Thermal runaway and propagation in Li ion batteries

Literature review

Dr Annika Ahlberg Tidblad

Background

- Proposal from China to include ”Propagation test” in EVS-GTR (EVSTF-08-58e)[1]
- OICA is questioning that:
  1. The proposed test procedure appropriately addresses the targeted battery failure scenarios
  2. Adds real safety to Li ion battery powered xEVs
  3. The proposed test method is reasonable, fair, repeatable and reproducible
- The industry has been asked to provide data to TF5.
- This review is representative of the prevailing knowledge and understandings of the international research community, as reflected by peer-reviewed publications, and covers the topics:
  - Causes and effects of internal short circuits (ISC)
  - Conditions leading to thermal runaway and the possibility of propagation
  - Explanations of the short-comings of existing test methodology to appropriately predict field failure behavior of batteries

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[1] https://www2.unece.org/wiki/display/trans/8th+Task+Force+meetings+in+Washington+DC

What failure scenarios are targeted?

Factors that may potentially trigger exothermic degeneration of the Li ion cell and initiate a thermal runaway

Trigger	How can it happen?	Addressed by other tests in the GTR
Overcharge	**Defective connectors. Faulty charging circuit**	**YES** **Overcharge test, (BMS sequential tests)**
External heat source	**Ground fire or other heat source in proximity of battery**	**YES** **External fire test, Overtemperature test (BMS sequential tests)**
Overcurrents	**Out of spec usage of battery caused by BMS failure**	**YES** **Overdischarge test, External short circuit test (BMS sequential tests)**
Internal short circuit by deformation	**Physical abuse of battery pack**	**YES** **Mechanical impact test, Mechanical integrity test**
Spontaneous internal short circuit	**Manufacturing defect**	**NO**

➡ The only trigger not already addressed in the GTR is **spontaneous internal short circuit.**

Merits of scientific explanation models (theory) as technical evidence in the GTR

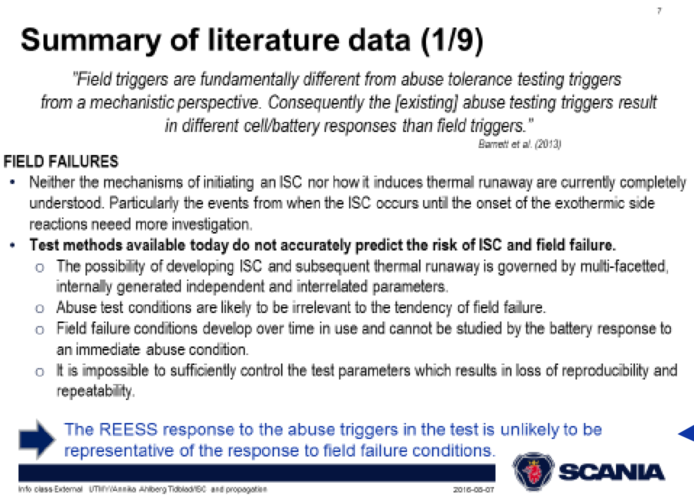
- Scientific knowledge and understanding is based on theoretical explanation models.
- The scientific model constructs are generalized knowledge building on commonalities identified from multiple experimental investigations and taking into account globally available information and data from a large number of sources:
  - Technical and practical experiences and observations
  - Experimental data from specific cases reported by various research groups
  - Explanation models (theory) from related and/or similar fields
- Regulation has to be universally and fairly applicable on a broad range of technical system solutions and battery technologies.

The theoretical explanation models that are universally applicable form a more solid and representative basis for regulatory development than isolated experiments on limited test populations.

Guide of how to use this document

Part 1 – Summary and conclusions

- Selected quotes from references
- Further explanatory text based on literature data
- Conclusive statement based on the information on the slide



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Summary of literature data (1/9)

> *"Field triggers are fundamentally different from abuse tolerance testing triggers from a mechanistic perspective. Consequently the [existing] abuse testing triggers result in different cell/battery responses than field triggers."*
>
> *Barnett et al. (2013)*

FIELD FAILURES

- Neither the mechanisms of initiating an ISC nor how it induces thermal runaway are currently completely understood. Particularly the events from when the ISC occurs until the onset of the exothermic side reactions neeed more investigation.
- **Test methods available today do not accurately predict the risk of ISC and field failure.**
  - The possibility of developing ISC and subsequent thermal runaway is governed by multi-facetted, internally generated independent and interrelated parameters.
  - Abuse test conditions are likely to be irrelevant to the tendency of field failure.
  - Field failure conditions develop over time in use and cannot be studied by the battery response to an immediate abuse condition.
  - It is impossible to sufficiently control the test parameters which results in loss of reproducibility and repeatability.

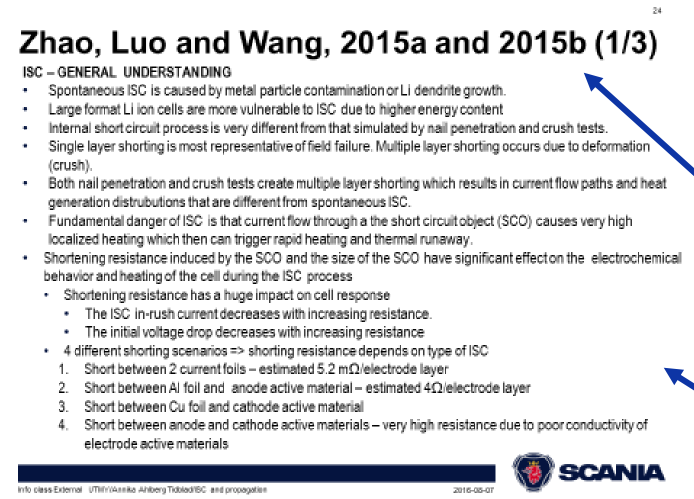
➡ The REESS response to the abuse triggers in the test is unlikely to be representative of the response to field failure conditions.

