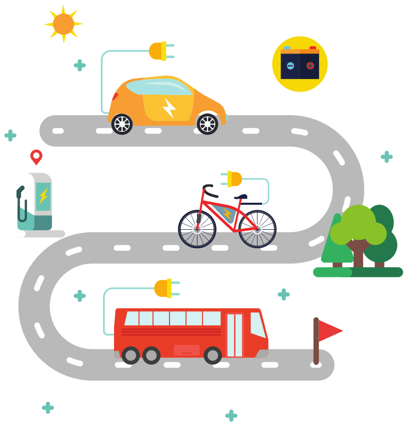

ELECTRIC MOBILITY FORUM

ENGAGE
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Electric Vehicle Safety: Thermal Runaway and Fire Characteristics & Suppression in Lithium-ion Batteries

August 31 , 2020
7:00 PM - 8:00 PM (IST)
WRI India

Speaker:
Dr. Judy Jeevarajan
Research Director – Electrochemical Safety,
Underwriters Laboratories Inc.

Moderator:
Shravani Sharma
WRI India

WRI INDIA
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SHAKTI
SUSTAINABLE ENERGY FOUNDATION


Battery Safety
Advancing safer energy storage through science
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About UL Battery Safety Group

Working for a safer world

RESEARCH: We conduct research and **share scientific data-driven knowledge** to drive safe, reliable, innovative designs to meet the world's increasing energy demands.
Findings of the research are presented in conferences and other public forums, and also through journal and newsletter publications.

OUTREACH: We conduct the **Battery Safety Summits** and **Battery Safety Council forums.**
The Summits and Council forums are platform to catalyze the safety, performance and innovation in the area of batteries for the growth of safe energy storage systems.growth of electric mobility and renewable energy through emphasis on battery performance, safety and innovation.

EDUCATION (awareness-building): We participate in **trainings,** and **webinars,** and share our **research findings** in different platforms like learning modules for students of different age groups.

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- Background
- Thermal Runaway in Lithium-ion Cells
- Fire Characterization
  - NMC Cathode Chemistry
  - LFP Cathode Chemistry
- Fire Suppression for Lithium-ion – Lab scale
- Summary

Introduction

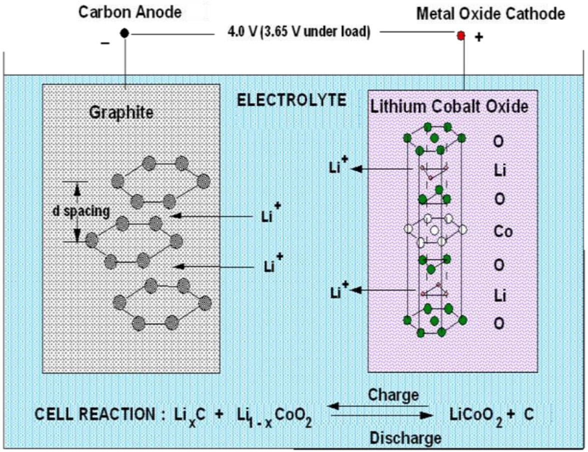
- Lithium-ion battery chemistry, first commercialized in the 1990s, has the highest energy density of rechargeable battery chemistries, has no memory effect, has long cycle and calendar life and good rate capability.
- It is used in a myriad of applications today from consumer electronics to electric vehicles and stationary grid energy storage as well as in sea and space applications.
- Associated with the high energy density is their propensity to experience fire and thermal runaway if not designed or used correctly.
- Due to the proliferation of the use of batteries of this chemistry, there are several hundred manufacturers of lithium-ion cells and batteries today; not all cell and battery designs are characterized stringently and they are not all certified especially the low-quality ones that are also inexpensive and can be purchased on-line with a fast turnaround time.
- Characterizing thermal runaway for the various combinations of cathode and anode chemistries, electrolytes and additives as well as the variety of formats, shapes and sizes that these cells and batteries come in, is a significant challenge.
- Determining the best fire suppressant for the same is also a major challenge for the li-ion battery industry that is especially used for electric vehicles.
- This presentation will address some of the challenges of thermal runaway characterization as well as the fire suppressants and fire suppressing methods.

