# LITHIUM-ION BATTERIES

Dr David Rose

Regional Director Singapore Office

Hawkins

Leaders in forensic investigation

# Overview and learning objectives

**Part 1**

- A quick overview of Hawkins
- Types of lithium battery
- Construction of cells and banks of cells
- Pros & cons of using lithium batteries
- The causes of energetic failures
- Fire investigation challenges

**Part 2**

- Classification
- Shipping according to International and National requirements.
- Common problems encountered during shipping.
- Fires on ships.
- Fires at recycling centres.
- Case Study of the proof of causation.

- In no particular order…………

# Background

- Hawkins was established in Cambridge in 1980.
- Originally focused on fire investigation, we have expanded to cover 50+ different areas of specialism.
- Specialises in forensic root cause analysis, expert witness services and engineering consultancy to the insurance, legal, risk management and commercial sectors.
- Hawkins is solely employee-owned, allowing us to deliver exceptional customer service and technical expertise to all our clients.
- We have over 100 experts with impressive academic credentials, diverse specialisms and practical industrial experience.

# International presence

# Our expertise

**Fire & Explosion**

- Vehicle & machinery fires
- Fires in buildings
- Fire stop and spread
- Fire modelling
- Explosions

**Road Traffic Collisions**

- Collison reconstruction
- Vehicle examinations

**Crime & Fraud**

- Forensic accountancy
- Insurance fraud
- Major crime investigation

**Cyber, Digital & Technology**

- 3D modelling
- Data recovery
- Digital forensics
- Video analysis

**Engineering**

- Electrical / Electronics
- Mechanical
- Chemistry & process
- Power & energy

**Built Environment**

- Acoustics & vibration
- Forensic Architecture
- Civil engineering
- Fire Engineering
- Flooding & hydrology
- Health & Safety

**Marine**

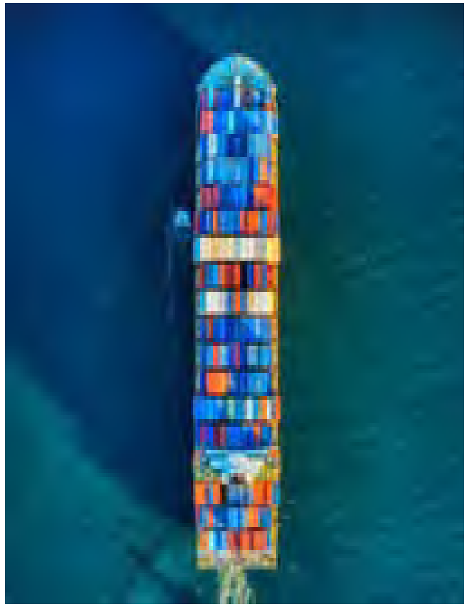
- Cargo spoilage
- IMDG / IMSBC cargo
- Liquefaction
- Master Mariner

**Materials, Chemistry & Biology**

- Contamination / pollution
- Metallurgy
- Composites
- Plant pathology

**Personal Injury**

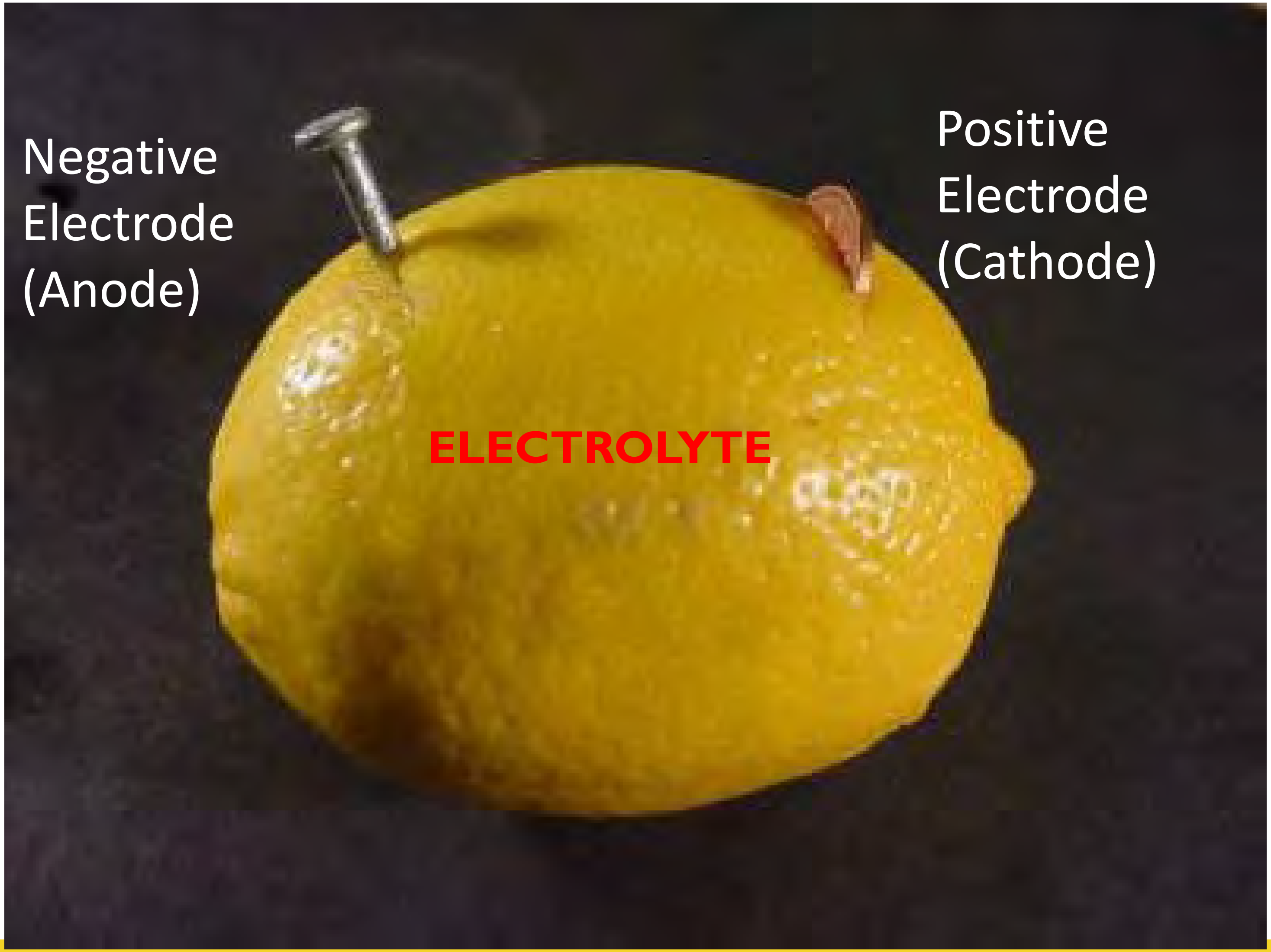
- Construction Injuries
- Falls from height
- Lifting operations
- Manual handling



