

UN SUB-COMMITTEE OF EXPERTS ON TRANSPORT OF DANGEROUS GOODS
3rd INFORMAL WORKING GROUP MEETING 2016

reliability.safety.power to the acculations!



PRO- LI-ION BATTERIES & SAFETY ASPECTS OF DAMAGED OR DEFECTIVE BATTERIES

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**UN SUB-COMMITTEE OF EXPERTS ON TRANSPORT OF DANGEROUS GOODS
3RD INFORMAL WORKING GROUP MEETING 2016
- UN TESTING REQUIREMENTS ON LARGE LITHIUM BATTERIES -**

HOSTED BY RECHARGE, COSTHA AND PRBA
MARCH 30 – APRIL 1, 2016, BORDEAUX, SAFT

Please note the Annex materials!
Konvolute with criteria, definitions e.c.



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Multi-stage safety concept is used to avoid battery failure.

- ▶ Start by carefully selecting all components...
- ▶ Coordinating them with each other...
- ▶ All safety functions are monitored, ...power output reduced or even switched off as required...
- ▶ Perform safety tests at the maximum limits of specification, and further in some cases way beyond the specs. ...

Nothing must happen during and afterwards these tests that could indicate any hazards for the user, **in transportation** or for the environment. Already during the development stage and when selecting the cells, use of simulation based on measured data is constantly correlated with real event sin the field – very high quality of predictions and safety level!

2016 : To trigger faults that would not be expected under normal transportation conditions.

➤ Transport safety screen.



- ✓ Cells and Batteries,
- ✓ **Automotive standard.**

- ✓ It is a fact, that transportation safety of automotive and qualified batteries is given: multimodal Exemption: Ok?! New UN number required?



- ✓ Cells and Batteries,
- ▶ “Less than 1 in 10 million - 1 in 40 Million cells”. In automotive with the new QSP’s the rate shall be significant lower! ?

**Next: New Safety Assessment
in Germany –(particularly Aviation)
Project started!**

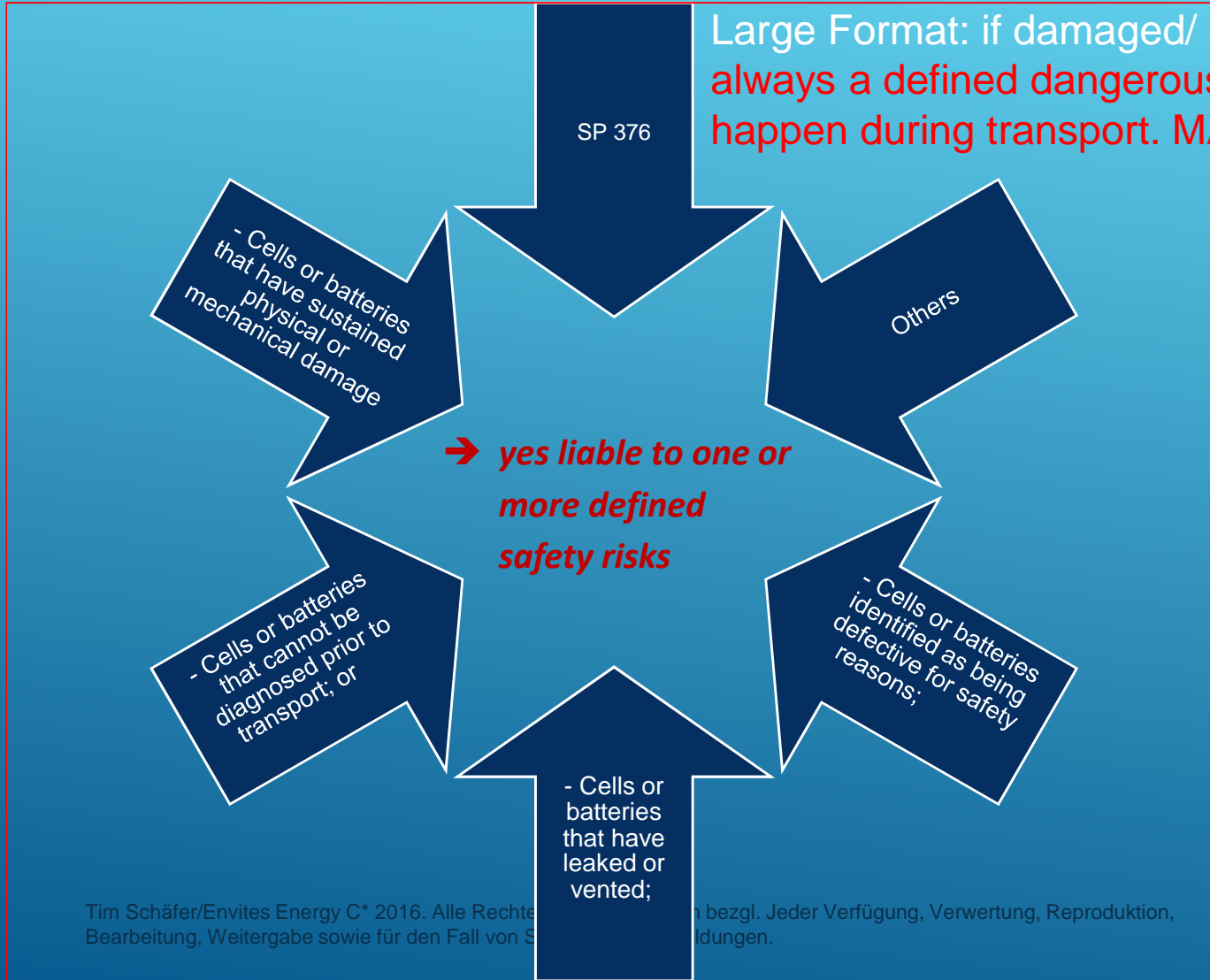
NEW SAFETY ASSESSMENT: INDISPENSABLE!