Info class External UTMY/Annika Ahlberg Tidblad/ISC and propagation 2016-08-07

Part 2 – Detailed notes from references

Information provided for transparency of data and conclusions summarized in Part 1

- Rererence information (full bibliography in reference list)
- Notes derived from text



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Zhao, Luo and Wang, 2015a and 2015b (1/3)

ISC – GENERAL UNDERSTANDING

- Spontaneous ISC is caused by metal particle contamination or Li dendrite growth.
- Large format Li ion cells are more vulnerable to ISC due to higher energy content
- Internal short circuit process is very different from that simulated by nail penetration and crush tests.
- Single layer shorting is most representative of field failure. Multiple layer shorting occurs due to deformation (crush).
- Both nail penetration and crush tests create multiple layer shorting which results in current flow paths and heat generation distrubutions that are different from spontaneous ISC.
- Fundamental danger of ISC is that current flow through a the short circuit object (SCO) causes very high localized heating which then can trigger rapid heating and thermal runaway.
- Shortening resistance induced by the SCO and the size of the SCO have significant effect on the electrochemical behavior and heating of the cell during the ISC process
  - Shortening resistance has a huge impact on cell response
    - The ISC in-rush current decreases with increasing resistance.
    - The initial voltage drop decreases with increasing resistance
  - 4 different shorting scenarios => shorting resistance depends on type of ISC
    1. Short between 2 current foils – estimated 5.2 mΩ/electrode layer
    2. Short between Al foil and anode active material – estimated 4Ω/electrode layer
    3. Short between Cu foil and cathode active material
    4. Short between anode and cathode active materials – very high resistance due to poor conductivity of electrode active materials

Info class External UTMY/Annika Ahlberg Tidblad/ISC and propagation 2016-08-07

Part 1

Summary and conclusions

Summary of literature data (1/9)

> *”Field triggers are fundamentally different from abuse tolerance testing triggers from a mechanistic perspective. Consequently the [existing] abuse testing triggers result in different cell/battery responses than field triggers.”*
>
> *Barnett et al. (2013)*

FIELD FAILURES

- Neither the mechanisms of initiating an ISC nor how it induces thermal runaway are currently completely understood. Particularly the events from when the ISC occurs until the onset of the exothermic side reactions neeed more investigation.
- **Test methods available today do not accurately predict the risk of ISC and field failure.**
  - The possibility of developing ISC and subsequent thermal runaway is governed by multi-facetted, internally generated independent and interrelated parameters.
  - Abuse test conditions are likely to be irrelevant to the tendency of field failure.
  - Field failure conditions develop over time in use and cannot be studied by the battery response to an immediate abuse condition.
  - It is impossible to sufficiently control the test parameters which results in loss of reproducibility and repeatability.

The REESS response to the abuse triggers in the test is unlikely to be representative of the response to field failure conditions.

Summary of literature data (2/9)

> *“While most ISC events result in poor battery performance,*
> *in rare cases, ISC can trigger thermal runaway.”*
>
> *Maleki and Howard (2009)*

FIELD FAILURES

- Field failures caused by ISC are very rare.
- Loss of battery function is the most common result of ISC.
- It is commonly assumed that foreign particles are triggers for ISC, however the majority of Li-ion cells containing foreign particles do not develop ISC and thermal runaway.
- ISC can develop from various sources: separator damage, contamination particcles, weld or solder splatter, desolution/deposition of electrode active materials, Li plating and dendrite formation.
- Rare incidents caused by slow development of ISC that mature to a point of thermal runaway.
- Field failure induction times lasts in the order of minutes while self heating is discernable before violent reactions occur.
- Cells that develop ISC in the field have typically passed industry standard safety testing (incl nail penetration and various other abuse tests).
- Cells and batteries can pass abuse tests without demonstrating true tolerance to the particular abuse situation tested.

Depending on the nature of the defect, an ISC may slowly mature to a point of a possible thermal runaway. Existing tests cannot detect batteries at risk.

Summary of literature data (3/9)

> *“The number of shorted electrode layers has a significant effect on the cell thermal response.”*
>
> Zhao *et al. (2015a)*

ISC UNDERSTANDING

- Single layer ISC is most representative of field failure. Multiple layer shorting occurs due to deformation (crush).
- The fundamental danger of ISC is that current flow through the short circuit object causes very high localized heating which can trigger rapid heating and thermal runaway of the cell.
- Mass transport of Li ions in the electrolyte is the most general characteristic that determines the rate of temperature increase.
- The electric resistance of the short distiguishes the ISC scenarios from each other.
- Current density and current distribution determine the local rate of temperature rise in the ISC area.
- Micro-shorts from isolated dendrites generally lack sufficient power to cause thermal runaway.
- Large format cells are more vulnerable to ISC than smaller cells due to larger electrode surface area and higher energy content.
- Insufficient cell capacity to power the entire ISC area results in lower maximum temperatures and lower risk of thermal runaway.

An appropriate test method must be able to control the number of shorted electrode layers to be representative of field failure behavior.

Summary of literature data (4/9)

> *"According to several studies there are four possible internal short-circuit scenarios:*
> *(i) the short between two current foils,*
> *(ii) the short between Al foil and anode active material,*
> *(iii) the short between Cu foil and cathode active material,*
> *(iv) the short between anode and cathode active material."*
>
> *Zhao et al. (2015a)*

ISC UNDERSTANDING

- Crucial factors that determine thermal runaway behavior:
  - Low electrical resistivity of anode active material leading to high power short
  - Onset temperatures for anode reactions are low compared to the cathode reactions
  - Inadequate heat transfer on the anode side resulting in large current flow, low reaction heats and poor heat distribution
- ISC between Al current collector and anode active material (type 3) is considered worst case scenario
- ISC between anode active material and cathode active material (type 4) is considered most benign due to the relatively poor conductivity in the electroactive materials
- ISC between the current foils is essentially the same as external short circuit.

An appropriate test method must be able to control the type of ISC formed in order to produce reliable results.