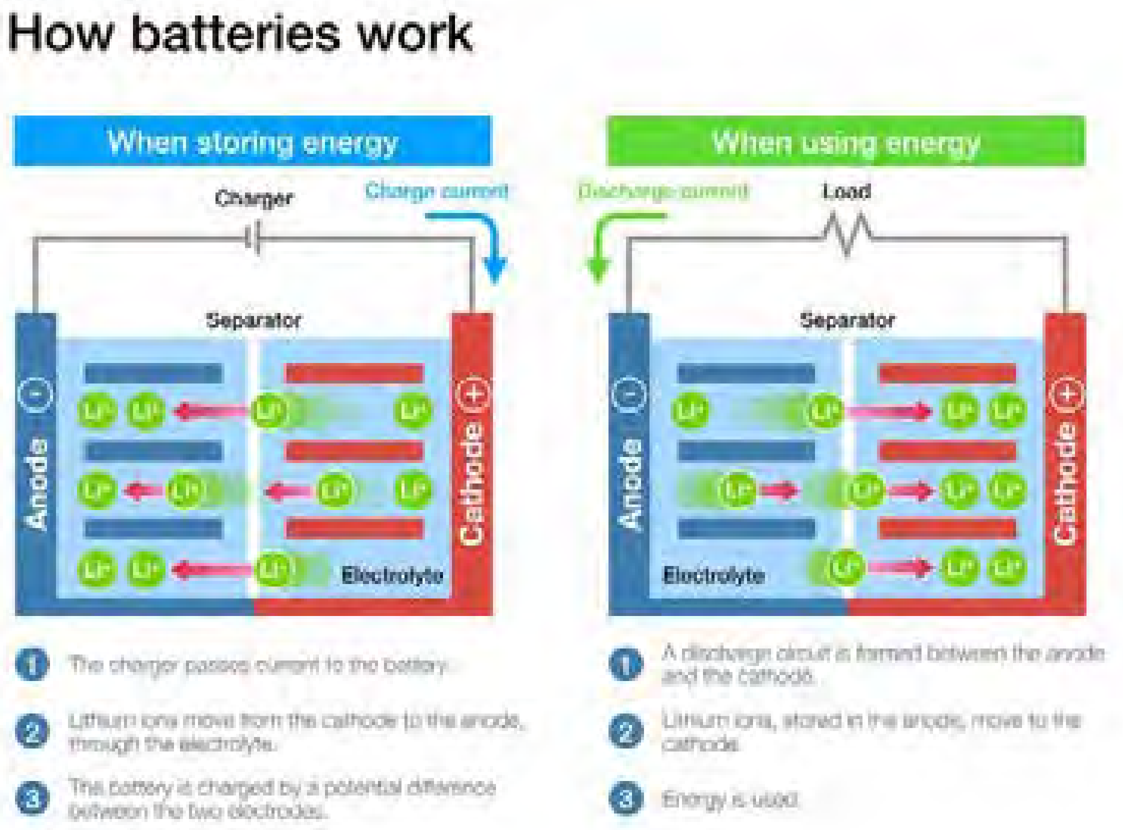
# PART I

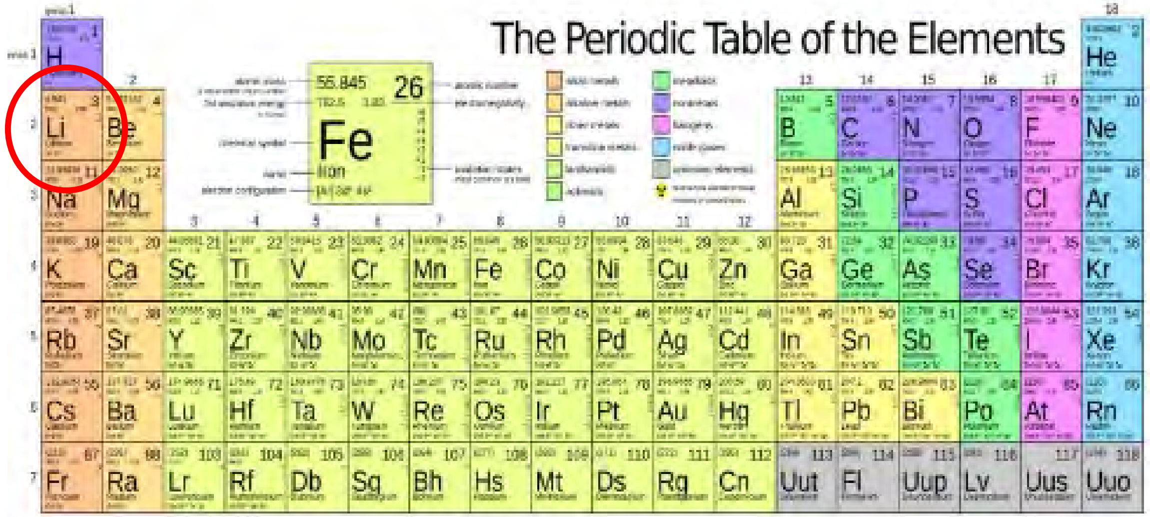
The Design and Construction of Cells

# How a battery cell works

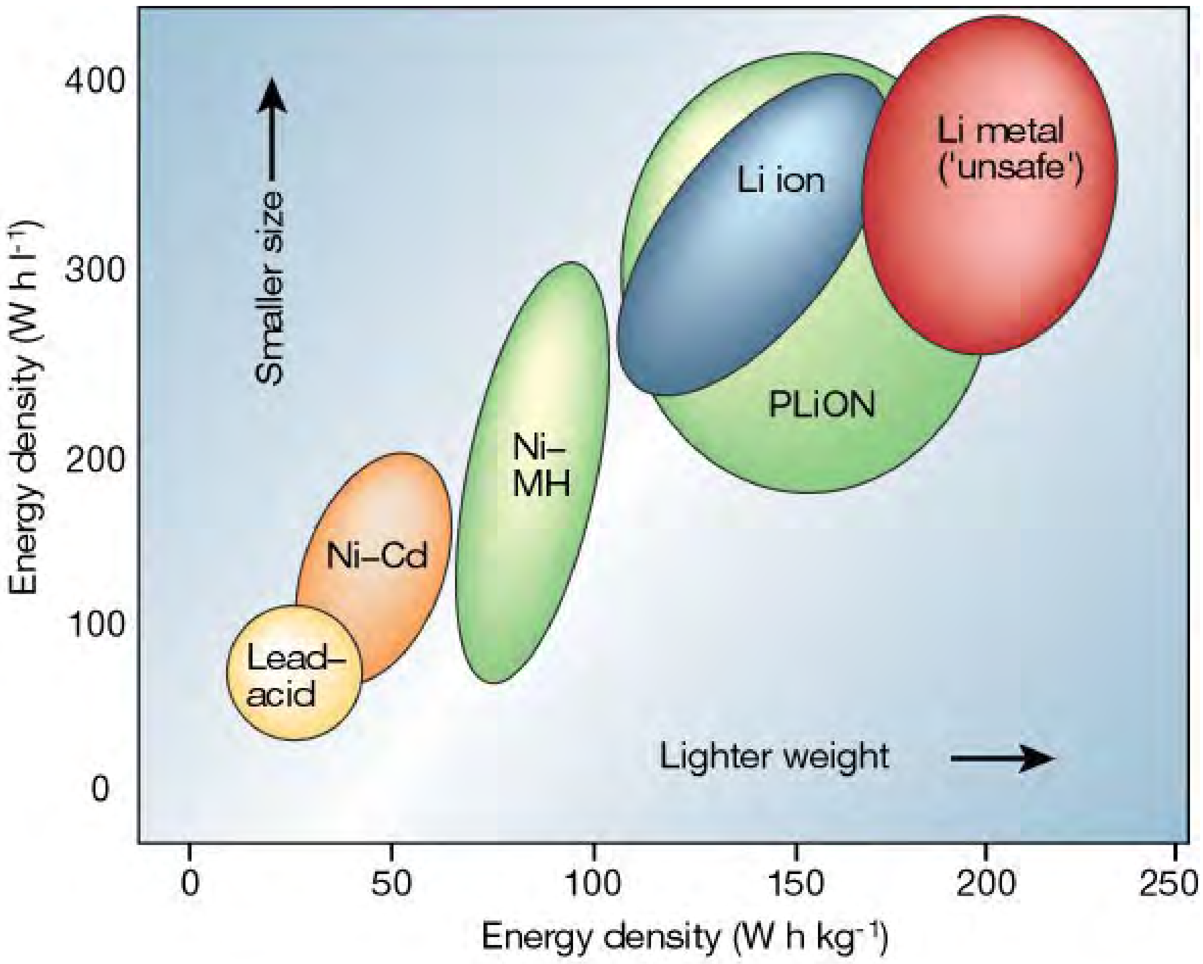


# Lithium-ion cell operation



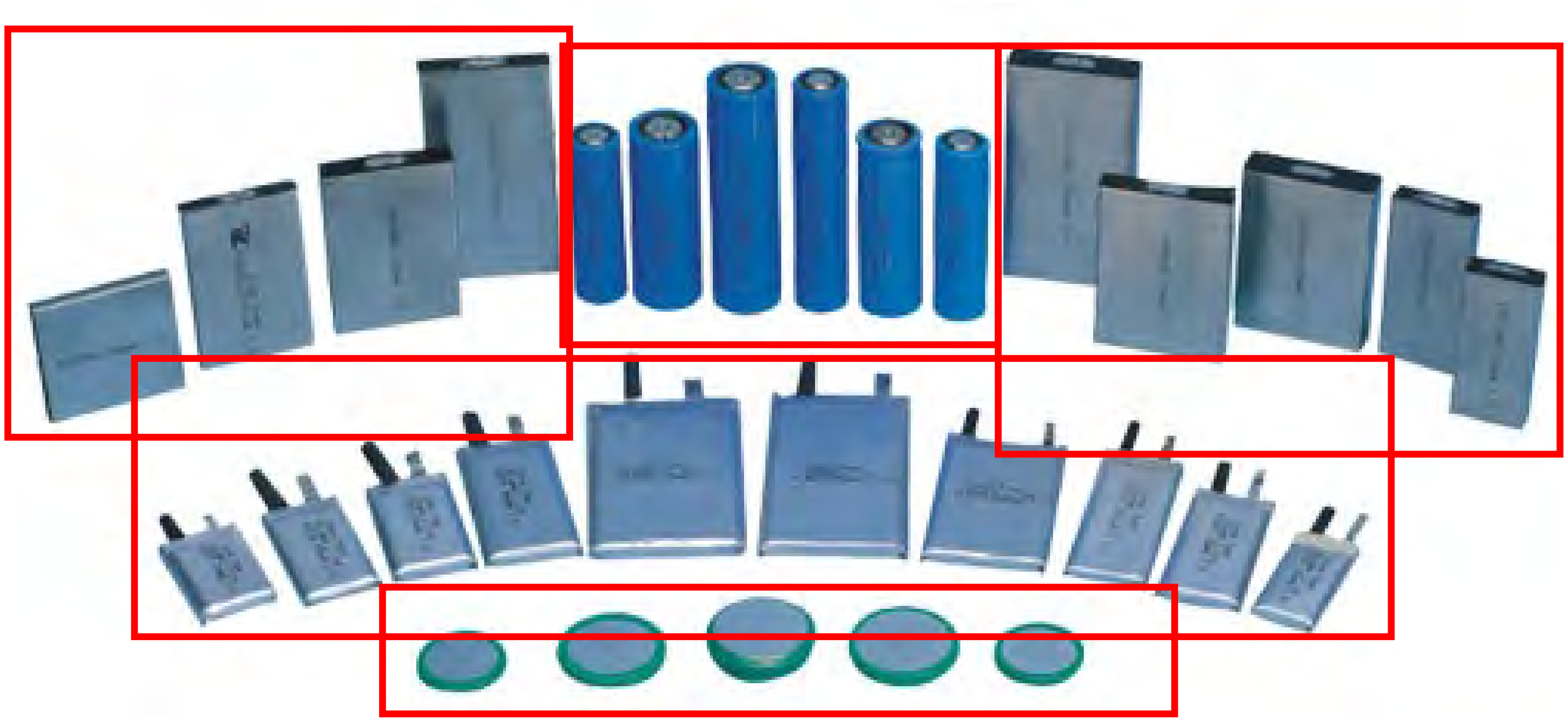
# Lithium battery applications





Sacrilege!

# Form factors



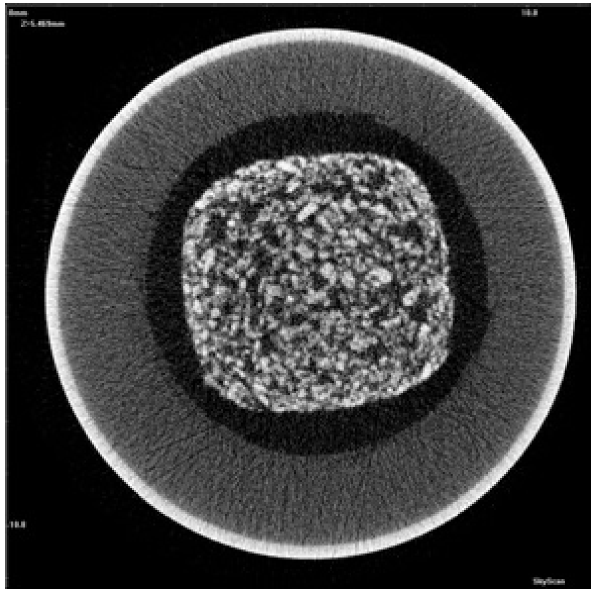
Source: Dr Quinn Horn

# 18650 cylindrical cells

- Slightly larger than AA cell
- 18mm x 65mm
- 3.7 V terminal voltage
- 1500 – 3500 mAh capacity
- Common size used in electric vehicles, electric bikes/scooters, laptops etc.