„TO BE, OR NOT TO BE: THAT IS THE QUESTION.”

WILLIAM SHAKESPEARE

GREEN OR RED! THERE IS ABSOLUTELY ONLY ONE CHOICE ON SAFETY OF LARGE FORMAT BATTERIES

3



1. *Rapidly disassembly*
2. *Dangerously react*
3. *Produce a flame or*
4. *Dangerous heat*
5. *Dangerous emission of toxic,*
6. *corrosive gas or*
7. *flammable gas or vapours*

→ **yes liable to one or more defined risks**



Source ZSW Ulm



Source FAA

Video: Typical risks of prismatic hardcase based battery *in abuse condition.*

ZSW ABUSE TEST RESULT/ FAA (2015)

ZSW= CENTER FOR SOLAR ENERGY AND HYDROGEN RESEARCH ULM GERMANY (E-LAB)
(ENVITES ENERGY CONTRACT)

- ▶ Risk of electrical shock.
- ▶ High fire load. Long time. Fire propagation.
- ▶ Battery can not be discharged (maybe).
- ▶ HF & flashback effect.



Safety Notes



Read all safety warnings and all instructions. Failure to follow the warnings and instructions may result in electric shock, fire and/or serious injury.

Save all safety warnings and instructions for future reference.

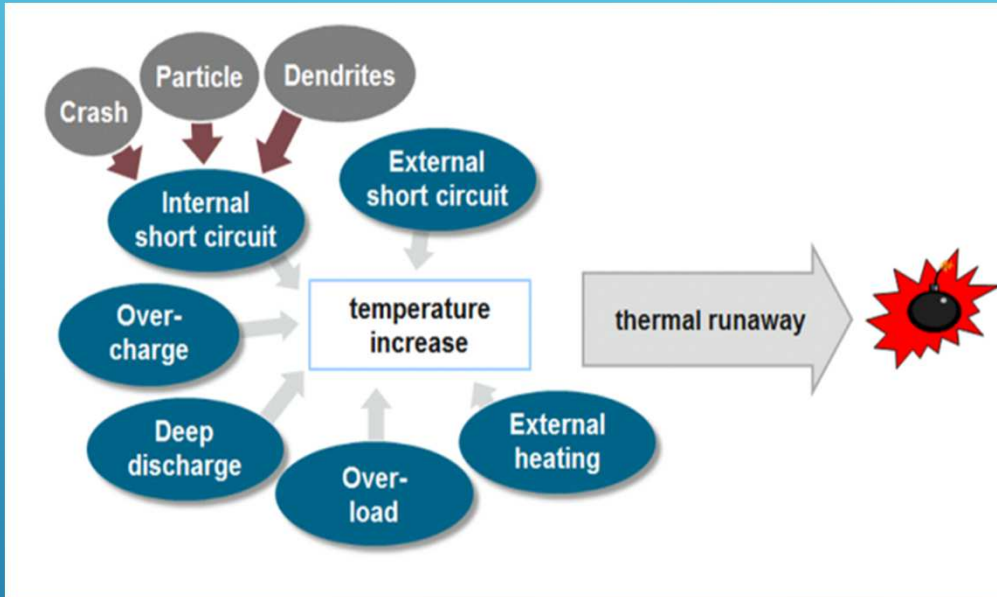
<p>Verätzungen durch Elektrolytleckagen</p>   	<p>Stromschlag bei beschädigten Gehäusen</p>     <p>BOMBEN - DO NOT TOUCH</p>	<p>Brandverletzungen</p>   
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Source: Mercedes-Benz Safety Center, Rastatt 5. Fachtagung Technische Rettung Feuerwehr und Fahrzeugicherheit Berlin

SP 376 , CRITERIA? ADDITIONAL POTENTIAL RISKS AND DANGER.

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Thermal runaway, Extremely rare in transportation (of qualified batteries).



Source: A. Kabza Study Battery Safety, BMVI Germany, NOW, PTJ, ZSW Ulm, 2016, based on Prof. Dr. Jürgen Garche ,UECT tutorial 2014

- In very rare cases, a battery may ignite, for no reason whatsoever. This does not necessarily have to lead to carries a thermal runaway or propagation. However, under certain circumstances, a battery then carries a seriously high fire load bearing subsidiary risks.



