and dielectric oils

Temperature profiles for a 5C discharge (0.02 W pumping power)

	Clearco STO50	Clearco PM-125	Midel 7131	Midel ICE
ν (cSt)	50	125	29	7.7 (@ 40°C)
μ (Pa.s)	0.048	0.134	0.0281	0.007
ρ (kg/m³)	960	1070	970	915
T_{PP} (°C)		-51	-60	-75
k (W/mK)	0.15	0.14	0.15	0.13
c_p (kJ/kg)	1.5	1.498	1.8	1.947
T_{ebol} (°C)			>300	
T_{FP} (°C)	>300	315	260	190



- The use of dielectric liquids is much more efficient than air, with a temperature reduction of about 25 °C at the end of the simulation time;
- the final temperature of 50 °C reached with air, may be well outside the safe range for commercial cells

Conclusions

- Even a **simple** model can provide reliable results in a very short time
- This is useful in many applications where the applicability of a given battery pack has to be assessed
- **Dielectric liquids** are generally much more efficient than air
- However, as shown before, the real cooling efficiency in all predictable scenarios has to be preliminarily assessed on a **case-by-case** analysis


рахмат
danke
謝謝
ngiyabonga
spas
teşekkür ederim
Баярлалаа
mersi
kia ora
barka
welalin
tack
спасибо
faafetai lava
vinaka
спасибі
blagodaram
dank je
misaotra
matondo
paldies
grazzi
mahalo
tapadh leat
kiitos
dankie
dhanyavad
nanni
nandri
mauruuru
köszönöm
thank you
gracias
хвала
asante
manana
bedankt
bayarlalaa
grácie
hvala
enkosi
akun
dankon
aciú
obrigada
tenki
murakoze
djiere dieuf
tau
mochchakkeram
дякую
mamnun
chokrane
dziękuję
chnorakaloutioun
gratias ago
gracies
sulpáy
taiku
go raibh maith agat
sobodi
dekuji
obrigado
mesi
didi madobia
sagolun
sukriya
kop khun krap
ありがとう
tanemirt
grazie
arigatō
takk
dakujem
trugarez
najis tuke
kam sah hamnida
rahmat
terima kasih
rahmet
ευχαριστώ
diolch
dhanyavadagalu
shukriya
merce
мерси
তোমাকে ধন্যবাদ
감사합니다
xièxie
merci

Grazie!