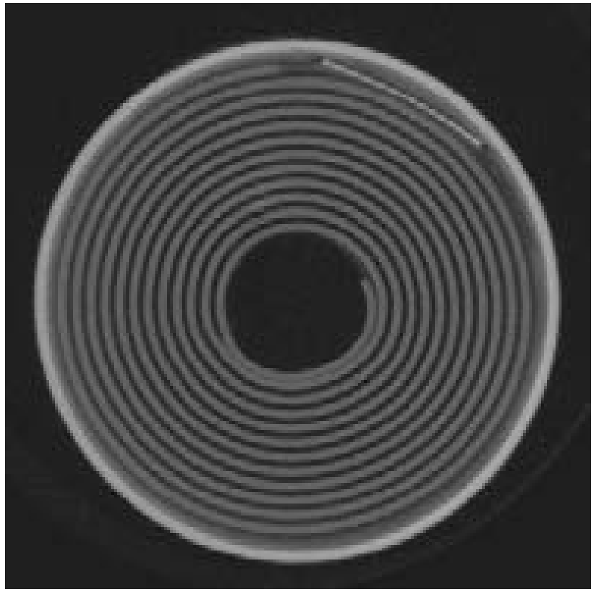
# CT Scans of different cell chemistries

Standard Alkaline



Nickel-metal hydride

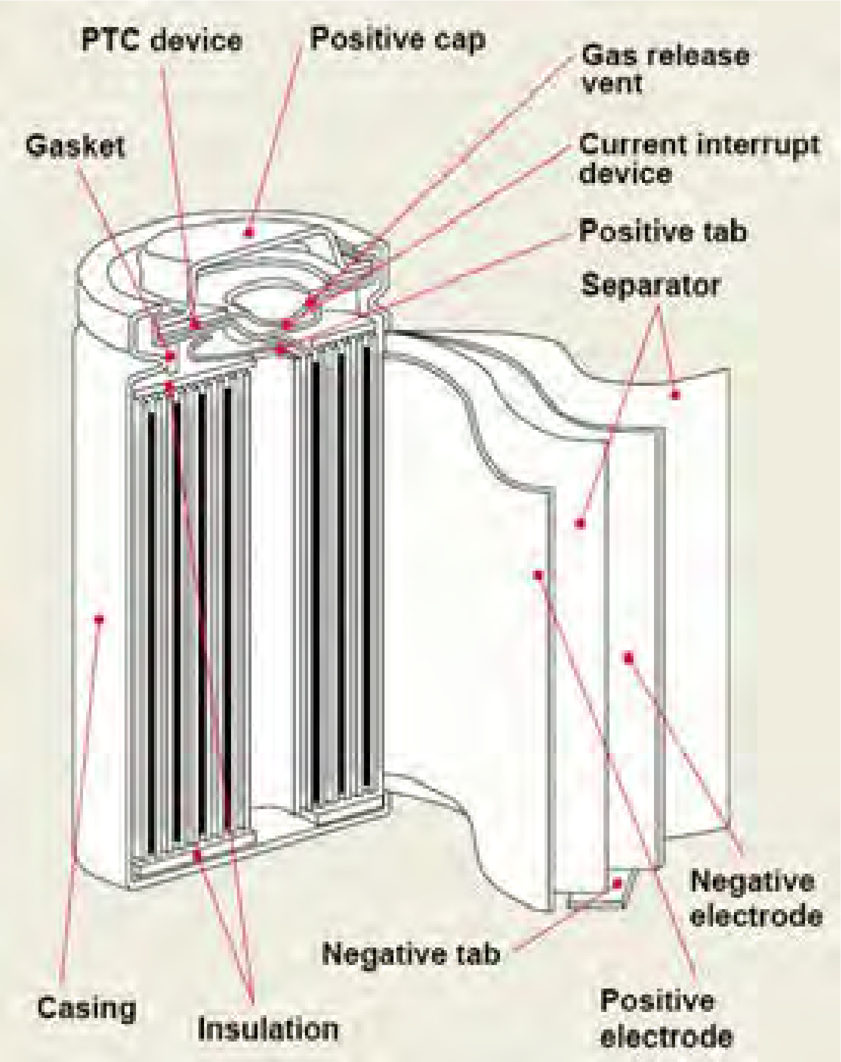
Lithium



Source: Dr Quinn Horn

# Construction of 18650 cells

**Safety devices:**
- PTC device
- Gas release vent
- Current interrupt device



# The active components of cells

The aluminium cathode is coated with a powdered metal oxide referred to as the active material. The active material used varies, as the choice affects the performance of the cell.

The copper anode is coated with a powered carbon material, which in many cases is graphite.

The electrolyte is typically lithium hexafluorophosphate (LiPF6) dissolved in an organic solvent (we cannot use an aqueous solvent as the Lithium would react with it).

# Naming convention

The predominant properties desired in a cell are low cost, high energy-density and a long life, but the selection of a cell design is a little more complicated than that....

This might be a good time to tell you about cell types....

- Li-ion cells are often marked with a three-letter code that describes the cell construction. The naming convention of cells is standardised to prevent confusion.
- Taking a cell marked "ICR 18650", the 'I' stands for Li-ion, the 'R' stands for round cell.

- The C indicates that a cobalt-containing oxide is the dominant component coating the cathode.
- 'N' stands for nickel/manganese oxide coated cathode.
- 'M' stands for a lithium manganese oxide based coating etc.

Hawkins

# Cathode properties

- Some cathodes offer excellent safety and lifespan, but at a higher cost and reduced performance compared with other formulations.
- Blending cathode materials can enhance the cell's performance.
- The drawbacks of Li-cobalt are a relatively short life span and low thermal stability.
- The cycle and calendar life of Li-ion with manganese spinel cathodes are limited, but low internal cell resistance enables fast charging and high-current discharging with moderate heat buildup.

# Anode properties

- The choice of active material on the anode is more limited.
- Graphite offers high electrical conductivity, low cost, and stable structure.
- Silicon offers higher energy density but faces challenges in terms of volume expansion and shorter cycle life.
- Some anode iterations will also 'dope' graphite anodes with a small amount of silicon to improve performance characteristics and energy density.
- Batteries with lithium titanate anodes are typically used in electric powertrains, UPS and solar-powered street lighting.

# Cell uses

- Its high specific energy makes Li-cobalt the popular choice for mobile phones, laptops and digital cameras.

- Li-ion cells with manganese spinel's low internal cell resistance enables fast charging and so these cells are used for power tools and medical instruments, as well as hybrid and electric vehicles.
- One of the most successful Li-ion systems is a cathode combination of nickel-manganese-cobalt (NMC). NMC is the battery of choice for power tools, e-bikes and other electric powertrains.

- Li-phosphate is often used to replace the lead acid starter battery. Four cells in series produce 12.80V, a similar voltage to six 2V lead acid cells in series.

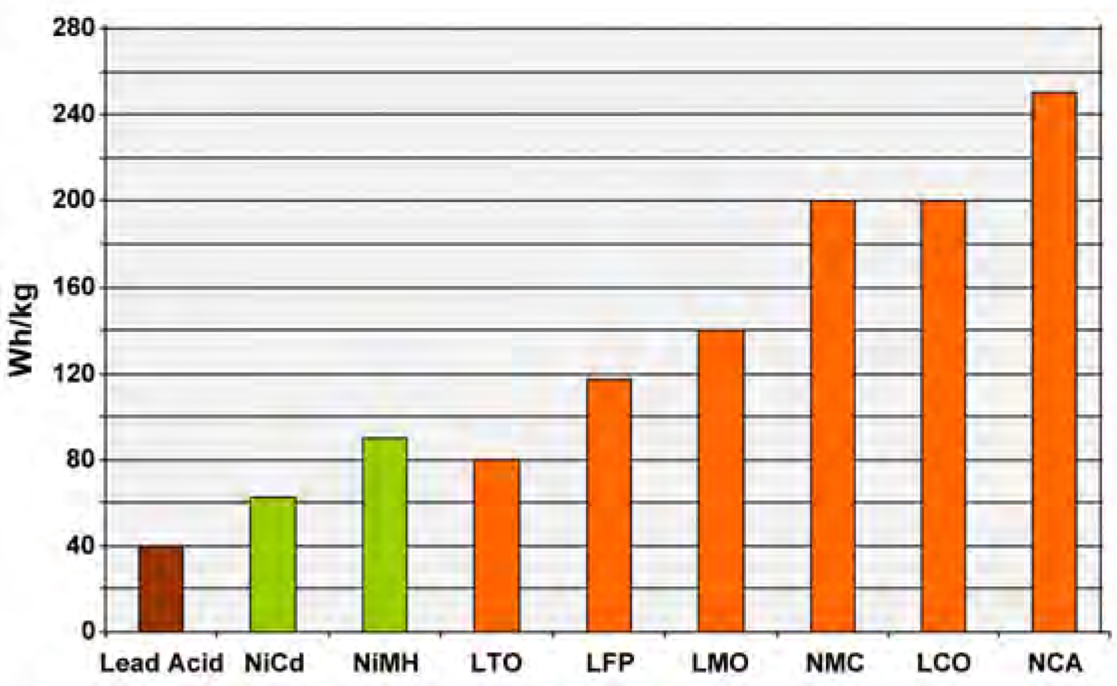
Hawkins

# Why use Li-ion cells?

- A commonly shown graph* gives a good answer. It compares the specific energy of lead-, nickel- and lithium-based systems. The Lithium-aluminium (NCA) cells look like clear winners.

However…

- In terms of specific power and thermal stability, Li-manganese (LMO) and Li-phosphate (LFP) are superior.




- Li-titanate (LTO) may have low capacity but this chemistry outlives most other batteries in terms of life span.

  It also has the best cold temperature performance.

* https://batteryuniversity.com/article/bu-205-types-of-lithium-ion

Hawkins

# Banks of 18650 cells (series and parallel)

The Battery Management System (BMS) is essential for the correct charging and discharging of the battery pack

# Types of lithium battery failures

**Non-Energetic**

- Loss of capacity
- Increase in internal resistance (lower current output)
- Occurs over time
- Most batteries fail in this way

**Energetic**

- Thermal runaway – controlled
- Thermal runaway - uncontrolled

# Causes of *energetic* lithium battery failures

- Manufacture
- Handling
- Use / Mis-use

# What could possibly go wrong?


# What could possibly go wrong?

# The phases of energetic lithium battery failures

Generally, there are four common phases

1- The initiating fault.

We have discussed these

2 - Thermal runaway

3 - Off gassing.

4 - Fire.

# Evolved gases

- A Li-ion cell involved in a thermal runaway will often release a white vapour cloud that contains many different chemicals. These include hydrogen gas, a very flammable material.

- The main hazard comes from what the battery cells are contained within. For example, many vehicles and consumer products contain significant quantities of plastic that liberate vast quantities of toxic smoke during a fire.

- The chemicals produced by a battery failure and a plastic fire are broadly the same, which given the component parts of a cell is not surprising.

- The more exotic chemicals liberated by a battery fire are water-soluble so perhaps not all is lost?