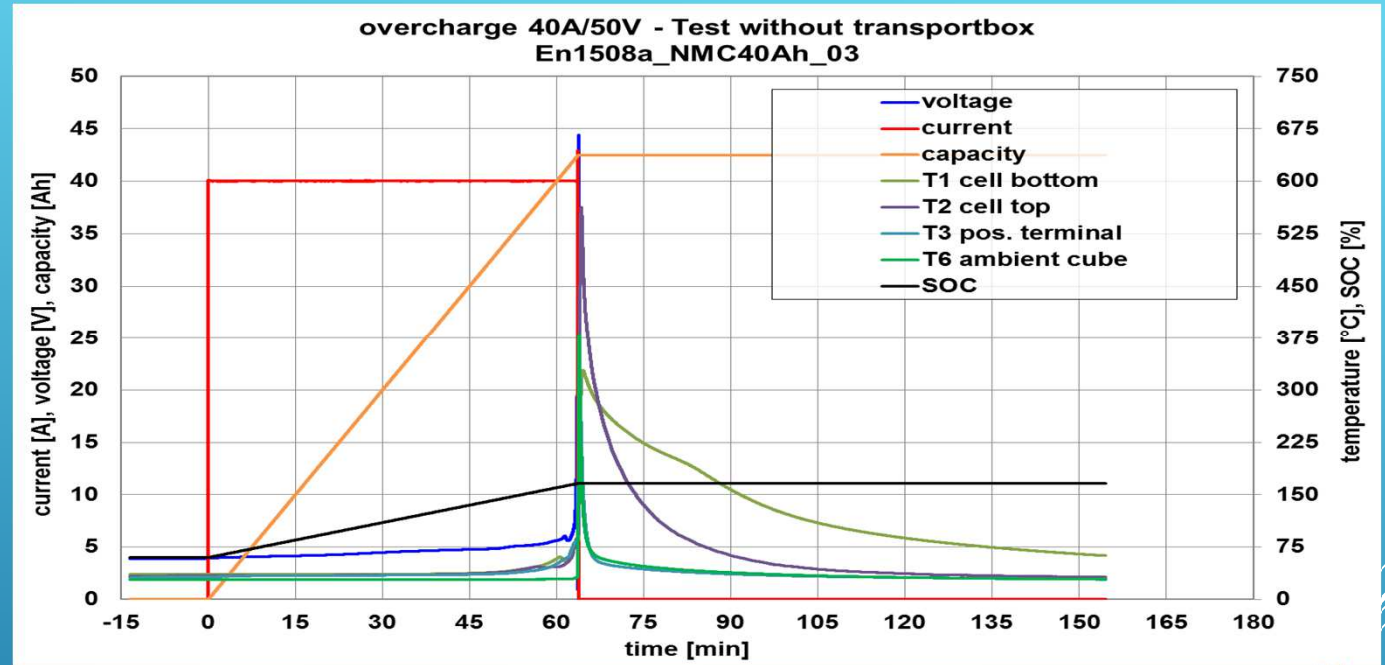
28 – 120 g HF/kWh Battery

Source: Prof. Dr. J. Garche, AABC Europe, January 2016, Mainz

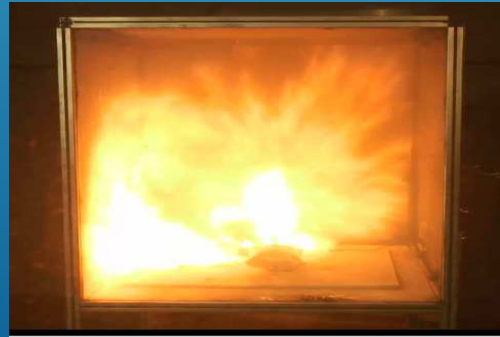


Cell in the box for overcharge

Abuse condition!



Start SOC about 60%. Overcharge for 64 minutes, cell inflation, cell opening, emission of gas and material, ignition, fire, rupture.



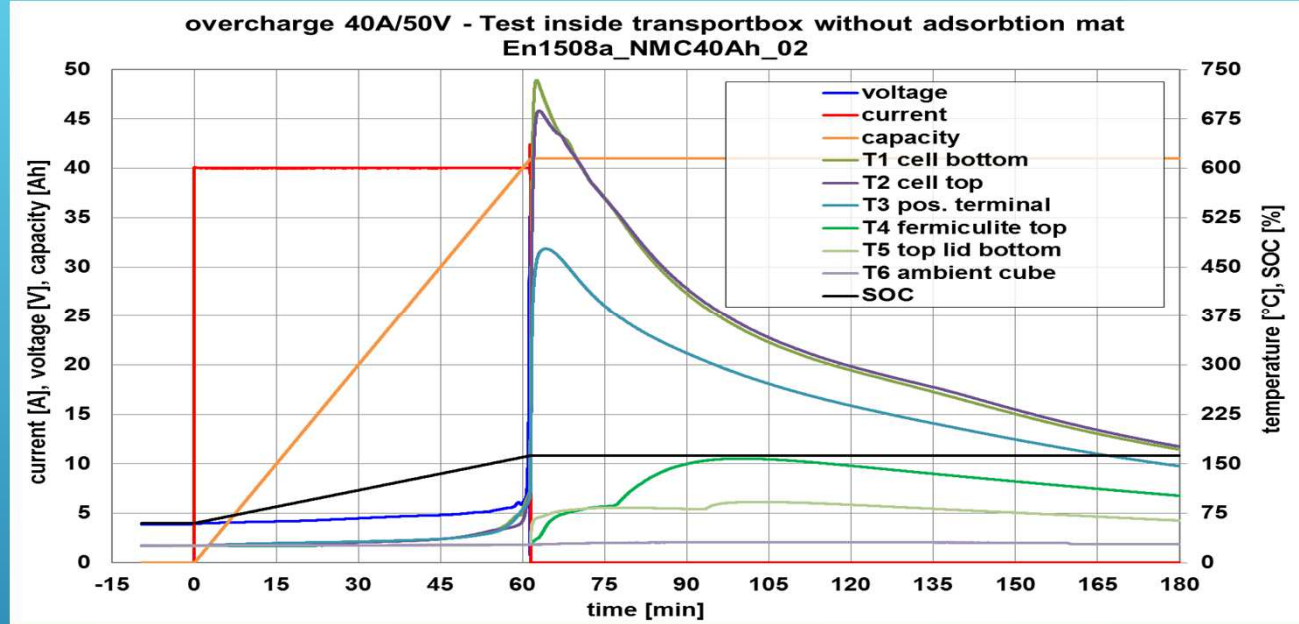
Test cell with packing in wood box and Vermiculite



box with bottom fermiculit



Cell embedded



Start SOC about 60%. Overcharge for 62 minutes, cell inflation, cell opening, emission of gas, 1m³ space permanently filled with white smoke, cell destroyed, molten pouch, emission of black material trapped in the Vermiculit