Summary of literature data (5/9)

> *”The assumption that a battery material (e.g. cathode chemistry) is more safe due to a higher onset temparture for decomposition is a fallacy.”*
>
> *Barnett et al. (2013)*

ISC UNDERSTANDING

- There is no evidence to support that any of the existing Li ion battery is immune to the possibility of thermal runaway
    - Anode decomposition is generally lower temperature trigger for initiating themal runaway.
    - Higher cathode decomposition temperatures can at best increase the threshold energy for inducing thermal runaway (not the power).
- Thermal performance of a cell depends on the contact between the can and the jelly roll
    - In prismatic cells, less 10% of the heat is dissipated through the current collectors.
    - Heat flux is mainly conducted along the long side of the jelly roll which emphasizes the importance of the cell design and the ability of the jelly roll to dissipate heat to the exterior of the battery.
- Since heat dissipation is a key factor determining if thermal runaway will occur, test methods that compromise normal thermal flows have a high risk of negatively affecting test results, leading to unrepresentative behavior.

➡ The graphite anode decomposition plays a major role for initiating thermal runaway. The ability of the cell to effectively dissipate heat is a key factor.

Summary of literature data (6/9)

> *"The common experimental methods that attempt to create an ISC distort the overall cell integrity, create shorts in multiple locations, or sink heat and current to the cell can. Thus, analyzing ISC's in finished Li-ion cells is limited by imperfect experimental methods."*
>
> *Maleki and Howard (2009)*

LIMITATIONS OF CURRENTLY USED TRIGGER METHODS

- **Current thermal runaway trigger methods induce cell structure breach, electrolyte release and venting – which is not often seen in field failures involving ISC**
- The side-effects caused by the test methods are difficult to control and minimize
- Lack of control of test parameters leads to added complexity and loss of reproducibility and reliability in test results.
- Destructive tests provide no information about electrochemical and thermal coupling that determines the cell behavior during ISC process.
- Traditional testing practice of removing a limited sample population for safety testing with external abuse triggers is clearly inappropriate for determining tolerance against ISC and thermal runaway.
- Risk of ISC formation, thermal runaway and propagation cannot be assessed with traditional external abuse tolerance test methods. Efforts must focus on engineering solutions that allow early detection and prevention of occurrence.

⇨ Currently used trigger methods suffer from lack of reproducibility and reliability and create unrepresentative conditions.

Summary of literature data (7/9)

LIMITATIONS OF CURRENTLY USED TRIGGER METHODS

- Existing trigger methods are not equivalent and do not generate the same thermal runaway processes
    - **Overcharge –** most severe since additional energy is added to the cell.
        - Heat generation is not localized as overcharging affects the whole cell.
        - Thermal behavior is not representative of ISC.
    - **Nail penetration –** Multiple layer ISC with 2nd heat source added in the form of venting flammable gases.
        - No control of the type of ISCs formed.
        - Localized heating, but thermal flow is affected by the nail. Thinner nail with low conductivity causes more severe condition.
        - Volatile electrolyte can escape the cell confinement and react with air, thus creating a second heat source.
            - Oxygen released from cathode active material and solvents is not sufficient to generate enough heat for thermal runaway.
            - Venting of the cell increases oxygen availability for combustion of emitted species and increases the amount of heat generated by 2-3 times.
    - **Heater –** Multiple layer large area ISC
        - Heating from outside in instead of inside out disables cell enclosure function as heat sink.

Currently used trigger methods create ISC conditions that are more severe than field conditions, which can result in unrepresentative battery responses.

Summary of literature data (8/9)

NEW TRIGGER METHODS ARE NEEDED TO IMPROVE TEST RELEVANCE

- Essential to control the type of ISC formed and other critical test parameters to improve repeatability and reproducibility of test, as well as the predictability of REESS thermal response in case of a thermal event.
- Prefered thermal runaway trigger methods should only induce ISC over few electrode layers to be representative of field failures.
- Examples of experimental laboratory methods which limit the ISC to single or few electrode layers include:
  - Cell surface pinching
  - *Insertion of low melting point alloy particle(Note: This method is not practical for regulation due to the necessity of significant manipulation of cell and battery.)*
- Advanced 3D battery modeling is a useful tool for increasing fundamental understanding of ISC and related cell processes and the results can be used to develop novel assessment methods for safety behavior of cells and battery packs in transport application.

More research is needed with focus on:

1. ISC and related cell processes leading up to thermal runaway.
2. The coupling of thermal and current flows inside the cell and battery and how these impact on thermal runaway and propagation behavior.
3. Innovative test methodology to adequately simulate field failure conditions

Summary of literature data (9/9)

> *”Cooling might be effective; if the battery cell is sufficiently colled the temperature increase and thermal runaway can be delayed or hindered.”*
>
> *Zavalis et al. (2012)*

SAFETY ENHANCING METHODS THAT CAN MITIGATE EFFECTS OF ISC

- Effective cooling strategies can mitigate thermal runaway if applied appropriately.
- Cell designs that facilitate thermal transfer from within the cell to an external heat sink, e.g. good contact between the jelly roll and the cell casing.
- SOC window during operation of the battery, however, mass transport in the electrolyte is the rate determining process for temperature increase.
- Design and packaging of cell and/or battery to limit oxygen availability.
- Various cell safety devices, including but not limited to
  - Separators and/or electrode materials that melt at elevated temperatures and increase cell internal resistance
  - Ceramic coating microlayers on separator to avoid shrinking and piercing by dendrites
  - Ceramic coating on electrode surfaces
  - Additives to inhibit start-up of exothermic side reactions
  - Conventional safety devices-overpressure vents, thermal fuses, CID and PTC

➡ Forcing thermal propagation as a test requirement precludes technical development intended to prevent the occurrence of thermal runaway.