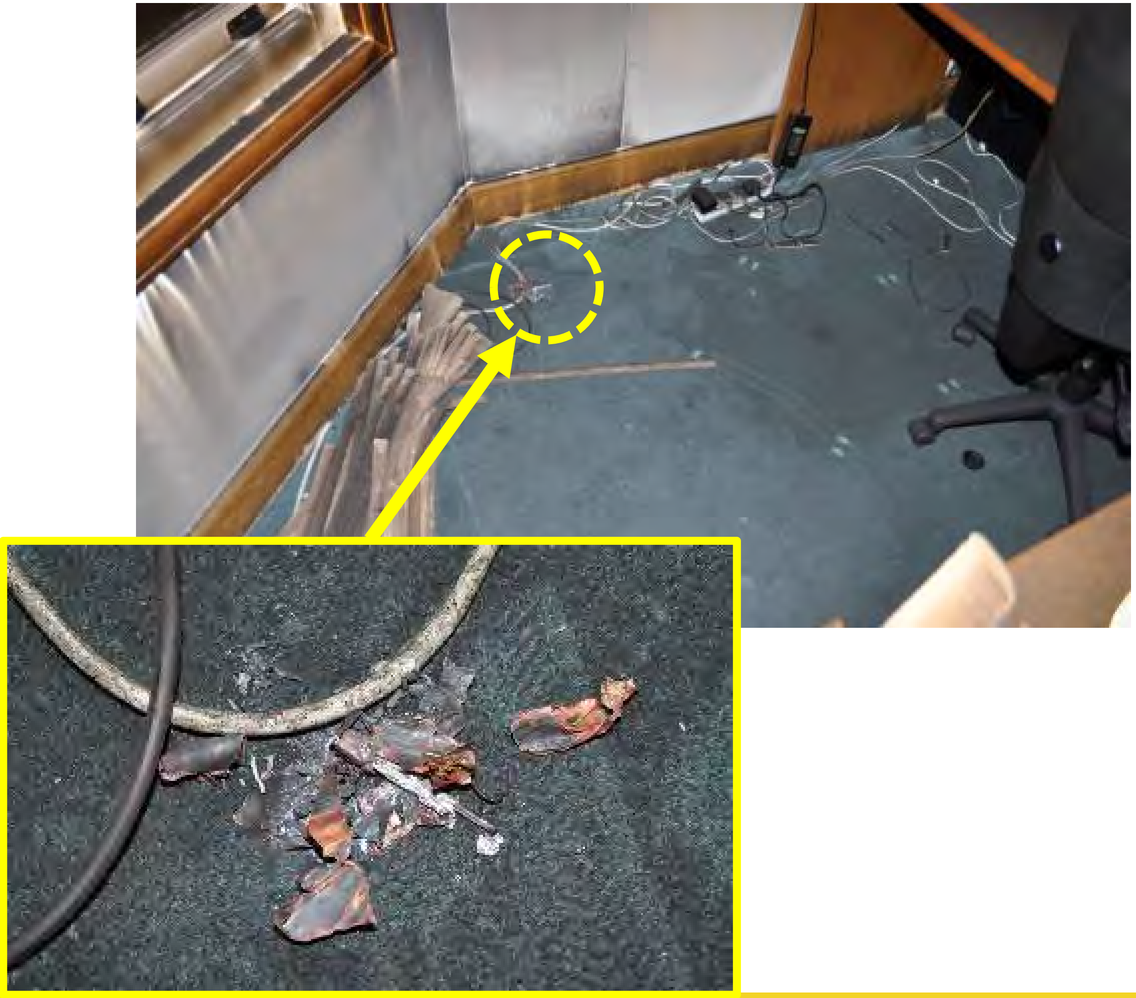
# Time for a video


[E-bikes explode in fireball after they were first extinguished at Seaford Meadows | 7 News Australia (youtube.com)]

# Fire investigation challenges

- Cause or effect?  Sometimes difficult to tell if cell failure was the cause of the fire or not.
- Proving the provenance of the cell.
- Was the fire deliberate?
- What was the failure mechanism?
- Are there exemplar cells available for inspection / analysis?
- Some cells have no circuit protection.
- Has the cell been projected across a compartment and started a fire remote from the charger?
- Do we have to excavate a large area to find all the component parts?

# Fire investigation challenges



# Investigation techniques

- Get exemplars!

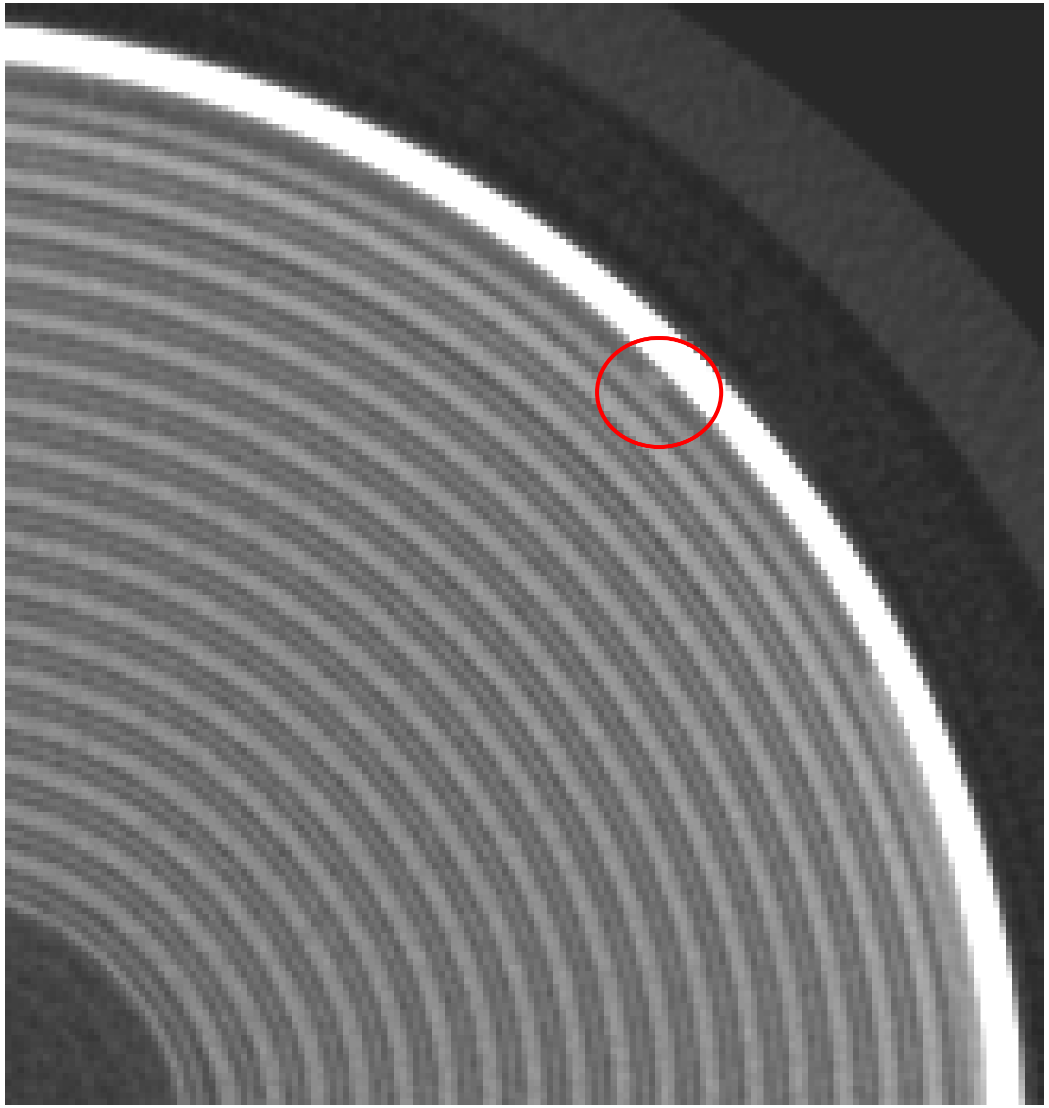
- The physical evidence of a causative battery fault is generally subtle.
  - A physical disassembly risks disturbing / destroying that evidence.

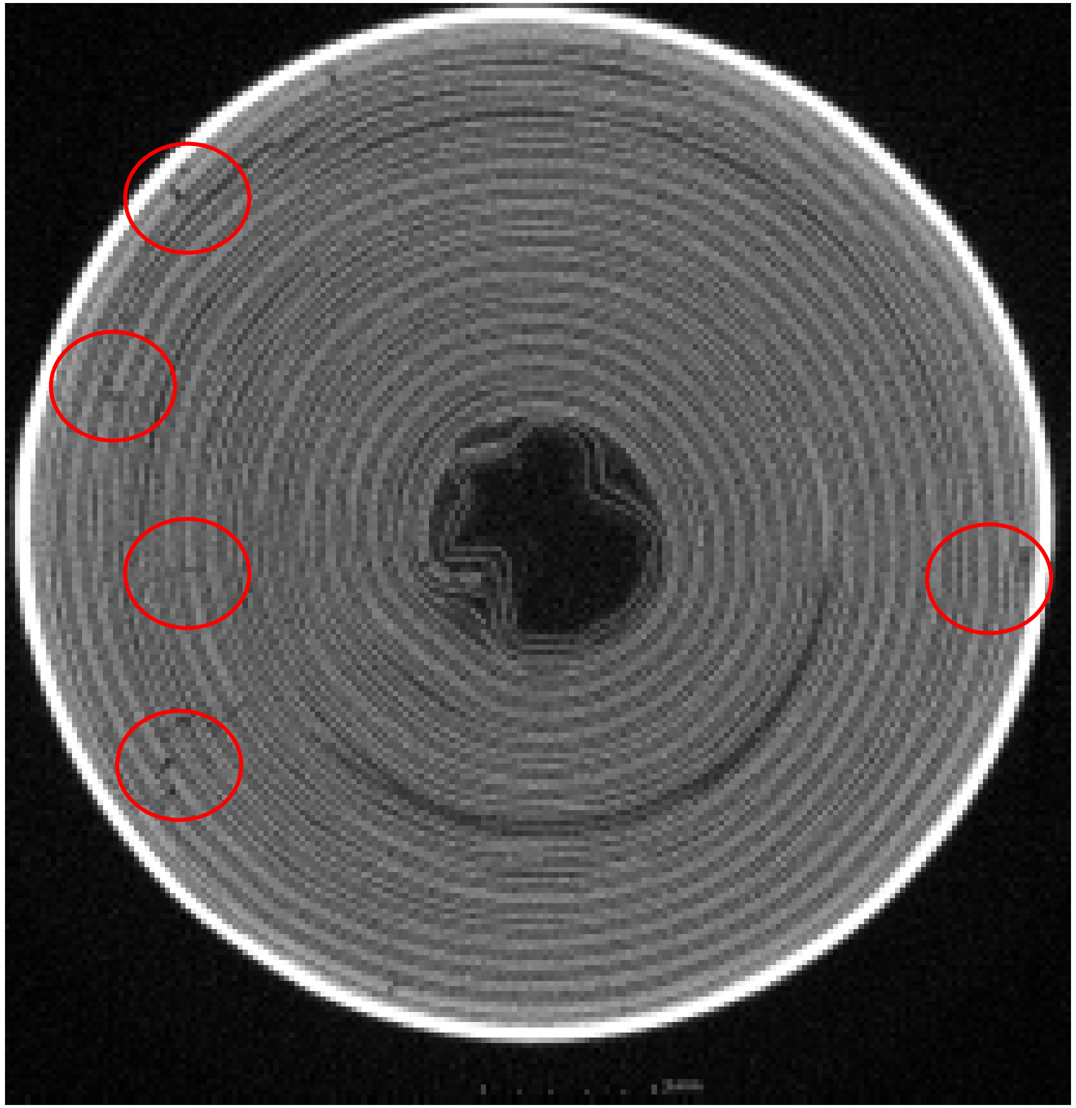
- Micro-CT scanning and X-rays are non-destructive methods to internally examine a cell.
  - Followed by a physical disassembly if required.

- Chemical and state of charge analyses.

- SEM-EDX and ICP-OES or ICP-MS.