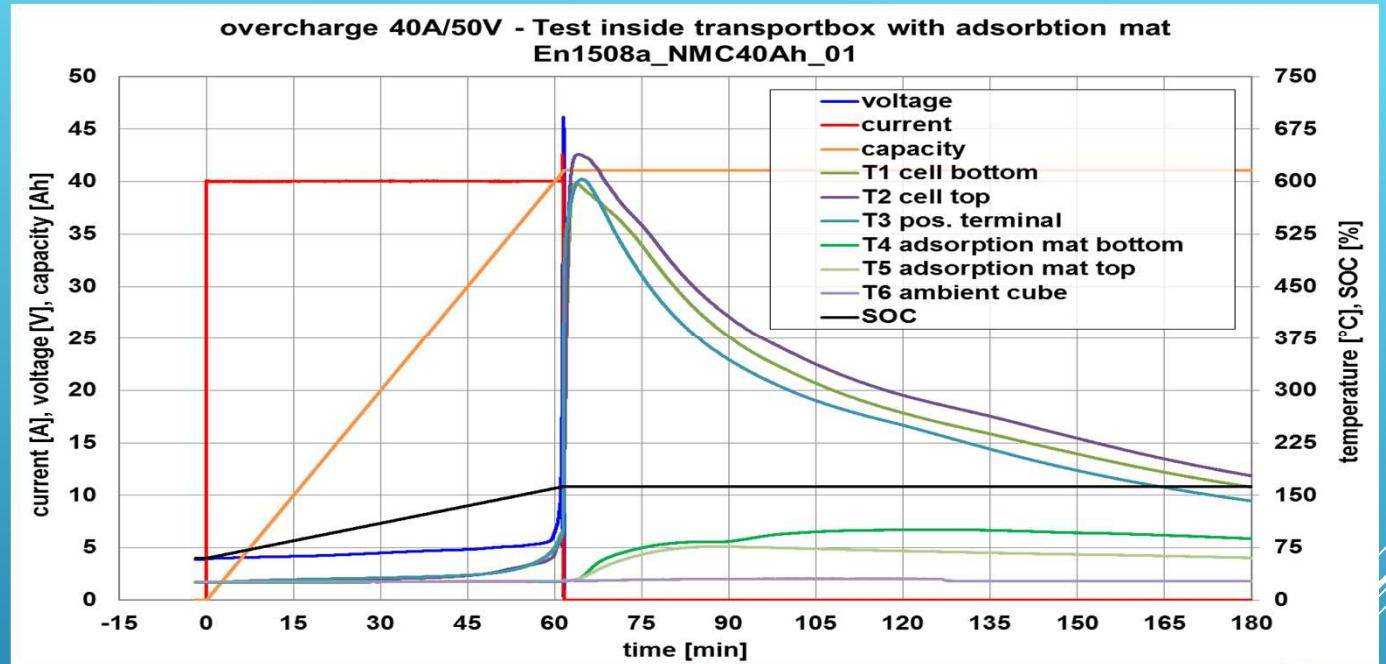




Cell embedded in Vermiculit



Bag with absorption agent (about 100g) at the top of the packaging



Start SOC about 60%. Overcharge for 62 minutes, cell inflation, cell opening, emission of gas, 1m³ space permanently filled with white smoke, cell destroyed, molten pouch, emission of black material trapped in the Vermiculit

Abuse condition!



ANNEX 1 DRY CLOUD = NO RISK EVEN IN THERMAL RUNAWAY



Source National News and Pictures, Dubai, Envites Energy, Nordhausen 2016



reliability.safety.power to the acculations!

What next?

We are working on new packagings
- minimizing all the risks,

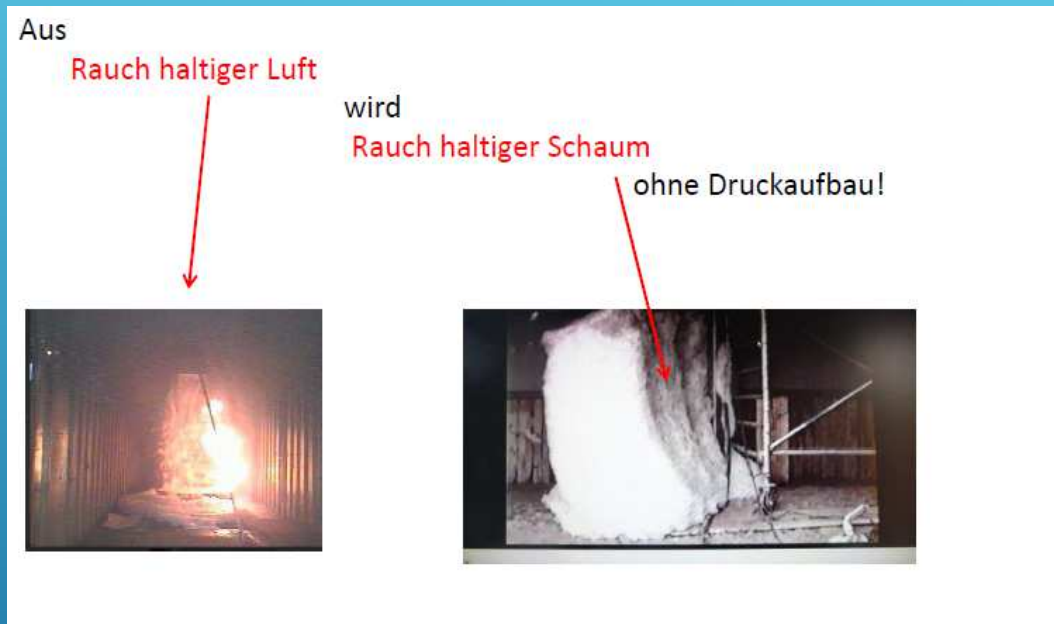
Focus: <700 Wh.