Trigger methods considered by the authors

- Blunt rod identation - UL
- Cell surface pinching (indentation)- Motorola
- Forced internal short circuit (FISC) – BAJ
- Nail penetration
- Oven test – UL
- External short circuit of cell
- Overcharge
- Crush test
- Metal defect particle dissolution/deposition on anode - TIAX
- Low melting point alloy particle inserted during production

Conclusions (1/4)

GENERAL

- There is significant evidence and agreement in the scientific and technical community that existing test methodologies, including the proposed propagation test method and thermal runaway triggers,
  - Fail to control critical parameters of thermal runaway,
  - Fail to accurately simulate critical ISC and thermal runaway parameters for the test purpose.
- There is a substantial risk that test data obtained from the proposed trigger methods for thermal runaway (overcharge, nail penetration and heater), will misrepresent actual field failure behavior of REESS.
- There is an inherent risk that unsafe battery designs can pass the proposed propagation test without having tolerance to field failure conditions
- The proposed test method implies compromising and/or disabling critical safety features of the cell and REESS that are in place to mitigate the effects of a thermal event, which increases the probability of false test fails
- Safety risks involving cell response to ISC and likelihood of propagation can be mitigated by cell and battery system designs, cell specific safety devices, appropriate cooling strategies and operational management of the REESS

➡ The well-documented inherent flaws of existing test methods justifies consideration of alternative approaches for ensuring propagation safety, e.g. a documented approach as proposed by OICA, until appropriate test methods have been developed

Conclusions (2/4)

RECOMMENDATION FOR FUTURE DIRECTION

- Traditional abuse tolerance to external triggers and field failures due to internal triggers need to be managed differently from each other
- Recent advancement and development in 3D battery modeling and simulation provides valuable and detailed information and new understanding of critical parameters driving thermal runaway processes
  - This knowledge forms the foundation for development of new assessment methods and criteria targeting relevant internal processes to ensure safe REESS performance in the event of field failure.
  - Increasing knowledge and understanding of critical parameters enables improved cell and battery designs as well as control of operating parameters which aim at preventing field failures from occuring.
- Efforts should focus on preventing the thermal runaway process from happening by developing methods for early detection and warning that there is an increased risk that a thermal event may be evolving,
  - Develop new sensor technology that can detect early warning signs that an ISC is evolving
  - Enables low cost system integration of sensor technology and prophylactic diagnose functions into the battery pack.

➡ Approach to prevent occurrence of thermal events and early warning technology is contradictory to a thermal propagation test.

Conclusions (3/4)

***Internal short circuits –** No screening tests or effective mitigation is [currently] available.*

Doughty (2013)

CONSIDERATIONS FOR DEVELOPMENT OF A TEST PROCEDURE

- Minimum requirements on a future propagation test procedure for REESS safety assessment against internal failure processes caused by ISC include:
  - ○ The ISC trigger should only involve few electrode layers in the cell in order to be representative of field failures
  - ○ The heat generation from the triggering method should be localized around the ISC and not global in the whole cell
  - ○ Cell integrity must be maintained to avoid secondary heat sources, e.g. escaped volatile electrolyte
  - ○ Test parameters must be controlled as well as correctly replicate and represent field failure conditions
    - Type of ISC formed by the trigger method
    - The total ISC area
    - The resulting ISC resistance
    - Thermal flow patterns and distribution in the triggered cell
    - Current distribution and flow patterns in the triggered cell

Development of innovative test techniques and methodologies is necessary since traditional external abuse triggers are inadequate.

Conclusions (4/4)

> *"There are no adequate test methods available today to accurately predict the risk of ISC and field failure."*
>
> *Barnett et al. (2013)*

- The data presented in this review are representative of the current accepted technical and scientific understanding of ISC, thermal runaway and possibility of propagation.
- IWG EVS should consider ALL the knowledge and data available in the international research community when developing an evaluation method of propagation safety for regulation.
- The principles for scientific and technical work practice are based on objectivity and a positivistic approach to knowledge constructs and advancements.
- Prerequisites for challenging and/or deviation from generally accepted scientific knowledge demand:
    1. Compelling evidence that falsifies existing knowledge and understanding

    OR

    2. Satisfactory demonstration that the chosen approach successfully and accurately addresses the intended objectives despite the inherent shortcomings of the method.
- TF5 has not successfully provided evidence that either of these conditions are fulfilled by the proposed propagation test method.

The known shortcomings of the proposed propagation test method are severe and show that it is premature to consider regulation in phase 1. The flaws of the method cannot be fixed by mere adjustment PASS/FAIL criteria

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Part 2

Detailed notes from references

Zhao, Luo and Wang, 2015a and 2015b (1/3)

ISC – GENERAL UNDERSTANDING

- Spontaneous ISC is caused by metal particle contamination or Li dendrite growth.
- Large format Li ion cells are more vulnerable to ISC due to higher energy content
- Internal short circuit process is very different from that simulated by nail penetration and crush tests.
- Single layer shorting is most representative of field failure. Multiple layer shorting occurs due to deformation (crush).
- Both nail penetration and crush tests create multiple layer shorting which results in current flow paths and heat generation distrubutions that are different from spontaneous ISC.
- Fundamental danger of ISC is that current flow through a the short circuit object (SCO) causes very high localized heating which then can trigger rapid heating and thermal runaway.
- Shortening resistance induced by the SCO and the size of the SCO have significant effect on the electrochemical behavior and heating of the cell during the ISC process
  - Shortening resistance has a huge impact on cell response
    - The ISC in-rush current decreases with increasing resistance.
    - The initial voltage drop decreases with increasing resistance
  - 4 different shorting scenarios => shorting resistance depends on type of ISC
    1. Short between 2 current foils – estimated 5.2 mΩ/electrode layer
    2. Short between Al foil and anode active material – estimated 4Ω/electrode layer
    3. Short between Cu foil and cathode active material
    4. Short between anode and cathode active materials – very high resistance due to poor conductivity of electrode active materials

Zhao, Luo and Wang, 2015a and 2015b (2/3)