# CT scans of subtle manufacturing defects?





# State of charge and chemical analyses

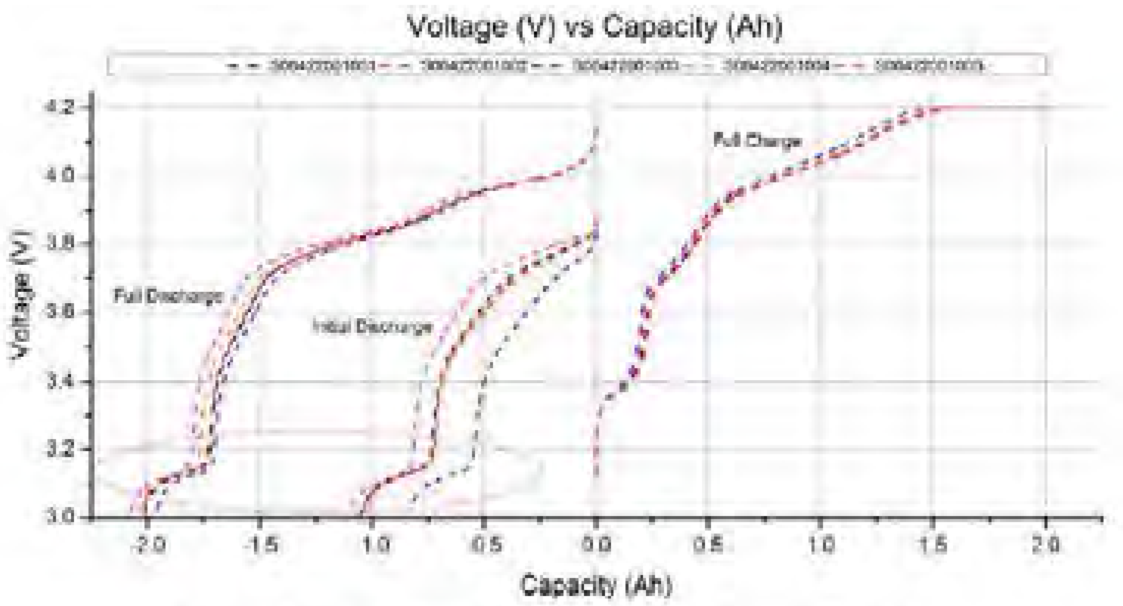



Figure 1: Voltage (V) vs Capacity (Ah) for all samples tested

All five cells exhibit highly unusual voltage profile during all three steps plotted in Figure 1. An additional voltage plateau appears consistently in the low SOC region, at approximately 3.1 V during discharge (marked red in Figure 1). Such plateau is uncharacteristic for cells utilizing any lithium transition metal oxide cathodes, e.g. lithium cobalt oxide ($LiCoO_2$). On the other hand, the indication "ICR" in cells' name suggest lithium cobalt oxide being the cells' cathode.

Such phenomenon may have various causes, among others contamination of either electrode active material.

- I had cells tested in the lab to determine their state of charge followed by:
- 1. X-ray CT (no defect found)
- 2. Cell disassembly and sample extraction
- 3.) ICP-OES

- The ICP-OES results indicated contamination of active materials during slurry processing on a massive scale.
- It was concluded that labelling the cells "ICR 18650" violated the naming convention of IEC 61960, because cobalt-containing oxide was not a dominant component of the cathode.

Hawkins

# Failure test 1


Source: UK Association of Fire Investigators (UK-AFI), 2017 Training Event (Youtube video)
https://www.youtube.com/watch?v=eg40qEktCew

# The damaged laptop battery pack

# Failure test 2

# The damaged Li-Po pouch battery pack

# Failure test 3

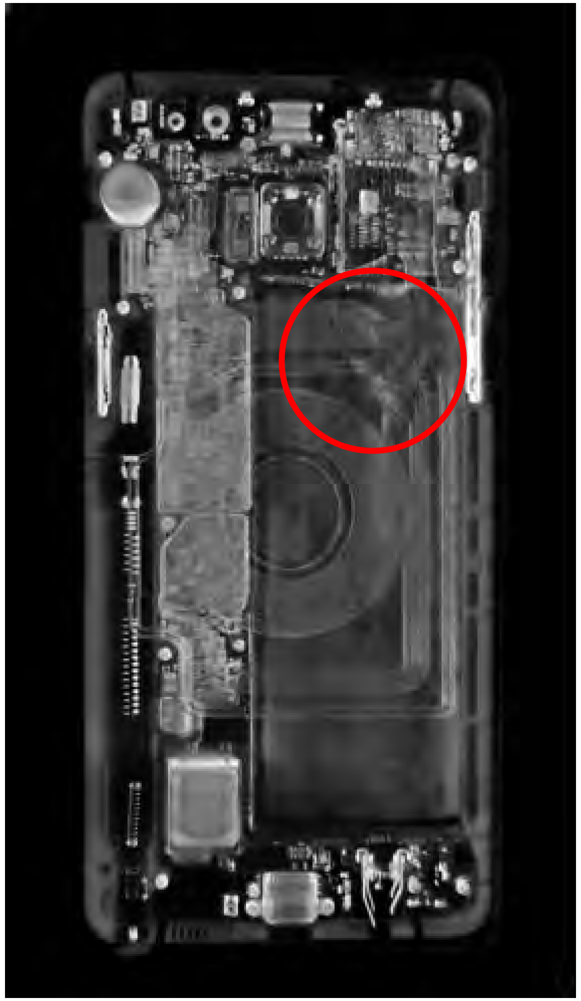
# The thermally damaged laptop

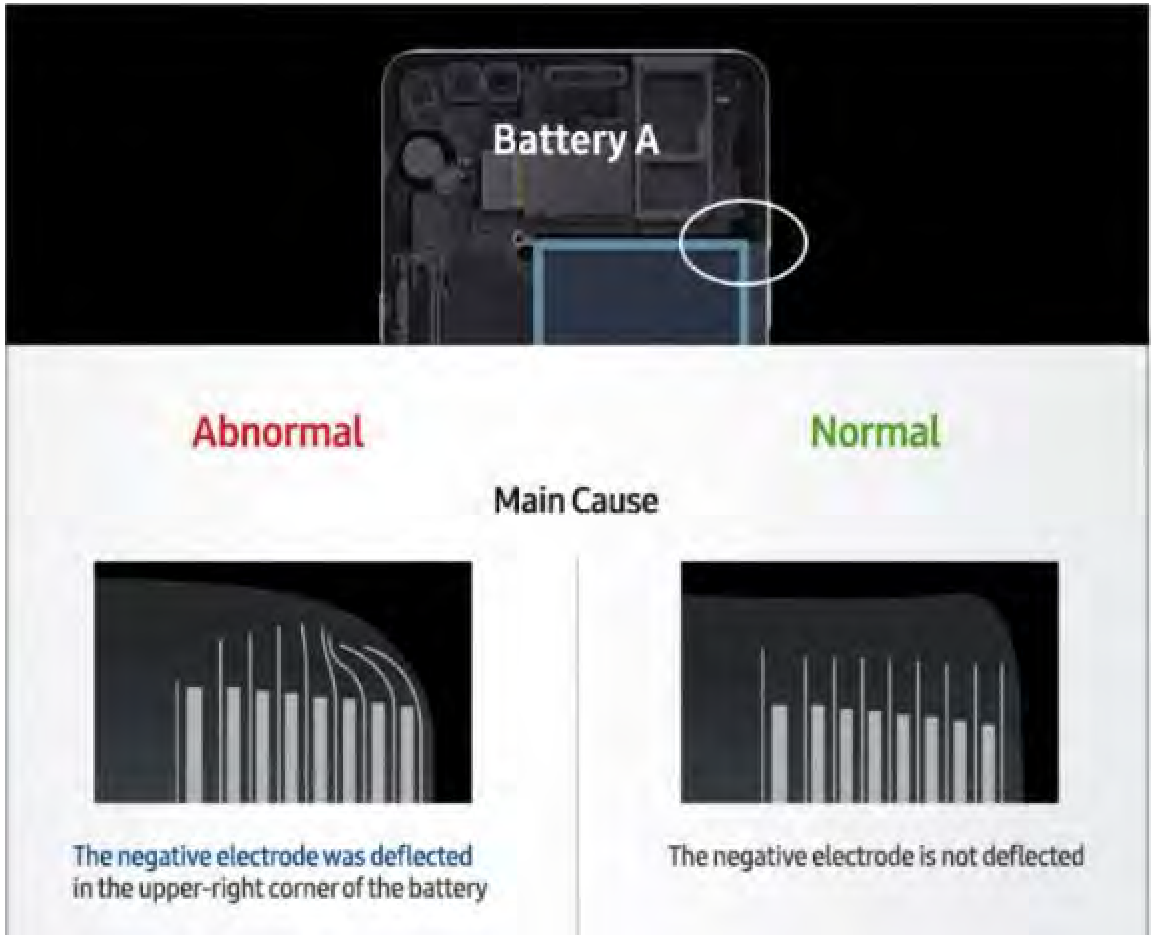
# External Short Circuit


Source: https://www.youtube.com/watch?v=KR7_xwQbYp0 (Guardian Wires)

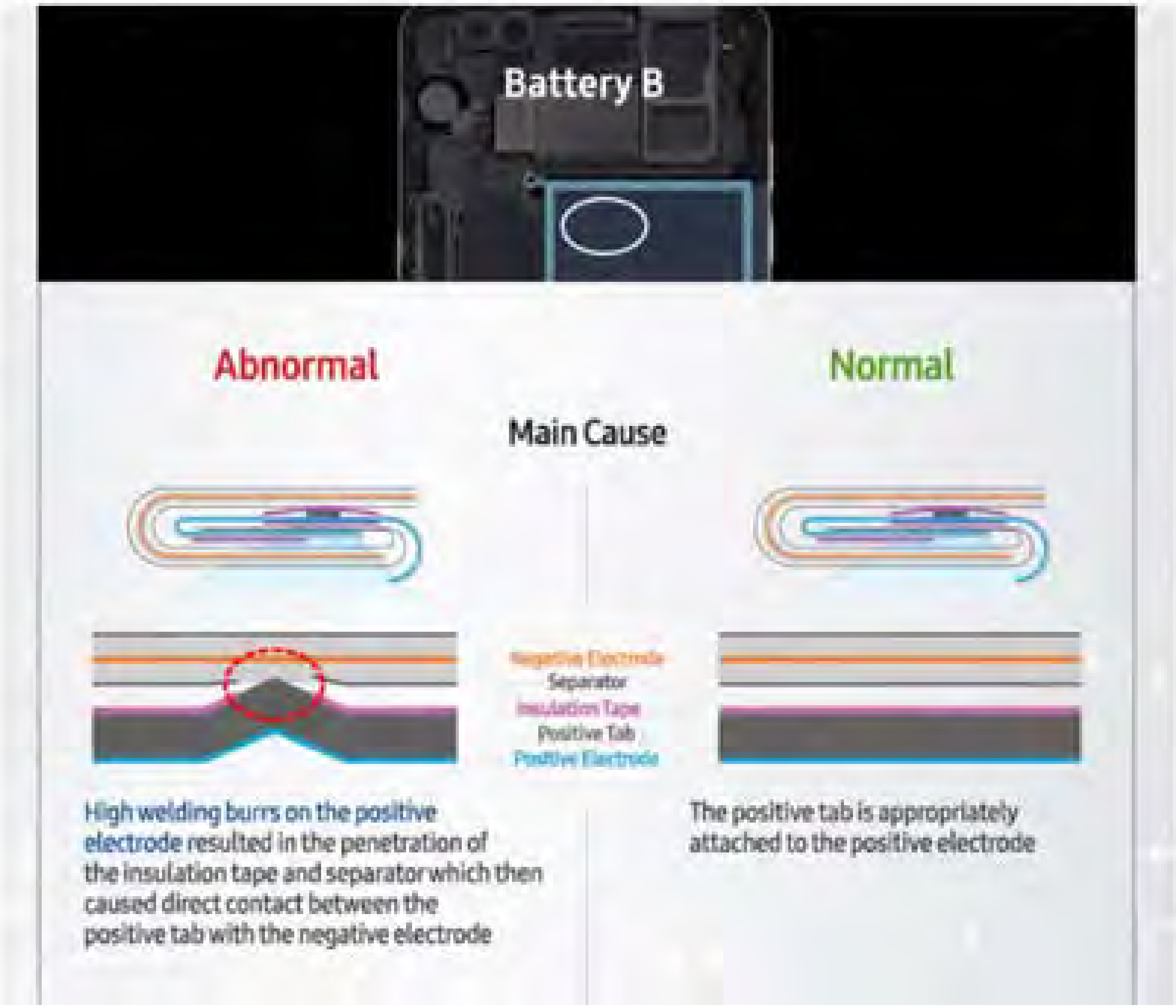
Hawkins
Leaders in forensic investigation