The Suppression of Battery Fires : A new way? Dry Cloud.

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Innovative Process Dry Cloud: EN Norm or NFPA compliance.

(DIN/EN13565-2 as example)



- 600 x foaming
- > 1.200 °C
- Strong stick effect.
- 9 hours stable
- Easy installation, not much costs overall
- Environment clean material

FROM SMOKE TO DRY CLOUD- PRESSURELESS STABLE FOAM FOR HIGH FIRE LOADS
LIKE LITHIUMBATTERIES

Specific Risk/Hazard	Dry Cloud
Jet flames	Strong suppression - no longer perceptible.
Fire	Strong suppression and cooling, stop the propagation effect, reduce the event on minimum: fast and efficient.
Smoke & Pressure	Since smoke is transferred into dry cloud material (solid), sustainable foam. No pressure!
HF- H2 – others , Can be breathed?	Tbd one step to neutralize /Inhibitor- no danger! No restriction on breathing, no dangerous heat (outside containment).
Ignition of explosive gas mixtures / Backfire in the flue gas/Explosion	No free Gas, not possible. No open fire.
Environmental hazard in cleaning or disposal	Material itself is not environmentally dangerous, after the event some used material shall be special waste, in the EU regs no problem to handle.
How long does it works?	It is an engineered solution, for certain application you find normal inspection regime for, durable and returnable for many years. Dry Cloud ist stable still Happy Landing.

DRY CLOUD TECHNOLOGY FOR AVIATION SAFETY- LITHIUM-ION BATTERIES ARE SAFE!

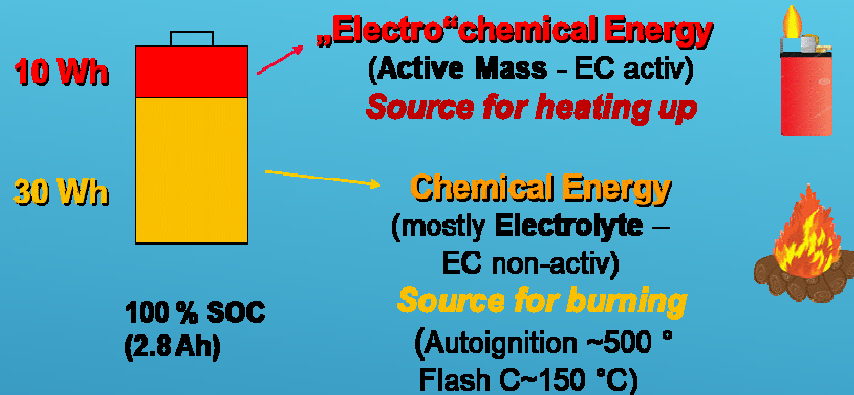
SPECIFIC HAZARDS VS. DRY CLOUD

ANNEX 2 GERMAN STUDY OF BATTERY SAFETY:

RECOMMENDATIONS FOR ACTION FROM “STORAGE AND TRANSPORT”

8 EXAMPLES

30% SOC and practice?



REVIEW 1. -2. WG MEETING WASHINGTON

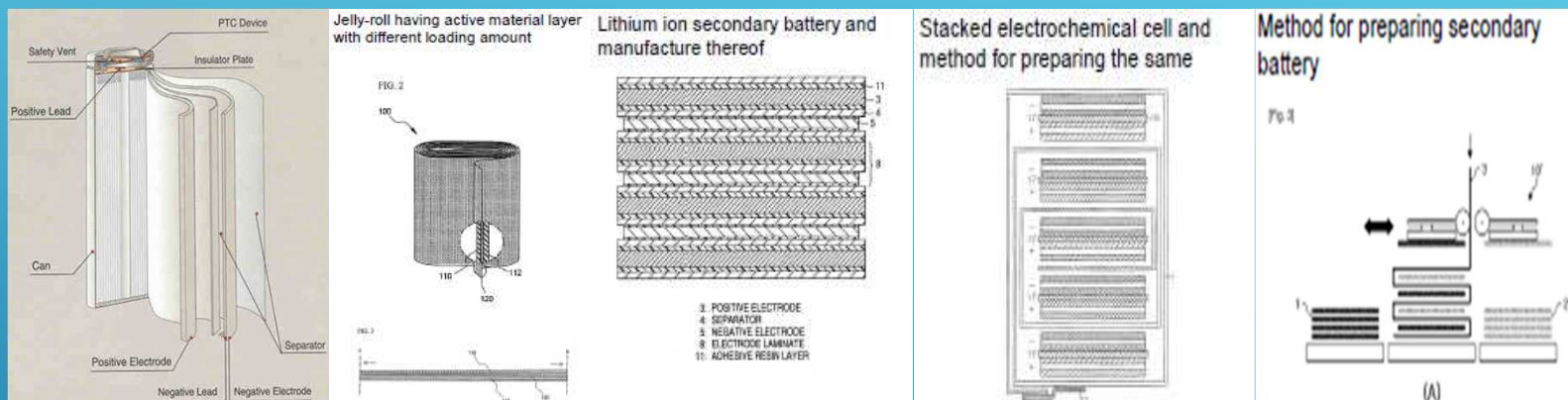
Scientifically battery (+ -)cells are referred to as electrochemical or galvanic cells, due to the fact that they store electrical energy in the form of chemical energy and because the electrochemical reactions that take place are also termed galvanic. Galvanic reactions are thermodynamically favorable (the free energy difference, ΔG , is negative) and occur spontaneously when two materials of different positive standard reduction potentials are connected by an electronic load (meaning that a voltage is derived). The material with the lower positive standard reduction potential undergoes an oxidation reaction providing electrons by the external circuit to the material with the higher positive standard reduction potential, which in turn undergoes a reduction reaction.