Thermal Runaway in Lithium-ion Cells and Batteries

- What is "Thermal Runaway"?
- Wikipedia: thermal runaway
  - A repeating cycle in which excessive heat causes more heat until the operation c eases, or an explosion occurs. Examples are lithium-ion batteries, germanium-based bipolar transistors, etc. In the latter case, high temperatures cause current to leak, heat up even more and eventually become unstable or self-destruct.
- Typical Definition in Lithium-ion Standards:
  - **Thermal runaway is defined as an accelerating release of heat inside a cell due to a series of uncontrollable exothermic reactions manifesting as an uncontrolled increase in cell temperature.**

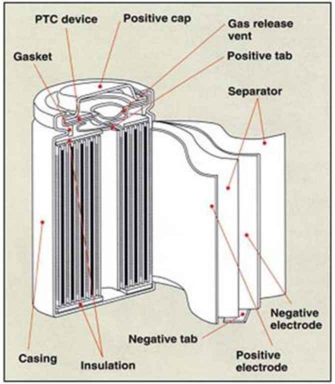
Lithium-ion Cell

Charge and Discharge Process



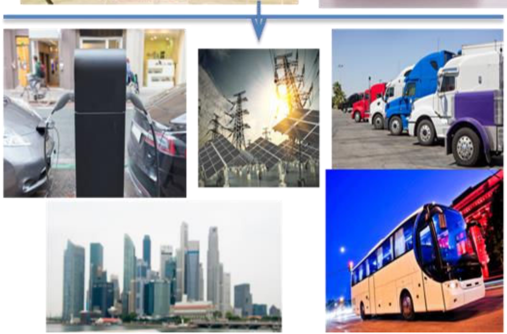
Components of a Lithium-ion Cell

1. **Cathode:** The positive electrode of the cell (for discharge).
2. **Anode:** The negative electrode of the cell (for discharge).
3. **Electrolyte:** The medium that provides the ion transport mechanism between the positive and negative electrodes in a cell. (This can be aqueous or non-aqueous)
4. **Separator:** A microporous material that keeps the cathode and anode from touching each other.



Li-ion Battery Designs and Challenges

Low Voltage/ Low Capacity



High Voltage/High Capacity

Incidents of Li-ion Fires

Fire Incidents in Portable Applications

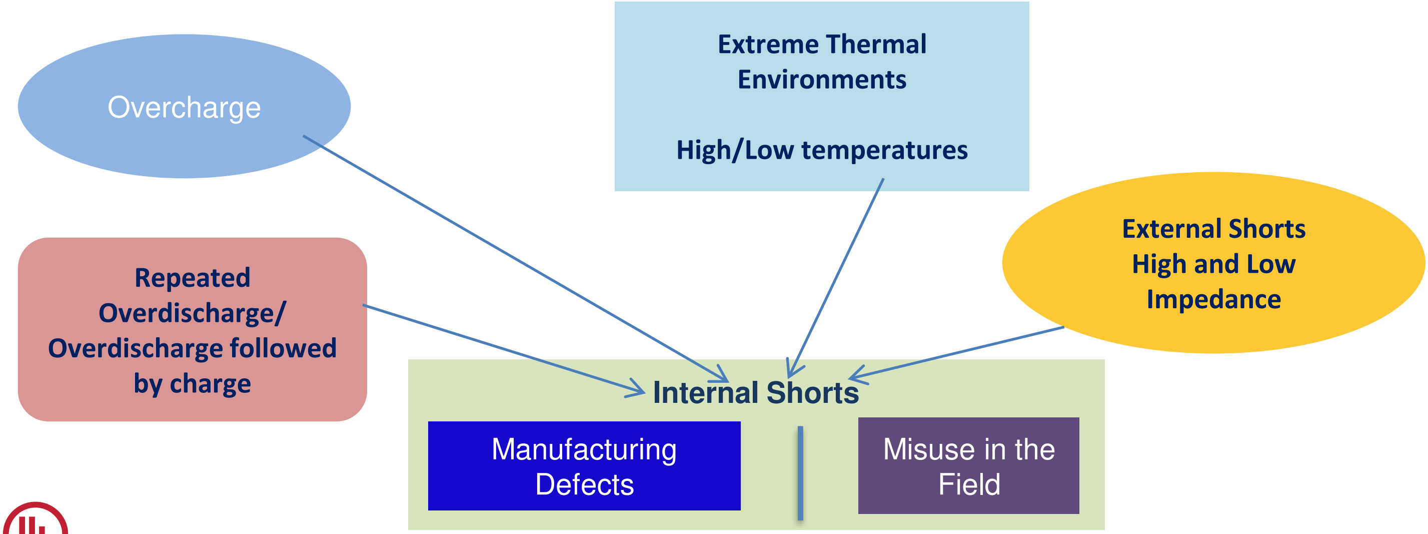
Lithium polymer fire burns down shop

Fire Incidents in Cell Manufacturing Facilities

Fire in Battery Recycling Facility


Li-ion Cell Hazards
Thermal
BRRRRR
Mechanical
Electrical

Hazard Causes - Electrical



Hazard Causes - Electrical

Overcharge

Over-voltage / High-rate Charge

Electrolyte Decomposition (formation of gases such as H_2, CO and CO_2

Cathode destabilization and release of Oxygen

Lithium metal dendrites (can pierce the separator causing short circuit)