ISC – GENERAL UNDERSTANDING, continued

- Typical discharge behaviors
  - High resistance short => limited reduction of OCV, controlled shorting current, unlikely to evolve thermal runaway
    - The lower the in-rush current, the more the discharge progess resembles constant rate discharge.
    - The initial voltage drop is small
  - Low resistance short => large shorting current causing Ohmic heating in SCO and tabs, large voltage gradient and shorting current limitted by Li ion transport in the electrolyte. May evolve to thermal runaway but depends on thermal flow paths activated in the cell.
    - The inital in-rush current is high, but rapidly drops due to Li ion depletion at the cathode, resulting in increasing cell resistance and lower electrolyte conductivity
    - The initial voltage drop is large
- Global warming of the cell in field conditions is unlikely to cause thermal runaway.
  - Global warming is typical of low resistance short due to the ISC resistance being negliglible to cell internal resistance
- Worst case local warming occurs when the ISC resistance is close to cell internal resistance (nail penetration), and thermal runaway is likely to occur.
- The poor reproducibility of nail penetration experiments is explained by the high sensitivity to various test parameters that cannot be precisely controlled by existing test methodology
- Test methods should be designed to precisely control the shorting resistance (type of short formed) and number of shortened electrode layers in order to quantify Li ion ISC behavior.

Zhao, Luo and Wang, 2015a and 2015b (3/3)

TRIGGER METHODS AND THEIR LIMITATIONS

- **Nail penetration and crush** = multiple layer ISC
  - Current and heat flows are different from spontaneous ISC
    - In multiple layer ISC, the current flow path forms a closed current loop in each of the electrode layers and very little current flow in the tabs. Heat generation distribution equal to all electrode layers and global heating of the cell.
    - In single layer ISC, a large current flow from the unshorted layers to the SCO forms, through the electode tabs. This creates localized hot spots at the location of the ISC and in the tabs.
  - **Trigger methods induce cell structure breach, electrolyte release and venting – which is not often seen in field failures involving ISC!**
    - These side-effects are difficult to control and minimize
    - Leads to added complexity and loss of reproducibility and reliability in test results
  - Destructive tests provide no information about electrochemical and thermal coupling that determines the cell behavior during ISC process, hence fails to replicate the process targeted by the test.
- Nail penetration testing is a highly dynamic process and very sensitive to test parameters. The current test methods fail to control these parameters.
  - The nail diameter affects the shorting resistance and the thermal mass of the nail
    - Larger nail results in lower temperature rise during the nail penetration process and more uniform heating of the cell (global heating)
    - The thermal conductivity of the nail affects the likelihood of thermal runaway

Zavalis, Behm and Lindbergh, 2012 (1/2)

- Heat generation during short circuit is caused by electrochemical processes inside the cell
- Thermal behavior also dependent on thermal and geometric properties of the cell
- The temperature rise in a short-circuited Li ion cell is not well understood. Particularly the events from when the ISC occurs until the onset of the exothermic side reactions need more investigation.
- Mass transport of Li ions in the electrolyte is the most general characteristic that determines the rate of temperature increase.
- The electric resistance of the short distiguishes the scenarios from each other (3 types studied in paper)
  1. External short circuit
  2. Nail penetration – simulates cell level damage
  3. Impurity induced short circuit (1μm particle) – simulates production contaminant, dendrite formation or vibration damage inside the battery cell
- Current density and current distribution determine the local rate of temperature rise
  - Scenario 1 resulted in more heterogeneous heat distribution than scenario 2
  - Scenario 3 resulted in only local hot spot around contaminant particle
- For a single-layer short, the time scale for initiating exothermic side reactions around the short is approx 10s.
- Local current density distribution determine the temperature distribution. Scenarios leading to local hot spots increase the risk of developing thermal runaway.

Zavalis, Behm and Lindbergh, 2012 (2/2)

- Common understanding is that electrode area (i.e. cell size and dimensions) affect the ISC current
  - True for scenario 1 and 2 which high electronic conductivity and current collectors crate and efficiant route for electron transfer within the cell
  - False for scenario 3 due to the relatively high electric resistance within the cell layer which limits current production to a small region on the electrode
  - Impurity induced short circuit (1μm particle) – simulates production contaminant, dendrite formation or vibration damage inside the battery cell
- **Cooling can inhibit initiation of exothermic side reaction if applied appropriately**.
- Additional mitigating safety measures include:
  - Separators and/or electrode materials that melt at elevated temperatures and increase cell internal resistance
  - Additives to inhibit start-up of exothermic side reactions
  - SOC window during operation of the battery

Spotnitz and Franklin, 2003 (1/3)

SURVEY OF ABUSE TOLERANCE TO

- Oven test
- External short circuit
- Overcharge
- Nail penetration

GENERAL UNDERSTANDING

- Nail, crush and external short circuit tests are somewhat similar but have significant differences
    - Heat is generated by rapid discharge in all tests
    - All 3 tests allow uniform discharge of cell
    - The nail test localizes heat generation to nail location
    - The crush test leads to localized heat generation at the point of shorting. If conductivity is good, then the crush test will behave like an external short circuit test
    - Nail test allows volative electrolyte to come into contact and react with air
- The onset temperature for thermal runaway varies inversely with the degree of lithiation of the negative electrode (anode)
- Thermal stability promoted by increased Li contents in the cathode
- Electrolyte composition affects the thermal stability

Spotnitz and Franklin, 2003 (2/3)

GENERAL UNDERSTANDING, continued

- The positive electrode (cathode) is responsible for thermal runaway for SOC in the range 50-100%
- The negative electrode (anode) is responsible for thermal runaway for SOC in the range 150-200%
- On overcharge, metallic Li can react with electrolyte
- Li metal can react with binder
- Battery discharge releases energy due to entropy changes, overpotentials and ohmic resistance
  - Heat of entropy changes is relatively small compared to ohmic heating

EXOTHERMIC REACTIONS PROPOSED TO TAKE PLACE

- SEI decomposition – exothermic at 90-120 ^{o}C – contributes some heat but is overshadowed by the heat of reaction from the anode/solvent reactions
- Intercalated Li reaction with electrolyte – exothermic at temperatures >120 ^{o}C
- Intercalated Li reaction with fluorinated binder – Binder reactions do not release significant amounts of heat
- Electrolyte decomposition – exothermic at elevated temperatures >200 ^{o}C
  - contributes significant amounts of heat
  - Lower porosity materials will significantly reduce the amount ot energy
- Positive electrode active material decomposition – exothermic and gIve off oxygen
- On overcharge, metallic Li can react with electrolyte
- Li metal can react with binder
- Battery discharge releases energy due to entropy changes, overpotentials and ohmic resistance
  - Heat of entropy changes is relatively small compared to ohmic heating