High Energy Density Lithium Batteries. Edited by Katerina E. Aifantis, Stephen A. Hackney, and R. Vasant Kumar
© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
ISBN: 978-3-527-32407-1

BATTERIES VS. BATTERY CELLS, NOT ONLY CELLS ?

Tim Schäfer/Envites Energy 2015 www.envites.de envites@envites.de 2. Defintions & 3. Testing Lithium (ion) Batteries
2nd Informal Working Group Meeting 2015-2016
Lithium Batteries ans UN Manual of Tests and Criteria, Washington, DC

- ▶ **Battery Cells** are made of different design, especially with more than one electrode assembly or cell inside (winding, stacking, e.c.). The amendment proposal shall be the base for more clarity and sustained understanding.



- ▶ **“Cell means a (single) encased electrochemical unit (one positive and one negative electrode) which exhibits a voltage differential across its two terminals, and may contain its protection devices.”**

CELL = BATTERY CELL

- ▶ “Cell means a single encased electrochemical unit (one positive and one negative electrode) which exhibits a voltage differential across its two terminals, and may contain its protection devices.”
- ▶ “**Battery** Cell means a (**single**) encased electrochemical unit (**at least** one positive and one negative electrode) which exhibits a **voltage** differential across its (**two (?)**) terminal(s), and may contain **its** protection devices **or other features**.”

Proposal: secondary cell (Li): definition

- **Li-Ion (intercalation), or**
- **Ox-reduction of Li between negative or positive electrode**

→ IEC /EN 62620 (2015)

- IEC 61960 Ed2 “secondary single cell whose electrical energy is derived from the oxidation and the reduction of lithium. It is not ready for use in an application because it is not yet fitted with its final housing, terminal arrangement and electronic control device”.
- IEC 62660 “secondary single cell whose electrical energy is derived from the insertion/extraction reactions of lithium ions between the anode and the cathode.”

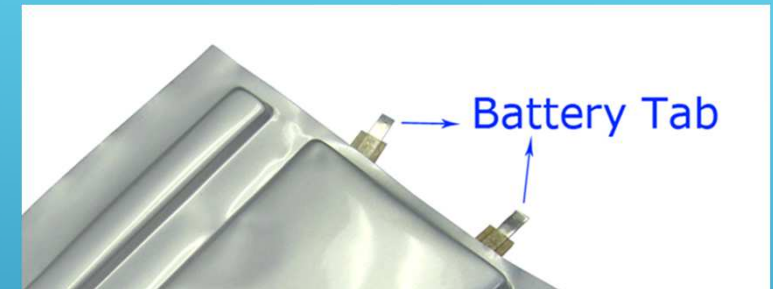


Battery terminals are the electrical contacts used to connect a load or charger to a battery cell, single cell or multiple-cell battery, a battery assembly. These terminals have a wide variety of designs, sizes, and features that often not well documented.

Tabs are Battery Cell terminals in regard of this Manual.



Some Battery Cells offer only 1 real terminal or more, sometimes 5 terminals...



- **Charge Voltage** – The voltage that the battery is charged to when charged to full capacity. Charging schemes generally consist of a constant current charging until the battery voltage reaching the charge voltage, then constant voltage charging, allowing the charge current to taper until it is very small.

Voltage

- ▶ The theoretical standard cell voltage, E_0 (cell) can be determined using the electrochemical series and is given by the difference between the standard electrode potential at the cathode, E_0 (cathode), and the standard electrode potential at the anode, E_0 (anode) [2] as

$$E_0 \text{ (cathode)} - E_0 \text{ (anode)} = E_0 \text{ (cell)}$$

- **Terminal Voltage (V)** – The voltage between the battery terminals with load applied. Terminal voltage varies with SOC and discharge/charge current.
- **Open-circuit voltage (V)** – The voltage between the battery terminals with no load applied. The open-circuit voltage depends on the battery state of charge, increasing with state of charge.

WHAT`S ABOUT A BATTERY CELL NOT ACTIVATED IN TRANSPORTATION ?

- **Nominal Voltage (V)** – The reported or reference voltage of the battery, also sometimes thought of as the “normal” voltage of the battery.

- 1. Safety and Li-Ion Batteries.
- 2. Damaged or defective Batteries (with potential risk tendency) in transport.
- 3. Review 1.-2. WG meetings Washington and Annex 1 and 2

Many Billions of batteries are safely transported annually:
It must be remembered that on the field, roughly 6 billion Lithiumbatteries have been shipped 2015, yet the field failure rate is very low.

What is the actual percentage danger prone batteries?
What events are based on the residual risks Li-ion batteries actually?

which accounts for the relative safety of cells and battery packs in the field (estimate of failure rates of lithium ion rechargeable battery cells is less than 1 in 10 million¹ with some estimates of failures of 1 in 40 million cells.²

Source: BMVI –Germany: Studie Batteriesicherheit 2016

1. B. M. Barnett, E. P. Roth, K. E. Thomas-Alyea, and D. H. Doughty, "Abuse Tolerance versus Field Failure: Two Different Issues for Lithium-Ion Safety," presented at the *International Meeting on Lithium Batteries*, June 2006.
2. J. Dahn and G. M. Erlich, "Lithium Ion Batteries," p. 26, *Linden's Handbook of Batteries*, 4th edition, T. B. Reddy, Ed., McGraw Hill, 2011.