High Temperatures
Venting
Fire
Thermal Runaway

Overdischarge

Undervoltage / High Rate Discharge

Dissolution of Copper Current Collector

Cathode showed heavy copper plating

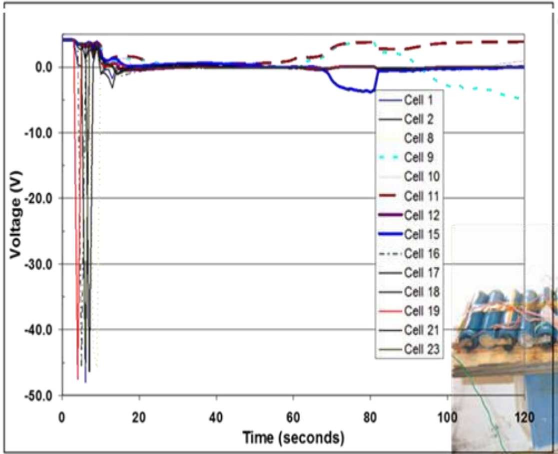
Delaminated area, where active material was adhered to separator

J. Nemanick *et al.*, International Batt Seminar, March 2016

Benign Internal Shorts

Hazard Causes Electrical (contd…)

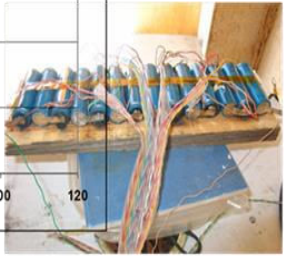
External Short - High and Low Impedance



Only venting observed, no fire

Cell Voltages in bold – No visible signs of Venting or damage, but no voltage;

All others vented with Obvious leakage or discoloration



Rapid cell venting within the first 10 seconds

Internal Short

- **Manufacturing Defect**
- **Field Failures**

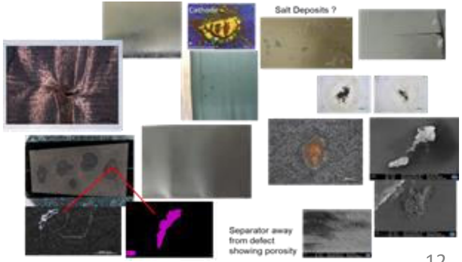
Manufacturing Defect

Major defects can be screened by manufacturers

Subtle defects need to be identified and screened out during acceptance testing. Defects include poor manufacturing (creases, tears, delamination, etc.), introduction of foreign or native object debris,

Field Failures

Avoided by **use within manufacturer's specification** (I, V, T); **stringent cell and battery selection and screening criteria**; **stringent monitoring and control** (I, V, T); **cell balancing**, **health checks** (with issue-recognizable tests); **good thermal design.**