Spotnitz and Franklin, 2003 (3/3)

TRIGGER METHODS, LIMITATIONS

- **Overcharge –** most severe since additional energy is added to the cell
  - Rate of overcharge current affects venting behavior – lower current rate (<1.5C) is less likely to cause cell to vent than high current rate (>2C)
  - Runaway mainly due to metallic Li reacting with solvent.
- **Nail penetration**
  - Allows uniform discharge of cell
  - Concentrates heat locally due to nail
  - Volatile electrolyte can escape the cell confinement and react with air, thus creating a second heat source
  - Rate of nail and depth of penetration has large impact on temperature increase
  - Fast and deep results in significantly lower temperature (~150 ^{0}C) than slow and shallow (~600 ^{0}C)due to relative rates of heat removal and heat generation
- **Crush test**
  - Allows uniform discharge
  - Local heat generation at shorted areas
  - If cell is designed for good internal electric contact, then the cell behaves like a cell exposed to external short circuit
- **Oven test –** the temperature rise is greates at the can surface and decreases towards the core. When thermal runaway occurs, the heating of the core increases and ultimately creates a negative thermal gradient from the core to the can surface

Santhanagopalan, Ramadass and Zhang, 2009 (1/3)

PARAMETERS AFFECTING CELL RESPONSE TO ISC

- **Importance of ISC area**
  - Microshorts from isolated dendrites typically burn out of the membrane and do not contain sufficient power for the short to propagate
  - Persistent shorts which results in sufficient heat generated lead to onset of abuse reactions – this is more likely for larger ISC area
  - If the cell capacity is insufficient to supply power to the entire ISC area, then this leads to decreasing maximum temperature
- **Impact of initial cell temperature** – in preheated cells the margin for safety is reduced due to temperature dependence of rate constants and mass transport parameters
- **Importance of capacity** – a larger cell heats up faster
- **Importance of SOC** – a higher SOC shows a progressive exponential rise in the rate of temperature increase
  - SOC directly relates to degree of lithiation of the anode
  - Critical cut off SOC for onset if thermal runaway is about 87% for type 2 ISC
- **Importance of oxygen availability** – combustion process is limited by oxygen amount available for reacion
  - Oxygen released from cathode active material and solvents is not sufficient to generate enough heat for thermal runaway
  - Venting of the cell increases oxygen availability and increases the amount of heat generated by 2-3 times
- The origin of thermal runaway is almost always coming from the anode

Santhanagopalan, Ramadass and Zhang, 2009 (2/3)

- **Impact of the nature of the ISC**
  - Copper/Aluminium (type 1)
    - Similar to low resistance external short circuit
    - Due to extremely good heat conductivity of Cu and Al, the localized heat accumulation around the ISC is minimal
    - The rate of temperature is initially very high for a few seconds, but then quickly decreases as the shorting current decreases
  - Copper/cathode active material (type 2)
    - By virtue of cell design, this type of short is fairly infrequent
    - The ISC resistance is controlled by the cathode material, which is the poorest conductor among the 4 components, which results in a minimal current flow and a limited temperature rise caused by Joule heating
    - The power liberated is rarely enough to trigger exothermic reactions
  - Aluminium/anode active material (type 3)
    - Crucial factors that subscribe thermal runaway behavior
      - Low electrical resistivity of anode active material leading to high power short
      - Onset temperatures for anode reactions are low compared to the cathode reactions
      - Inadequate heat transfer on the anode side resulting in large current flow, low reaction heats and poor heat distribution
      - Considered worst case scenario of ISC

Santhanagopalan, Ramadass and Zhang, 2009 (3/3)

- **Impact of the nature of the ISC, continued**
  - Cathode active material/Anode active material (type 4) – most probable short scenario
    - Preferred case due to poor conductivity of cathode
    - The temperature rise is limited to a few degrees above ambient as the current leaks across the short.
  - The power generated by a type 1 short is about 3-4 times higher than a type 3 short but the maximum temperature for a type 1 is significantly lower.
- A fully lithiated anode is more likely to be prone to thermal runaway due to the presence oc highly reactive nascent lithium with high heats of reaction (exothermic)

EXPERIMENTAL VERIFICATION OF MODEL

- Nickel particle was inserted between different layers of the cell in order to create the 4 types of ISC
- Experimental curves show the same qualitative trends as predicted by model under identical conditions
- Changing the electroactive materials and/or alternative cell designs can alter test results

SAFETY CONSIDERATIONS

- Safety can be enhanced by appropriate design of packaging material and enclosures to limit oxygen availability

Lundgren et al., 2016

- Thermal performance of a Li ion cell depends strongly on the contact between the jelly roll and the cell can
- In a prismatic cell, heat flux is mainly conducted through the long sides of the jelly roll
- Less than 10% of the heat generated inside the jelly roll is dissipated through the current collectors
- The cell can is not limiting for thermal performance, the limitations lie in the heat transfer process within the jelly roll.
- Electrolyte limitations during high current pulses lead to development of uneven current distributions

Orendoff, Roth and Nagasubramanian, 2011 (1/2)