CONTENT

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- Objectives and requirements are defined by the key performance parameters.
- In the process, all aspects of a battery system always need to be validated.
- There are many factors that determine whether or not a system design is safe- and the battery cell itself naturally plays a central role.
- Safety tests on high level are always performed at all levels.
- In particular, will beeing able to translate the properties of the battery components into the overall properties of the battery and thus improve efficient the safety.
- A multi-level safety assessment is used.

SAFETY IS THE SINGLE MOST IMPORTANT CRITERION

- Since the development of lithium-ion-batteries started, we have already come a long way in terms of the safety of battery systems.
- Safety of modern cells has been significantly improved in comparison to cell behavior 10 or 15 years ago. (materials, design-in, **safety elements, qualification, process** & more.)
- In addition, major progress has been made with regard to our expertise in production and quality control.
- Hazard potential can already be dramatically reduced through careful selection of the appropriate system.
- Next integration is safety function of intelligent BMS/BMMS, including systems for monitoring the cell temperature and voltage (& more).
- Ultimately, the overall mechanical design takes into account all of the thermal and mechanical requirements.

A BATTERY IS TESTED IN DETAIL. BATTERIES ARE SAFE IN TRANSPORTATION.
THE CONTENTS WILL NOT LEAK.

Li-ion batteries are today classified as Dangerous Goods for transport according to the UN Model regulation for the Transport of Dangerous Goods.

- ▶ They are classified under CLASS 9 Dangerous Goods due to their dual hazard properties associated with their chemical and electrical content.
- ▶ The Manual of Tests and Criteria contains criteria, test methods and procedures to be used for classification of dangerous goods according to the provisions of Parts 2 and 3 of the United Nations Recommendations on the Transport of Dangerous Goods, Model Regulations, as well as of chemicals presenting physical hazards according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS). As a consequence, it supplements also national or international regulations which are derived from the United Nations Recommendations on the Transport of Dangerous Goods or the GHS.

1. QUALIFIED LI-ION BATTERIES ARE NOT DANGEROUS IN THE TRANSPORT !?

Batteries liable to risk in transportation only if damaged or defective, how many in the field?

“less than 1 in 10 million - 1 in 40 Million cells”. In automotive with the new QSP`s the rate shall be significant lower!

Many Billions of batteries are safely transported annually:
It must be remembered that on the field, roughly 6 billion Lithiumbatteries have been shipped 2015, yet the field failure rate is very low.

What is the actual percentage danger prone batteries?

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which accounts for the relative safety of cells and battery packs in the field (estimate of failure rates of lithium ion rechargeable battery cells is less than 1 in 10 million¹ with some estimates of failures of 1 in 40 million cells.²

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2. J. Dahn and G. M. Erlich, “Lithium Ion Batteries,” p. 26, *Linden’s Handbook of Batteries*, 4th edition, T. B. Reddy, Ed., McGraw Hill, 2011.

BATTERIES, QUALIFIED UNDER AUTOMOTIVE QSP`S ARE SAFE.

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In general, the following basic principles apply to the further development:

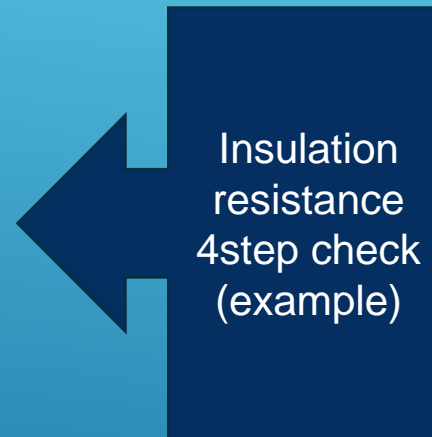
- The design of components and systems reflects the high quality and safety requirements in the industry and ensures that corresponding risk potential can be minimized.
- ▶ The monitoring of safety requirements for components and systems across the individual levels of product development and during production of the components and systems delivers high quality standards for the products (further in service, after market)
- ▶ Appropriate test methods are employed during the product and process development to continuously monitor the effectiveness of the measures.

To trigger faults that would not be expected under normal operation and transportation conditions.

PRINCIPLES : DEVELOPMENT OF LI-ION BATTERIES

QSP measures EV cell – example

- ... Aging 28 hours in >25 °C
- Precharge
- ...
- 2. Aging 24 hours in >25 °C
- 1st Grading
- 3. Aging 15 DAYs in 25 °C
- 2nd Grading
- Final Audit
- Stock-Test
- Transportation Integration check.