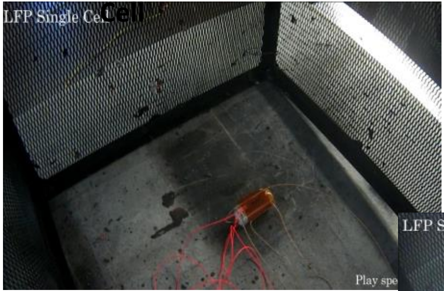
Thermal Runaway Process - Overcharge

Thermal Runaway – Single Cell Tests – Patch Heater

Nickel Manganese Cobalt (NMC) Cathode Lithium-ion Cell

Smoke only

Lithium Iron Phosphate (LFP) Cathode Lithium-ion Cell

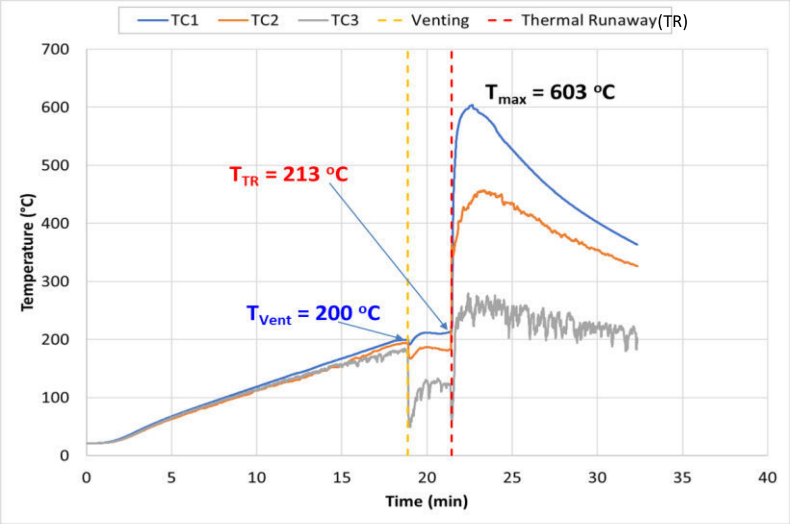


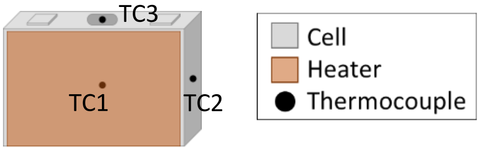
Cell 6 – Fire & Smoke

Variations in behavior between cells from the same battery

Cell 7 –Smoke only

Thermal Runaway – NMC Cell



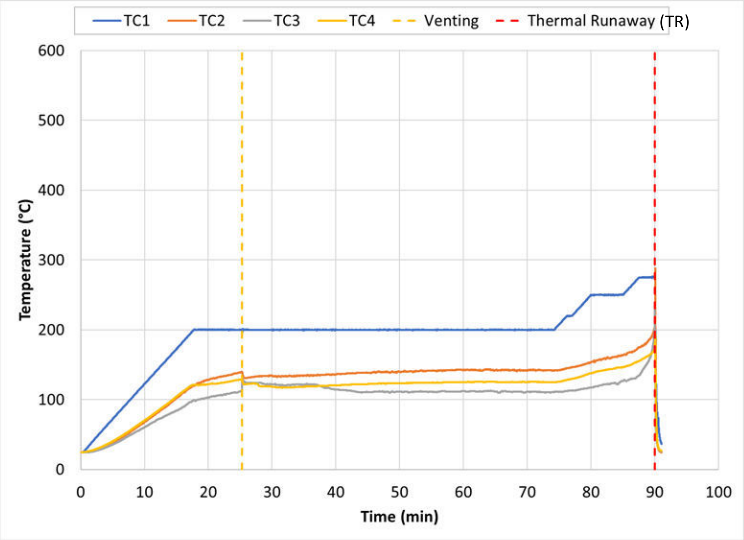


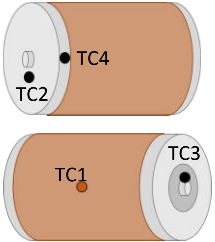
TC1 = Front (Under the heater)

TC2 = Side (Unheated end)

TC3 = Vent

Thermal Runaway – LFP Cell





TC1 = Side (Under the heater)

TC2 = Bottom (Unheated end)

TC3 = Vent (Top)

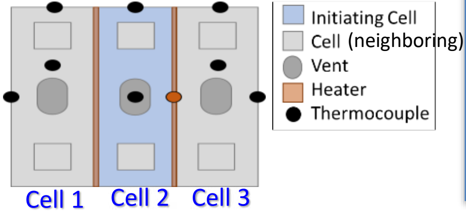
TC4 = Side (Next to the heater)

Thermal Runaway – Module Level

Patch Heater Method

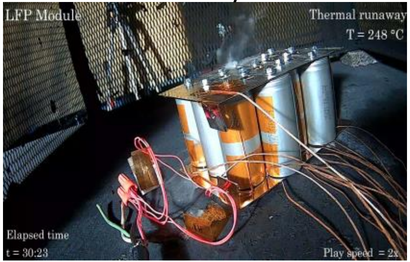
NMC Module

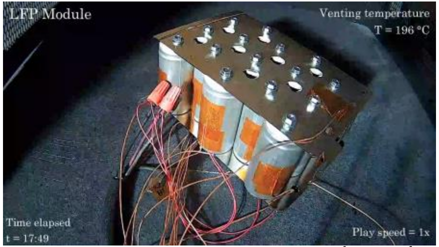
Fire and Smoke



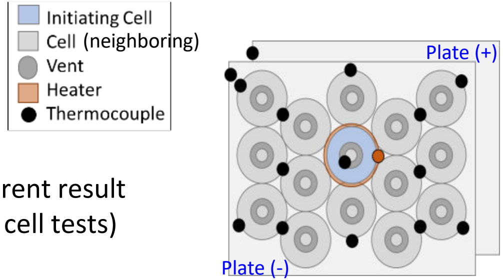
LFP Modules

Smoke only





Fire and Smoke



LFP modules showed different result (similar behavior as single cell tests)