# Samsung Galaxy Note 7 product recall





# Samsung Galaxy Note 7 product recall



# Case study – Electric rideable

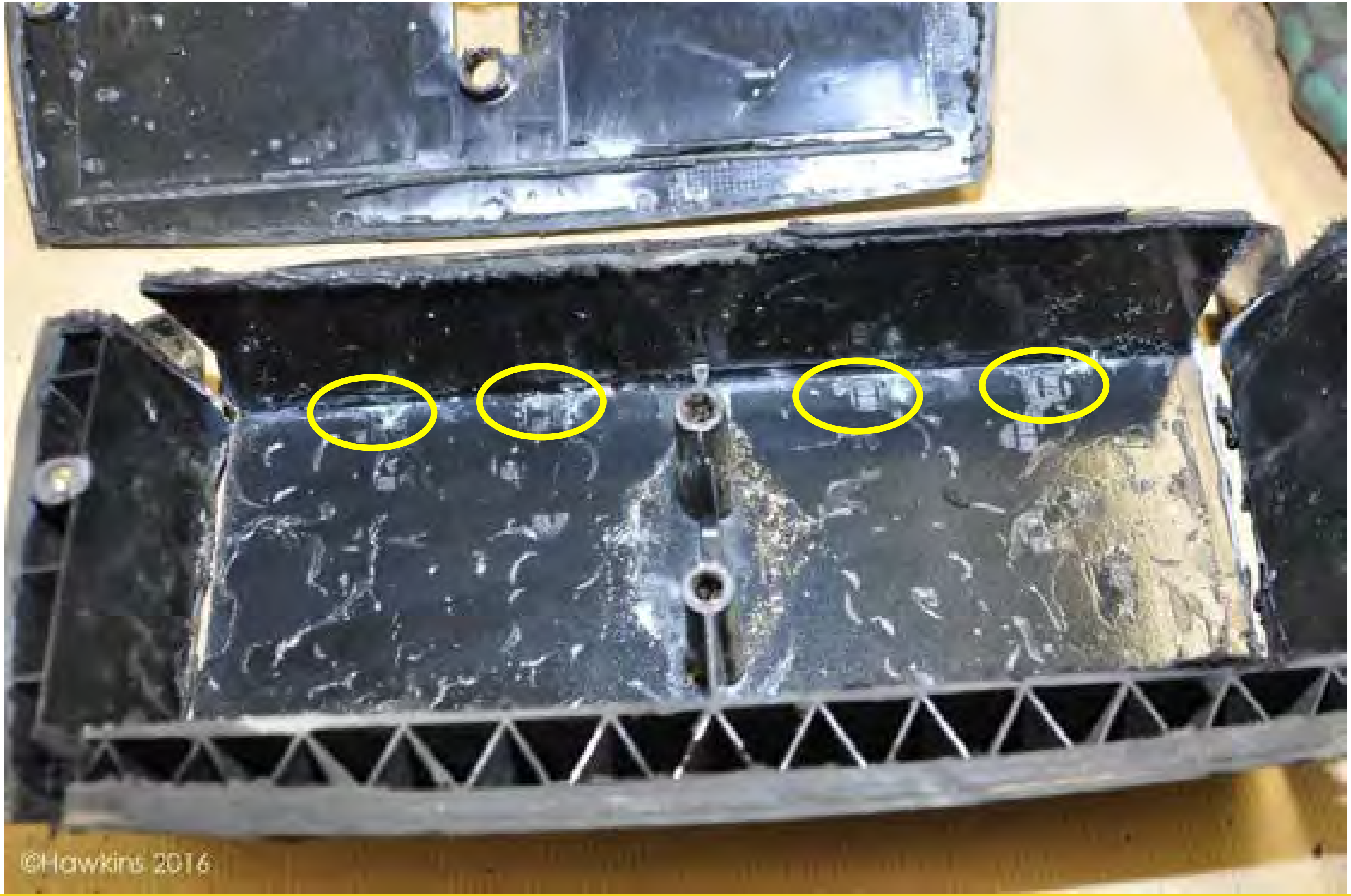
# Large battery pack

This battery pack = 96 Volts – consider electric shock risks

# Fire damage to two areas on the BMS PCB

Battery Management System (BMS) Printed Circuit Board (PCB)