ISC, GENERAL UNDERSTANDING

- Probability of failure is estimated to be very low, 1 in 5-10 million cells
- Field failure due to ISC are difficult to detect and predict
- Several of the test protocols adopted across the industry do not accurately similate ISC and following cell response
- ISC can develop from various sources, incl manufacturing defects: separator damage, contamination particcles, weld or solder splatter, desolution/deposition of electrode active materials, Li plating and dendrite formation
- ISC can develop over time under normal use or abuse conditions
- The type of ISC determines the cell response and subsequent consequences in terms of cell failure
    - Surface area
    - Short resistance
    - Location of short within the cell
    - SOC at the time of shorting
    - Cell capacity
    - Shorting components (anode-cathode, cupper-aluminium, cupper-anode, aluminium-cathode)
- Shorting parameters have significant impact on the cell heating – localized or homogeneous, amount of current passing through the short and the severity of cell failure
- In general, Cu-anode and anode-cathode shorts have the highest contact resistance (~100 mOhm) which limits current flow, localized heating and the shorting severity
- Al-Cu shorts have low resistance (<10 most mOhm), but the heat is readily dissipated byt the high thermal conductivity of Cu, resulting in homogeneous heating and generally no catastrophic failure

Orendoff, Roth and Nagasubramanian, 2011 (2/2)

ISC, GENERAL UNDERSTANDING, continued

- Al-anode is severe ISC as contact resistance is relatively low (~100 mOhm), thermal conducitivity of Al is lower than Cu, and localized heating occurs.
  - Degradation of anode SEI occurs at relatively low temperatures (80-100 ºC) compared to cathode decomposition (>180 ºC)
  - This leads to more heat generation and a higher likelihood of catastrophic failure compared to other ISC types
- Most ISC testing involves some form of mechanical deformation of the cell to point of ISC forming (cell indentation, nail penetration, surface pinching, forced ISC, etc)
  - Notable shortcomings including
    - Reproducibility
    - Inability to control the type of ISC formed
    - Restrictions on utitily based on cell configuration and packaging
- Non-mechanical test approach; dissolution and deposition of mechanical defect particles at the electrode surface causing dendritic growth at the anode
  - Reproducibility remains a challenge of this method
  - SOC at the time of shorting is hard to control

TRIGGER METHOD

- **Low temperature melting alloy particle (~30-60 ^{o}C)**
  - Reliability and reproducibility in larger cells (wound electrodes) needs improvement
  - Contact or interfacial resistance between defect and electrode remains a critical barrier to reliably trigger an ISC using this technique

Zavalis, 2013

- Less diffusion limitation within positive (cathode) material than for the negative (anode) material
- Large part of short circuit behavior can be attributed to mass transport limitations in the electrolyte
- Different thermal behavior for different types of ISC scenarios depends on the current flow (current distribution) and hence on differences in electric resistance. This implies that the distance the electrons travel between the point of reaction and the ISC along with the electric conductivity of the material the current flows thru is different for different shorting scenarios
- In nail penetration, the electrons will primarily travel in the nail and via the current collectors
    - Occurrence of hot spots depend on total heat and spacial distribution of heat generation as well as heat generation in the cell layer where the ISC has occurred
    - Heat generation is directly related to current distribution
- Cooling as a precautionary measure may be unrealistic if there are very large temperature gradients in the cell.

Maleki and Howard, 2009 (1/2)

ISC, GENERAL UNDERSTANDING

- Consequences of mechanical abuse and manufacturing defects depend on cell design, manufacturing quality and nature of ISC
- Majority of ISC result in poor battery performance
- Extremely rare that incidences of ISC triggered thermal runaway
- **Importance of cell design**
  - Up to 70% of cell energy can be released in <60 s causing significant self-heating, depending on cell design
  - Risk of thermal runaway depends on localized heating energy and the duration, separator shrinkage meting point and propagation, overall cell temperature increase
  - Very high risk of ISC leading to thermal runaway IF the uncoated section of the Al current collector contacts the anode surface
  - The anode heat propagation and SEI thermal stability play critical roles in controlling ISC events
  - Application of ceramic coating microlayer on separator to mitigate shrinking and melting
- Various test methods have been proposed to study thermal performance but it is difficult to create a small, isolated short inside a finished cell that mimics spontaneous ISC behavior
- Li ion cells are vulnerable to abusive conditions – especially overcharging
  - Electrical abuse: overcharge and external short circuit can be mitigated with control circuitry

Maleki and Howard, 2009 (2/2)

ISC, GENERAL UNDERSTANDING

- Modeling/simulation can be used to overcome shortcomings of physical tests
- Modeling results show reasonable agreement with experimental test data for nail penetration and surface indentation tesing
- Overall results show that nail penetration and surface indentation do not mimic high risk ISC events by creating heat sinking to the cell can or testing nail, potentially reducing risk of inducing thermal runaway
- Cell pinching provides more relevant ISC but has limitations in reproducing ISC conditions for prismatic cells with metallic cans
- Separator melting propagation depends on SOC and cell capacity – increasing risk of developing ISC when SOC and cell capacity are high
- Location of ISC changes themal response
  - Thermal build up near jelly roll bottom is more severe due to extra separator material filling out the space to can, creating heat flow limitation to can wall
- High risk ISC when there is a gap between jelly roll and the cell can internal wall or when ISC heat generation is sufficient to melt a signifacant portion of the separator

TRIGGER METHODS, LIMITATIONS

- **Cell surface pinching**
  - Reproducibility limitations for prismatic cells with metal can
  - Better agreement with experimental data than nail penetration and cell indentation
- **Nail penetration and cell indentation** do not mimic thermal behavior of high risk ISC
- **Combining experimental method with mathematical modeling can improve understanding of ISC response**

Barnett, Ofer, Sriramulu and Stringfellow, 2013 (1/5)

SAFETY FAILURES OF Li ION BATTERIES

- Can occur due to multiple triggers including overcharging, overheating, crushing, mechanical impact and external short circuits
- Rare incidents of slow development of ISC that mature to a point of thermal runaway
- Most safety tests performed in the laboratory do not replicate the field conditions under which safety incidents happen
- External abuse conditions have been extensively studied and several cell- and pack-level tests have been developed to evaluate abuse response.
- Technical solutions have been developed to manage cell and battery response to external abuse, and standardized test to asses external abuse tolerance have been developed.
- Rare safety incidents occur in the field involving spontaneous thermal runaway events usually involve cell and battery designs that have passed extensive abuse testing.
- Relatively little is know about the underlaying causes of field failures.
- The mechanisms of anode, cathode and electrolyte reactions have been extensively studied in the literature.
- Li ion cells with metal oxide cathodes do not contain sufficient oxygen to allow complete combustion of organic species, and a major fraction of solvent combustion can only occur outside of the cell.
- Cells and batteries can pass abuse tests without demonstrating true tolerance to the particular abuse situation tested.
- Tests to simulate ISC include particle insertion, controlled pinch tests, nail penetration or crushing of cells. However, although these tests exist, they are not standardized at the moment.