Thermal Runaway – Battery Level

Patch Heater Method

NMC Battery

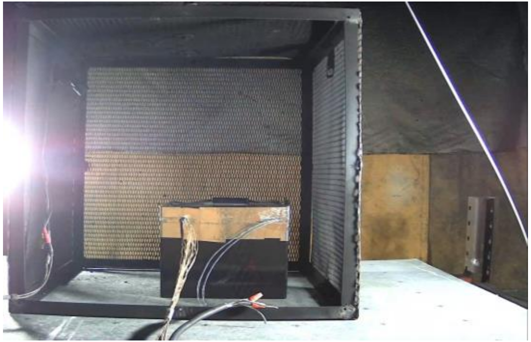
Fire and Smoke

15.2 V; 75 Ah

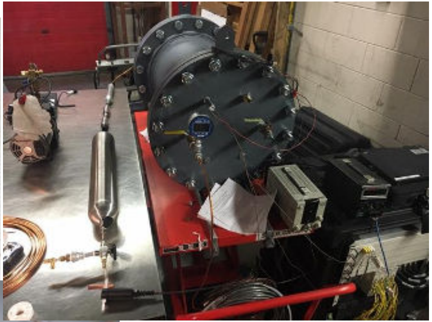
LFP Battery

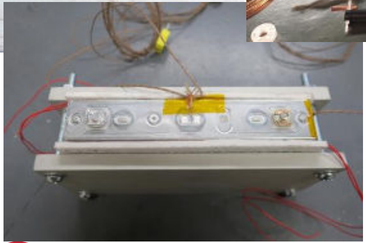
15.2 V; 82.5 Ah

Smoke only



Cell Gas Composition Test -NMC





25 Ah **NMC** cells (Automotive battery)
Volume of gas released during thermal runaway in a **single** cell – **41 Liters**

Component		Measured %	Component LFL
Carbon Monoxide	CO	23.76% **	10.9%
Carbon Dioxide	CO_2	26.65%	N/A
Hydrogen	H_2	36.03% **	4.0%
Methane	CH_4	3.55%	4.4%
Ethylene	C_2H_4	3.20%	2.4%
Ethane	C_2H_6	0.57%	2.4%
Propylene	C_3H_6	2.71%	1.8%
Propane	C_3H_8	0.15%	1.7%
Propadiene	C_3H_4	0.01%	1.9%
-	C_4 (Total)	0.83%	-
-	C_5 (Total)	0.09%	-
Hexane	C_6H_{14}	0.00%	1.0%
Dimethyl Carbonate (DMC)	$C_3H_6O_3$	1.08%	Not specified
Ethyl Methyl Carbonate (EMC)	$C_4H_8O_3$	0.46%	Not specified
Total	-	100	-
Individual C4 Components		-	-
Butane	C_4H_{10}	0.04%	1.4%
Butene	C_4H_8	0.60%	1.5%
Butadiene	C_4H_6	0.19%	1.4%
Individual C5 Components		-	-
Pentane	n-C_5H_{12}	0.09%	1.1%

** Gases above combustible volume

Cell Gas Composition Test -LFP

32 mm Diameter
70 mm Height

5.5 Ah Li-ion **LFP** cells (12 V replacement batteries for lead-acid)

Volume of gas released during thermal runaway in a single cell – **3 Liters**

Component		Measured %	Component LFL
Carbon Monoxide	CO	0.0%	10.9%
Carbon Dioxide	CO_2	21.60%	N/A
Hydrogen	H_2	54.00% **	4.0%
Methane	CH_4	6.10% **	4.4%
Ethylene	C_2H_4	3.46%	2.4%
Ethane	C_2H_6	1.13%	2.4%
Propylene	C_3H_6	1.51%	1.8%
Propane	C_3H_8	0.59%	1.7%
Propadiene	C_3H_4	0.0%	1.9%
-	C_4 (Total)	1.67%	-
-	C_5 (Total)	0.16%	-
Hexane	C_6H_{14}	0.05%	1.0%
Dimethyl Carbonate (DMC)	$C_3H_6O_3$	3.35%	Not specified
Ethyl Methyl Carbonate (EMC)	$C_4H_8O_3$	6.32%	Not specified
Total	-	100	-
Individual C4 Components		-	-
Butane	C_4H_{10}	0.38%	1.4%
Butene	C_4H_8	0.97%	1.5%
Butadiene	C_4H_6	0.27%	1.4%
Individual C5 Components		-	-
Pentane	n-C_5H_{12}	0.05%	1.1%