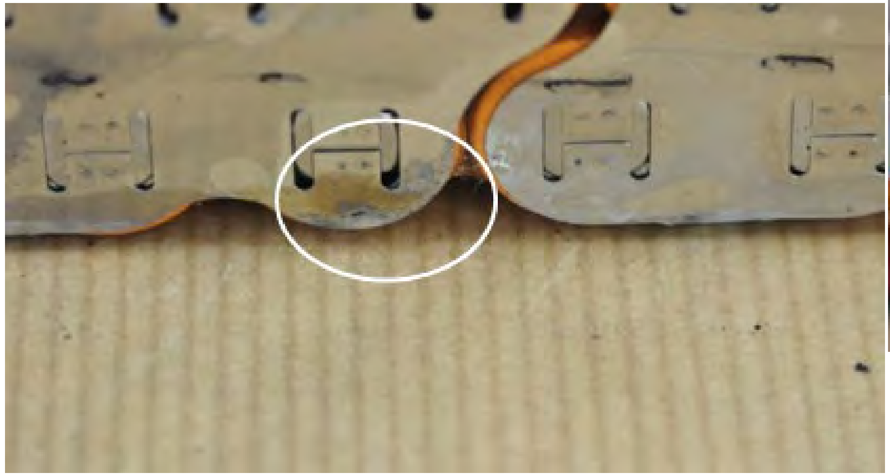
# Oxidation deposits within exemplar

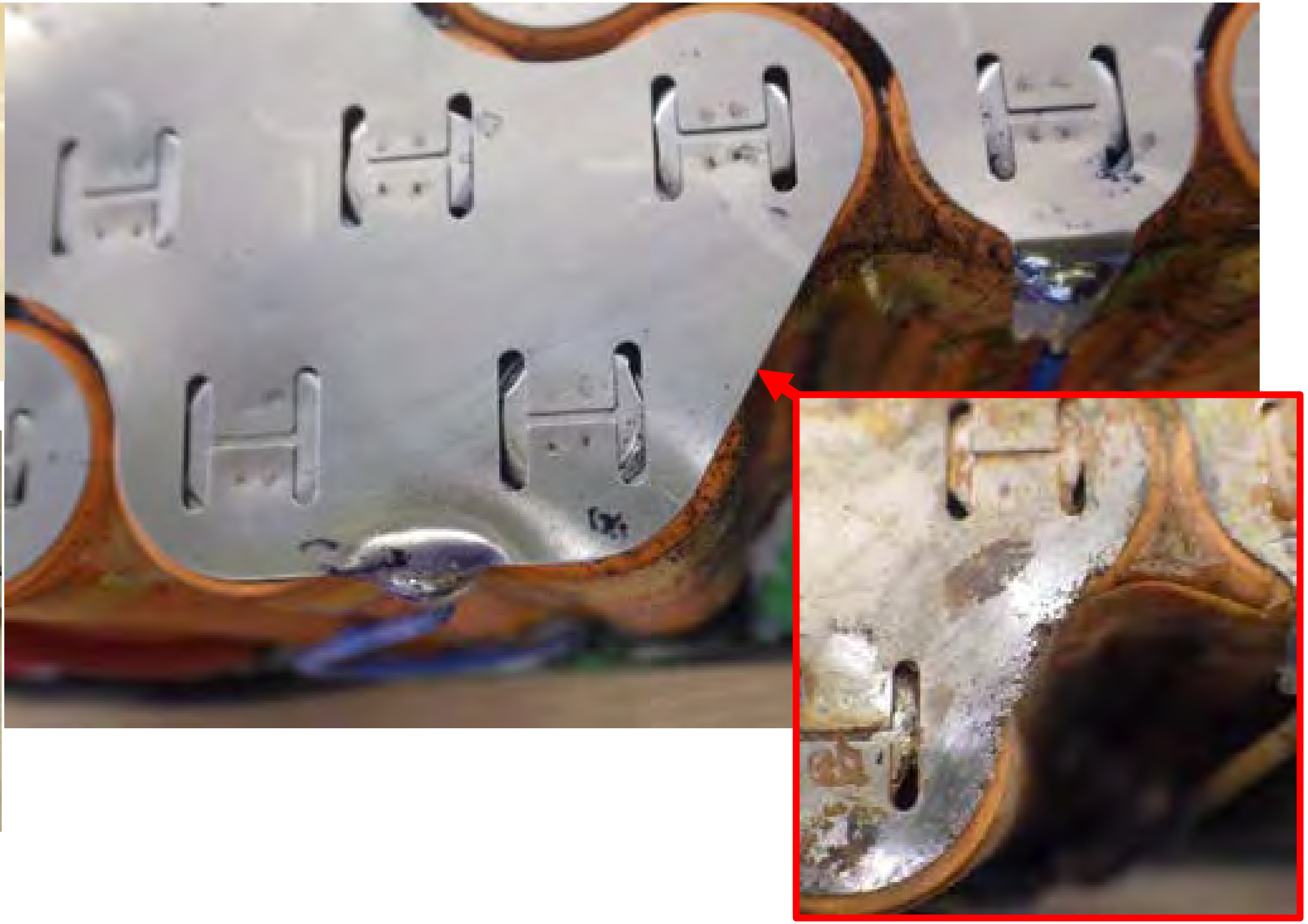


# Oxidation on the busbars (straps)

# Corrosion on incident busbars

# Comparison with the exemplar busbars





# Localised melting on PCB copper track

# Melting on copper tracks of the PCB

# Future energy storage

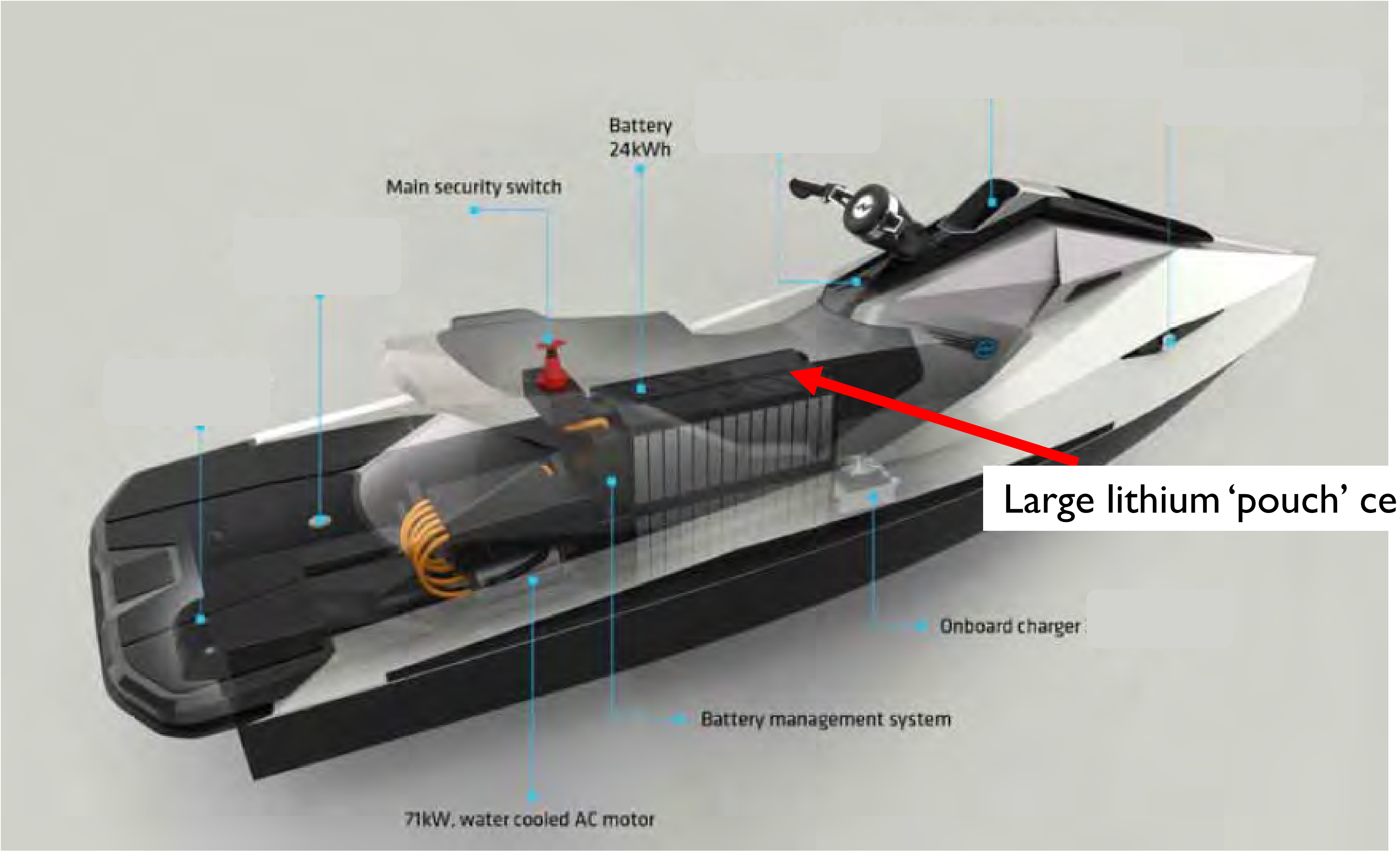
- Renewable generation is driving a need for storage.
  - To cope with fluctuating generation.

- Lithium batteries for electricity storage?
  - Possibly not, as demand for Li will soon outstrip supply.
  - Much research being conducted into alternative chemistries, such as sodium (Na-ion) or aluminium (Al-ion)*.
  - Alternatives have advantages such as better charge capacity, fire safety, cost / abundance of supply etc.

- Future technologies for Li-ion cells?
  - Solid-state Li-ion: High specific energy but poor loading and safety.
  - Lithium-sulfur: High specific energy but poor cycle life and poor loading – sulfur also swells when it absorbs Li.
  - Lithium-air: High specific energy but poor loading, needs clean air to breath and has short life – **high risk**.
  - Non-flammable electrolytes.
  - Replacing the $LiF_6$ to avoid generating hydrofluoric acid.
  - Lithium anodes instead of carbon or silicon.

- **Second hand batteries** – They are already here, and the market will only grow!

# But – we will see more retrofits!



# Future pmd or ev fire statistics?

- The numbers of fires can be controlled by legislation, public awareness and ultimately design and manufacturing improvements.

- But, with the numbers of cells in use increasing exponentially, will we see a fall in the numbers of fires? Perhaps..

Chart 5: Fires involving PABs, PMDs and PMAs in the last five years (2018 – 2022)

# Summary

- Lithium batteries are becoming increasingly useful.
- In the future they will get bigger (electrical capacity and the physical size).
- Current technology/chemistry is ‘sensitive’ to misuse.
- Cause vs effect remains a challenge for fire investigators.
- We will see more incidents as people retrofit electric motors into old technology or use second hand battery packs.
- Can the increase be curbed by legislation?

# PART 2

The Carriage and Disposal of Cells

Hawkins
Leaders in forensic investigation

# The Life Cycle of a Cell or Battery

- Stage 1 - Manufacture
- Stage 2 - Testing
- Stage 3 - Packing
- Stage 4 - Documentation
- Stage 5 - Shipment, Delivery and Sale
- Stage 6 - Use and Abuse
- Stage 7 - Disposal
- Stage 8 - Shipment (Again)?
- Stage 9 – Recycling

# Classification

- **<u>All</u>** Li-ion cells and batteries are classed by the United Nations (UN) as Dangerous Goods (DG).

- Assigned to 'Class 9', miscellaneous dangerous substances and articles, as they do not meet the test criteria of the other 8 classes of dangerous goods.
- Lithium batteries transported by themselves are assigned to the following UN entries:
  - ★ UN 3090, Lithium metal batteries, or
  - ★ UN 3480, Lithium-ion batteries.

- When inside or packed with equipment they are intended to power:
  - ★ UN 3091, Lithium metal batteries contained in equipment, or,
  - ★ UN 3091, Lithium metal batteries packed with equipment, or,
  - ★ UN 3481, Lithium-ion batteries contained in equipment, or,
  - ★ UN 3481, Lithium-ion batteries packed with equipment.

- EVs when cargo are UN 3171.

# Legal requirements

- They **must be proven to meet the requirements of the Manual of Tests and Criteria, Part III, § 38.3,** which is confirmed by a test report and be manufactured under a quality management programme.

- From January 2023 button cells contained in equipment, including circuit boards are exempt.

- In addition, each cell or battery must:
  - incorporate a safety venting device,
  - be equipped with an effective means of preventing external short circuit.

- Batteries containing cells connected in parallel must be equipped with an effective means to prevent dangerous reverse current flow.

# Testing

- All Li-ion cells and batteries submitted for transport **must** be tested except for small production runs (i.e. those sent for type testing) and damaged batteries.
- The cells and the packaging **must** be type tested.

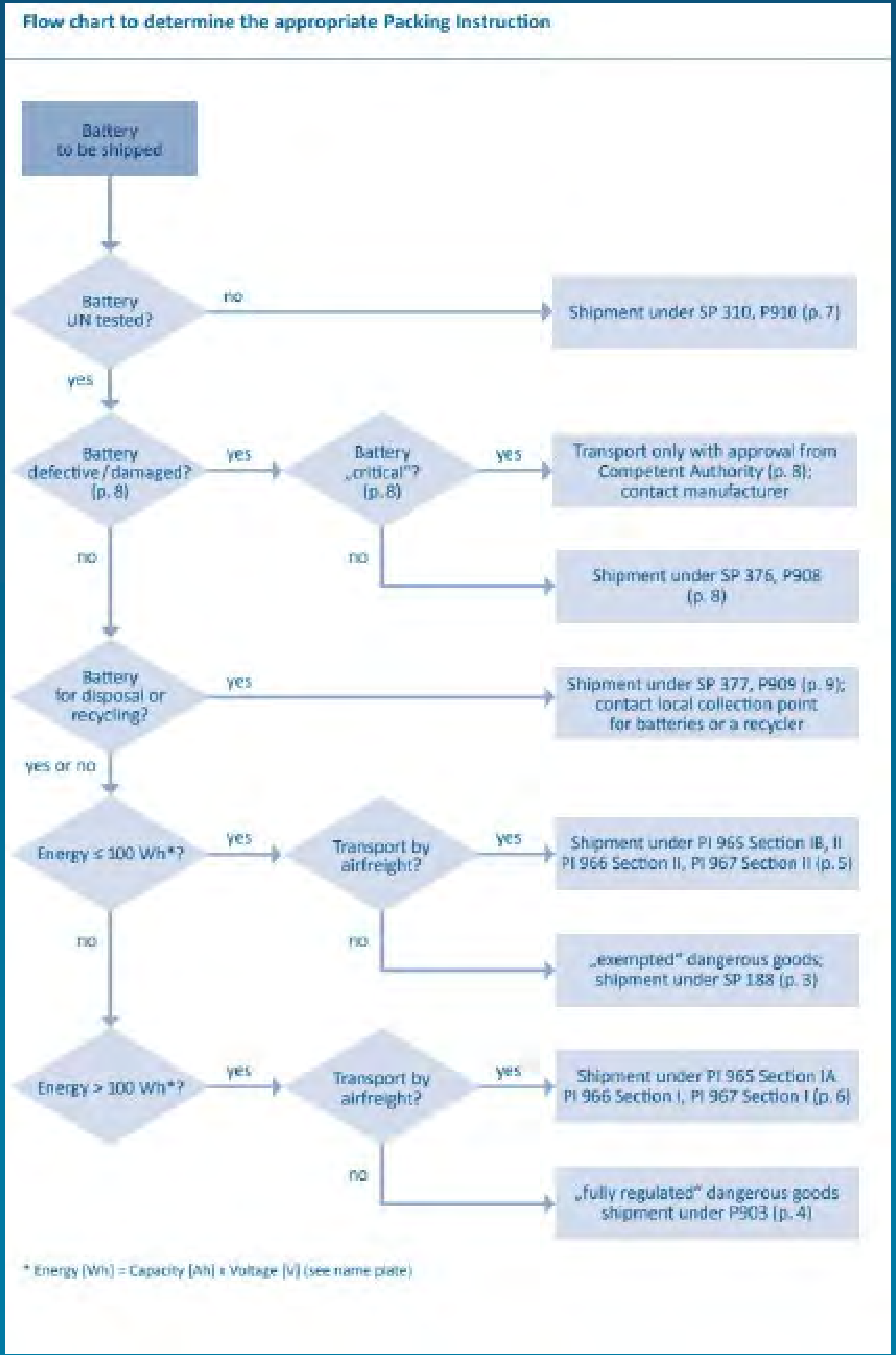
TESTING OF LITHIUM CELLS AND BATTERIES

| NO. | TEST | DESCRIPTION |
|---|---|---|
| T.1 | Altitude Simulation | Simulates air transport under low-pressure conditions |
| T.2 | Thermal Test | Assess seal integrity and electrical connections |
| T.3 | Vibration | Simulates vibration during transport |
| T.4 | Shock | Simulates possible impact during transport |
| T.5 | External short circuit | Simulates an external short circuit |
| T.6 | Impact | Simulates an impact |
| T.7 | Overcharge | Evaluates the ability of a rechargeable battery to withstand an overcharge condition |
| T.8 | Forced discharge | Ability of a rechargeable cell to withstand a forced discharge condition |

# Packaging

- To prevent physical damage and a short circuit.
- Depends on many factors, such as the mode of transport, the size and number of cells etc.
- The simplest way to show that the packaging is compliant with the requirements of the Codes is to use UN stamped packaging, but this is not always required.
- The most common way to ship cells is under what is known as Special Provision (SP) 188.
- Flow charts are available to help chose the packaging and labelling required etc.
- The packaging must be marked clearly in accordance with the requirements of the Code(s) and any applicable local legislation.
- For example, packages of Li-ion cells must be marked ‘UN 3480’, within a ‘Lithium Battery’ mark.
- Packaging containing damaged cells must be made to a higher standard and have a warning placard.