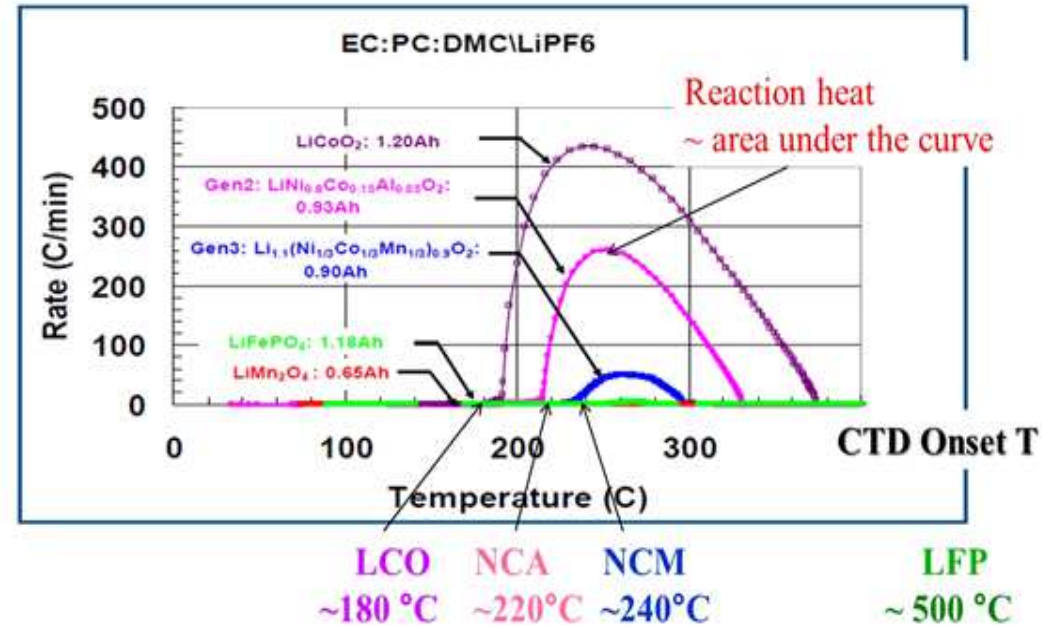
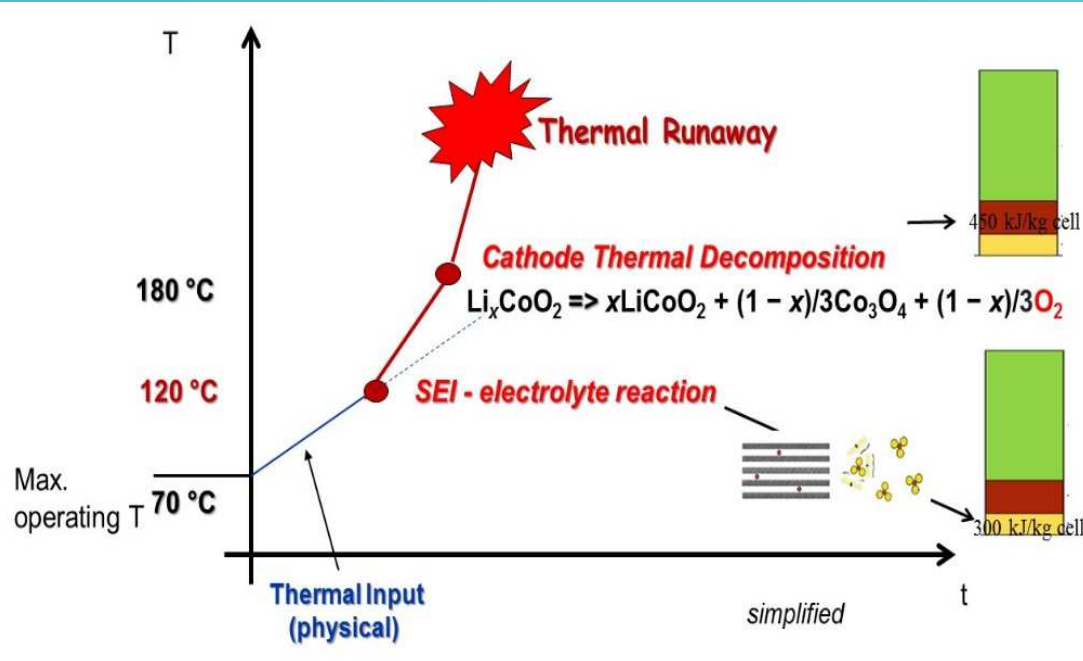
Source : Tim Schäfer TU Braunschweig Diagnose Batterien Februar 2015

EXAMPLE: CA. 20 DAYS TO CHECK THE QUALITY/SAFETY IN QSP/ENDCONTROL OF CELLS

27

- ▶ Before each transport batteries are tested/checked for safety/integrity. (damaged/defective).
- ▶ Automotive QSP.
- ▶ Development and production are driven and determinate by the principles of risk avoidance.
- ▶ System tests are performed in accordance with the recognized rules of sound engineering practice and in accordance with the relevant normative requirements.
- ▶ These include functional safety and reliability to ensure safe operation and transportation, when using the vehicle, as well as compliance with the applicable crash safety standards.
- ▶ A multi-level safety assessment is used to examine all safety aspects from the cell chemistry and layout to overall battery system or module.

CRITERIA FOR TRANSPORTATION SAFETY. AN (MULTIMODALLY) EXEMPTION FOR SUCH QUALIFIED BATTERIES IS THE NEED OF THE HOUR.





Jet flames,
Dangerous heat,
HF Phase,
Massive smoke, fast, DANGER! H2...
Long duration of fire: 13s25Ah roughly 1 hour, and more?
Propagation issue,
High fire load...

ABUSE, ...!

- 1. Safety and Li-Ion Batteries.
- 2. Damaged or defective Batteries (with potential risk tendency) in transport.
- ▶ **SP376 → SP 376** :Lithium ion cells or batteries and lithium metal cells or batteries identified as being damaged or defective such that they do not conform to the type tested according to the applicable provisions of the Manual of Tests and Criteria shall comply with the requirements of this special provision.

For the purposes of this special provision, these **may include, but are not limited to:**

- ▶ - Cells or batteries identified as being **defective for safety reasons**;
- ▶ - Cells or batteries that **have leaked** or vented;
- ▶ - Cells or batteries **that cannot be diagnosed prior to transport**; or
- ▶ - Cells or batteries that have **sustained physical or mechanical damage**.

CONTENT 2.

Thesis: Large Format: if damaged/ defective **for safety reason, always a defined dangerous risk moment could maybe happen during transport.**
MAYBE!