** Gases above combustible volume

Gas Analysis for Battery Packs

NMC 15.2 V; 75 Ah

Gas Component	Peak Release Rate (L/min)	Non-flaming (L)	Flaming (L)
Total Hydrocarbons (Propane Equivalent)	113.3	17	165
Carbon Dioxide	471.1	< 1	1403
Carbon Monoxide	33.8	< 1	90
Hydrogen	52.4	Below Detectable Limit (< 17.3 L/min)	83

LFP 15.2 V; 82.5 Ah

Gas Component	Peak Release Rate (L/min)	Venting (L)	Thermal Runaway (L)
Total Hydrocarbons (Propane Equivalent)	35.8	Below Detectable Limit (< 0.01 L/min)	357
Carbon Dioxide	< 1.8	Below Detectable Limit (< 1.8 L/min)	Below Detectable Limit (< 1.8 L/min)
Carbon Monoxide	< 0.1	Below Detectable Limit (< 0.1 L/min)	Below Detectable Limit (< 0.1 L/min)
Hydrogen	16.8	Below Detectable Limit (< 8.0 L/min)	196

Challenge with Gas Composition Analysis

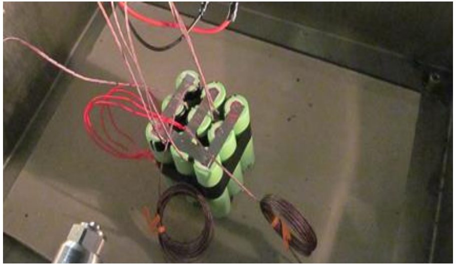
- HF which is produced in large quantities is not easy to detect as it condenses on the walls of the chamber and pipes
  - Prof. Mellander and Dr. Larsson have carried out experimental studies and modeling work to quantify the volume of HF produced
- Gas analysis of the Arizona Battery Energy Storage System (BESS) showed the presence of HCN above toxicity limits
  - Although li-ion cells do not produce HCN, components such as plastics, used in the manufacturing of BESS produce HCN as a byproduct when they burn
- Better analytical methods to determine HF concentrations need to be developed.

Fire Suppression Studies
Lab Scale

Li-Ion Module Fire Suppression Experiments

Experiment
Baseline (1 mm and 0 mm spacing)
N_2 Early release
N_2 Late release
Water Mist Early (side) release
Water Mist Late (side) release
Water Mist Early (overhead)
Water Mist Late (overhead)
Stat-X Early release
Stat-X Late release

9P Module Configuration



Cells in contact physically and electrically to simulate worst case configuration

Cell with heater

Venting and Thermal Runaway Detection Cues

Detection Cues:

- Cell temperature
- Light attenuation (smoke)
- Pressure
- Module voltage
- Visual (initial vent and thermal runaway)

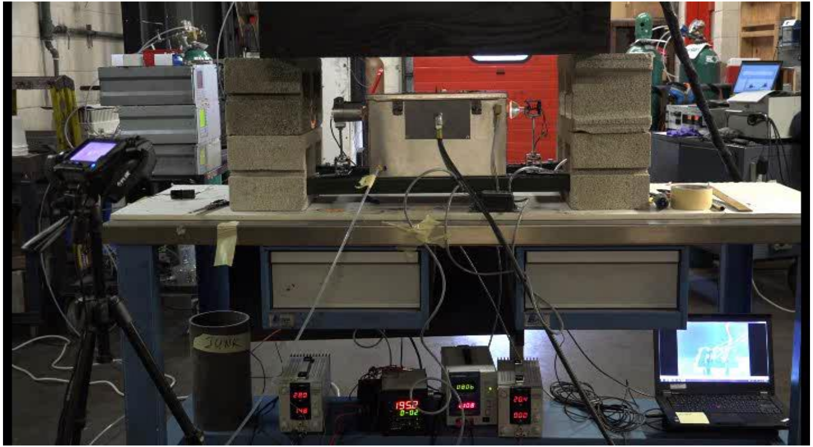
	T_{vent}
Baseline	~133°C
N_2 Early	~129°C
N_2 Late	~133°C
WM Early	~136°C
WM Late	~137°C
Stat-X Early	~127°C
Stat-X Late	~137°C