# How to choose?




Hawkins
Leaders in forensic investigation

# Documents

- Documents required vary depending on the SP and how a package is shipped. It is not straightforward!
    1. Land
    2. Sea
    3. Air
    4. Testing

- We can **ignore** air transport as they are banned from being transported as cargo by the UN and most Aviation Authorities without State of Origin and State of Operator approval. This is expensive.

- We can also ignore cells sent for testing (unless your friendly forensic scientist has taken an exhibit for you).

- Take an example of a consignment of cells into Singapore.

- 99% will be shipped under SP188 – Documents are required - plus a full Dangerous Goods Note (DGN) with associated declarations for the sea transport. **BUT** documents are also required for the road / rail transport legs in the country of manufacture and Singapore.

# Documents

- All DG, when transported by sea, must be declared on a DG transport document often referred to as the "DGN".

- The following information is **MANDATORY**:
  - Consignor name and address
  - Consignee name and address
  - The DG description for each dangerous substance identified by each UN number
  - Number and description of packages and total quantity of each item of dangerous goods.

- The DG description should be presented in the following order:
  - UN number,
  - Proper shipping name (supplemented as required),
  - Class (with subsidiary hazard/hazards in brackets if applicable),
  - Packing group (if applicable).

# More documents

Shipper's declaration:

The transport document must include a certification, as detailed by IMDG 5.4.1.6.1 that is to be signed and dated by the consignor.

*"I hereby declare that the contents of this consignment are fully and accurately described above/below (as appropriate) by the proper shipping name, and are classified, packaged, marked and labelled/placarded, and are in all respects in proper condition for transport according to applicable international and national government regulations".*

# Road transport

- The NEA in Singapore considers Li-ion batteries as **non-hazardous.**
- Licensing controls are taken care of by the Fire and Safety Act and the Environmental Protection and Management Act. They control the storage, transportation, importation and use of any dangerous goods.
- Companies in Singapore must have certification from the Singapore Civil Defence Force (SCDF) to use a hazmat-licensed truck for transporting dangerous goods. These trucks are equipped with specialized safety features and only certified drivers are allowed to operate them.
- Singapore also requires that transport of DG by road complies with the requirements laid down by the European Agreement for the Transport of Dangerous Goods by Road (ADR).

# Road & rail transport in other Countries

- Other Countries have a similar stance to Singapore and base road transport on the ADR.
- Rail transport is often governed by the International Carriage of Dangerous Goods by Rail Regulations.
- Some countries do not advertise the rules and regulations you need to comply with very well.
- We asked the Authorities in Malaysia for their requirements but have not yet received a reply.
- Lithium batteries shipped to Japan must be tested according to the Japanese DENAN standards. Lithium batteries fall under Category B of the DENAN law and therefore may be self-declared.

# Road & rail transport in other Countries

- Australian requirements are mostly ‘harmonized’ unless it is waste…
  - The Dangerous Goods (Road and Rail Transport) Act 2008 (NSW)
  - The Dangerous Goods (Road and Rail Transport) Regulation 2022 (NSW)
  - The Australian Code for the Transport of Dangerous Goods by Road and Rail, 7th Ed (The ADG Code)

- Transport regulations in South Korea generally comply with international UN regulations and restrictions. However, lithium battery transport in South Korea is regulated by the Ministry of Land, Infrastructure and Transport (MOLIT). As such they must also pass Korea Certification (KC) standard testing.

# Ship fires

These can range in severity from a single container to multiple holds.

Hawkins

# Shipping incidents

- Most cells come from China, but Korea is a major manufacturer also.
- Many ship fires each year are caused by Li-ion cells being transported as cargo. Often ~250,000 cells per container.
- Almost invariably mis-declared and packaged incorrectly.
- Almost always a possible recovery against someone in the supply chain.

# Ship fires

- The removal of fire damaged containers from a hold can take weeks.
- Then there is the excavation of the container or containers of interest.

Hawkins

# Shipping incidents


# Ship fires

These cells are often packaged like this:

# Shipping Incidents

- In every case I have seen the cartons and inner packaging was non-compliant.
- Almost every case involved incorrect paperwork. If the cargo is not declared properly there is the potential for insurers to decline the claim or recover their outlay.
- I have at least one case where I have shown the cells to be contaminated (as decided by the Court). A manufacturing defect in the cells meant that my client was able to recover their losses. Many millions of dollars. Other cases are in the pipeline.

# Mobile telephone parts

These cells are often packaged like this:

Hawkins

# Recycling centre fires

- Recycling centres need a 'government' licence to handle Li-ion cells. I think this is the same everywhere these days.
- Legislation can be used in prosecutions. Using Singapore for example we have:
- Section 24 of the Environmental Public Health Act (Cap 95) ("**EPHA**"), disposing of or causing or permitting to be disposed of industrial waste in or at a place that was not a public disposal facility, or a disposal facility established pursuant to a licence granted by the Director-General of Public Health under section 23(1) of the EPHA.
- Section 29(1) of the EPHA, bringing or causing to be brought dangerous substances or toxic industrial waste or the residue from the treatment thereof to a disposal facility without the written permission of the Director-General of Public Health.
- Regulation 36 of the Environmental Public Health (Toxic Industrial Waste) Regulations (Cap 95, Rg 11), failing to or failing to ensure that the employees, servants and/or agents store, use or otherwise deal with toxic industrial waste in such a manner as not to threaten the health or safety of any person or to cause pollution to the environment.

# Recycling centre fires

More legislation that can be used in prosecutions:

<u>Health & Safety Laws (e.g.)</u>

- Environmental Protection and Management Act (Cap 94A), failing to or failing to ensure the health and safety of employees, servants and/or agents of the facility, or to cause pollution of the environment.

<u>Environmental Laws (e.g.)</u>

- Regulation 11 of the Environmental Protection and Management (Hazardous Substances) Regulations (Cap 94A, Rg 4), failing to take adequate precautionary measures to prevent hazardous substances from spilling, dropping, or being released during transportation or failing to take necessary precautions to prevent a fire or an explosion.

Hawkins

# Recycling centre fires

- These fires are often severe because the ‘centre’ does not know what they are dealing with.
- This means they have not taken the necessary steps to segregate the cells, handle them appropriately and because they then try to fight the fire with water.
- If not aware of the nature of the consignment, the centre can leave the cells in storage for years. They can still catch fire if moved!
- Li-ion cells can fail so energetically that they act as mini-fireworks and start multiple fires around the compartment of origin. This can overwhelm ‘first aid’ fire-fighting.

Hawkins

# Careless disposal of cells 1

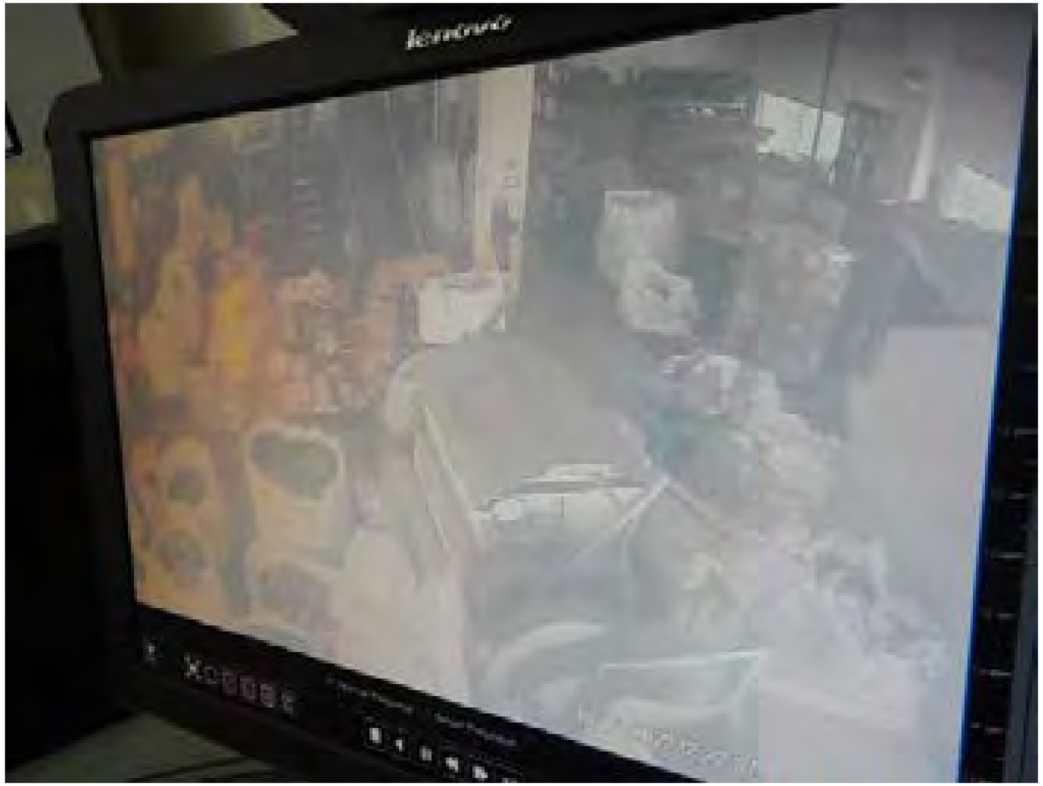
In one case there appeared to be multiple seats of fire.  Upon closer inspection I saw …



Hawkins

# Careless disposal of cells I

The CCTV footage proved to be most useful; 20 seconds separate the images.



# Careless disposal of cells 2


Hawkins

# Careless disposal of cells 2


Hawkins

# Any Questions?

David Rose
E: david.rose@hawkins.biz
T: +65 9117 2143