Internal short circuit is reported to attribute to a majority of field failures

Barnett, Ofer, Sriramulu and Stringfellow, 2013 (2/5)

KEY OBSERVATIONS FROM FIELD FAILURES

- Internal short circuit is reported to attribute to a majority of field failures in handheld and consumer applications.
- Internal short circuits are not discernable at the time of manufacture
- Internal short circuits occur in a frequency of 1 in 5-10 M cells for the most accomplished manufacturers
- Various processes and measures are practiced by cell manufacturers to reduce incidence of particle contamination
- Internal short circuits leads to a highly non-homogeneous temperature distribution, local temperature increase may exceed 200ºC per second
- **Cells that develop ISC in the field have typically passed industry standard safety testing** (incl nail penetration and various other abuse tests)
- Internal short circuits cannot be mitigated by standard safety electronics
- It is commonly assumed that foreign particles are triggers for internal short circuits
- The majority of Li-ion cells containing foreign particles do not develop internal short circuits and thermal runaway. **Loss of battery function is the most common result of ISC.**
- **Neither the mechanisms of initiating an ISC nor how it induces thermal runaway are currently completely understood**
- Field failure **induction times lasts in the order of minutes while self heating is discernable** before violent reactions occur
- Achieving Li ion systems which are totally free from the risk of developing a spontaneous safety event is not a quality problem
- **Historic testing for safety is focused on abuse testing although the actual safety events that occur are quite different!**

Barnett, Ofer, Sriramulu and Stringfellow, 2013 (3/5)

MECHANISM OF ISC FORMATION

- Several factors influence how particle contaminant develops into ISC:
  - Nature of metal particle – type of metal
  - Size and shape of particle
  - Rate capability of the cell
  - Separator permeation and themal properties
  - Charge/discharge history
  - Temperature distribution history
- The relative importance of the different factors is unknown.
- Possible mechanisms of ISC formation
  - Formation of metal dendrite between anode and cathode which dissolves and deposits on the anode surface
  - Li deposition and dendrite formation, however dendrites are unlikely to dissipate enough power to enable thermal runaway
  - Particle migration and separator puncture – particle migrates during volumetric changes in the cell charge/discharge cycle – less likely to develop a durable cathode contact capable of supporting a thermal runaway conditon
  - Lower power particle shorts induces separator melting which then eneables large area anode-cathode direct contact interaction
- ISC starts as a local thermal event in a very small area. Complex interactions determines if a thermal runaway will develop; temperature, concentrations, rate of reactions and heat transfer conditions.
- Energy dissipation in the short is a key factor in determining thermal runaway.

Barnett, Ofer, Sriramulu and Stringfellow, 2013 (4/5)

MEASURES TO MITIGATE EFFECTS OF ISC ON CELL LEVEL

- High puncture strength and high melt separators
- Porous ceramic coatings on electrode surfaces and/or separators

POSSIBLE TOOLS FOR QUANTITATIVE ASSESSMENT OF SAFETY

- ”Safe Zone” concept plot defining threshhold power and energy levels for a specified cell design and system configuration
  - Can be developed for any Li ion cell
  - Enables engineering assessment of the safety impact from various design changes and the relative risk of thermal runaway

EVALUATION OF ABUSE TOLERANCE VS FIELD FAILURES

- Field triggers are fundamentally different from abuse tolerance testing triggers from a mechanistic perspective. Consequently the abuse testing triggers result in different cell/battery responses than field triggers.
- Field failures typically occur during otherwise ”normal” operation, i.e. there is no external trigger driving a potentially unsafe condition to occur.
- There are no adequate test methods available today to accurately predict the risk of ISC and field failure.
- Traditional testing practice of removing a limited sample population for safety testing with external abuse triggers is clearly inappropriate for determining tolerance against ISC and thermal runaway.
  - The possibility of thermal runaway is a complex, multidimensional response surface and the ”one fits all approach” means that existing test methods can be gamed by unsafe designs that can be manipulated to pass without actually having true tolerance against ISC, thermal runaway and progagation.
  - Abuse test conditions are likely to be irrelevant to the tendency of field failure.

Barnett, Ofer, Sriramulu and Stringfellow, 2013 (5/5)

- **The assumption that a certain battery material (e.g. cathode chemistry) is more safe due to a higher onset temparture for decomposition is a fallacy!**
  - Anode decomposition is generally lower temperature trigger for initiating themal runaway
  - Higher cathode decomposition temperatures can at best increase the threshold energy for inducing thermal runaway (not the power)

RECOMMENDATION FOR FUTURE DIRECTION

- Traditional abuse tolerance to external triggers and field failures due to internal triggers need to be managed differently from each other
- Efforts should focus on preventing the thermal runaway process from happening by developing methods for early detection and warning that and ISC may be evolving, for example develop new sensor technologythat can detect early warning signs and which enables low cost system integration into the battery pack.

Balakrishnan, Ramesh and Kumar, 2006

SAFETY MECHANISMS IN Li ION BATTERIES

- Conventional safety devices
  - Safety vents
  - Thermal fuses
  - Other circuit breakers - thermistors
- Self-resetting devices
  - Ceramic PTC materials – fuse like action
  - Conductive polymer PTC devices
- Separators
  - Shut down
  - (Ceramic coating, Maleki and Howard, 2011)
- Electrolytes
  - Non-flammable (fluorinated and organophosphorus solvents and molten salt electrolytes, e.g. ionic liquids)
  - Redox shuttles – prevents overcharge and overdischarge conditions
  - Shutdown additives
  - Alternative conductive salts
- Coatings