Experiment	$T_{thermal\ runaway}$
Baseline	~210 °C
N_2 Early	~190 °C
N_2 Late	~200 °C
WM Early	~200 °C
WM Late	~197 °C
Stat-X Early	~215 °C
Stat-X Late	~210 °C

T_{vent} & $T_{thermal\ runaway}$ occur in a relatively narrow and repeatable range
Both temperatures are reliable predictors of CID /vent opening and thermal runaway for this cell design

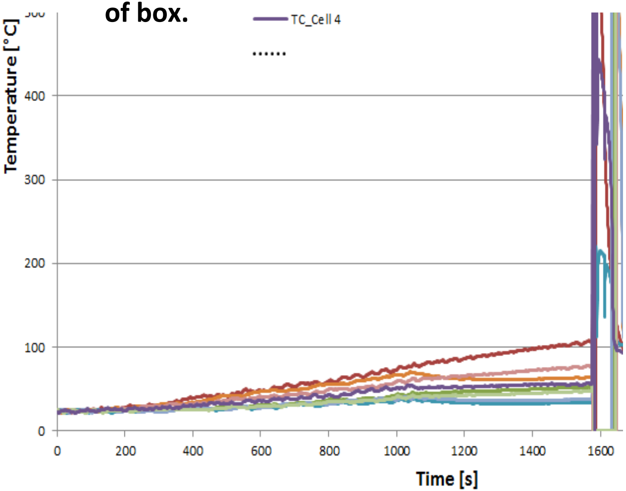
Stat-X : A potassium carbonate-based fire extinguisher

Fire Suppression - Baseline Test – No fire Suppressant



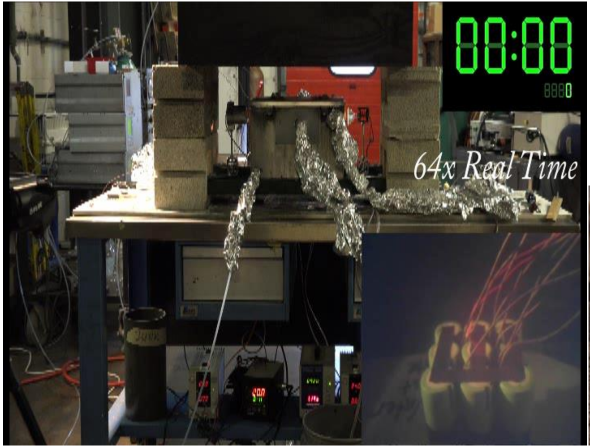
Early Release Water Mist

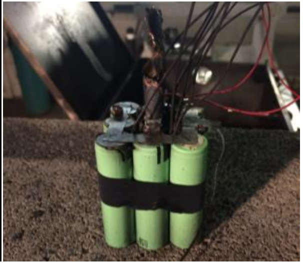
Early water mist: cools cells near trigger cell, however all cells exceed $T_{thermal\ runaway}$ (~200 °C). Flames visible outside of box.

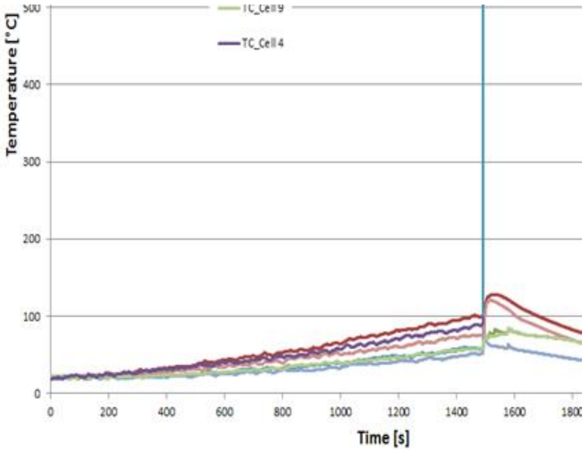


Late Release Water Mist

Late water mist: Suspect that thermal runaway may have affected two other cells; Flames contained inside the box

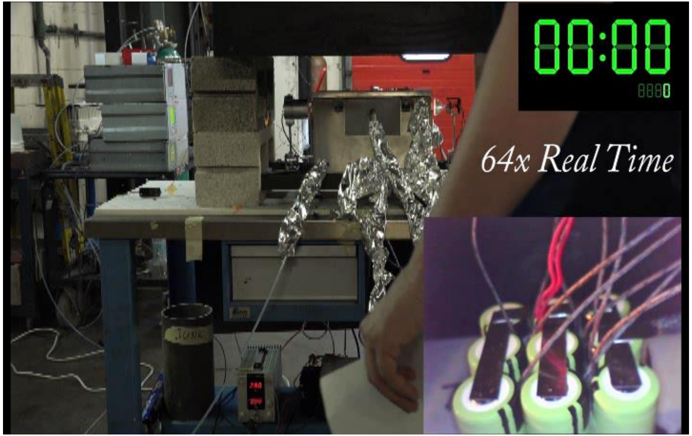


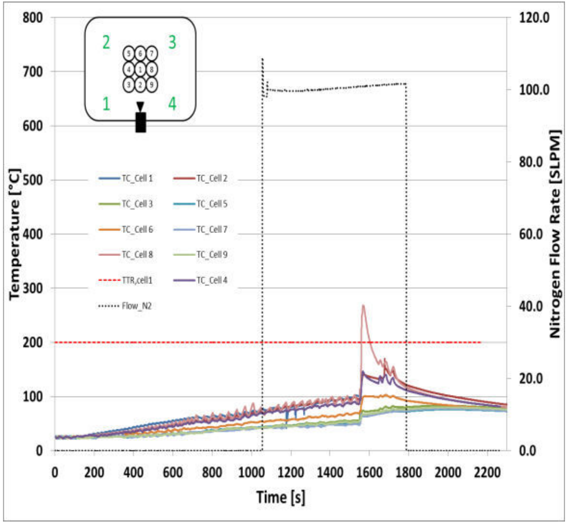




Early Release N_2

- Single cell in thermal runaway
- No flames after thermal runaway, in or out of box

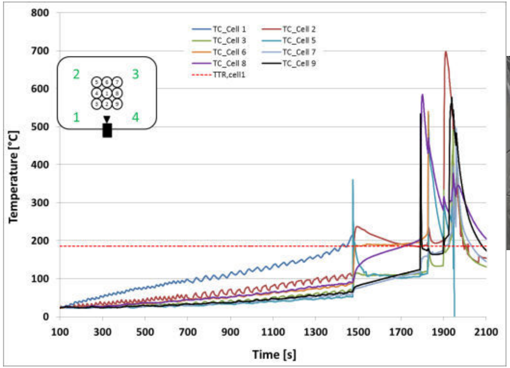




Fire Extinguisher – Potassium Carbonate Type

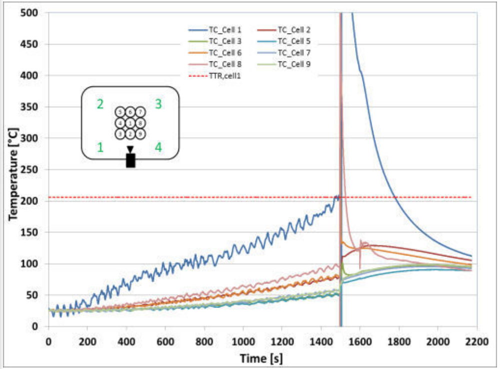
Early Release

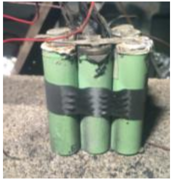
- Thermal runaway propagated to all cells
- Short fire outside the box.



Late Release

- Thermal runaway propagated to two cells.
- Very short fire outside the box after thermal runaway was observed.





Summary of Test Results

Experiment	$T_{rupture}$	$T_{thermal\ runaway}$	Propagation beyond cell 1	Flame outside box?
Baseline	~133°C	~210 °C	Yes (all)	Yes; sustained fire
Water Mist Early (side)	~136°C	~200 °C	Yes (all)	Yes
Water Mist Late (side)	~137°C	~197 °C	Yes	No
Water Mist Early (Overhead)	127	No	No	No
Water Mist Late (Overhead)	134 °C	~194 °C	Yes	Yes
N_2 Early	~129°C	~190 °C	No	Small or no sparks
N_2 Late	~133°C	~200 °C	No	Small or no sparks
Stat-X Early	~127°C	~215 °C	Yes (all)	Yes – at beginning and end
Stat-X Late	~137°C	~210 °C	Yes (2)	No; Small sparks

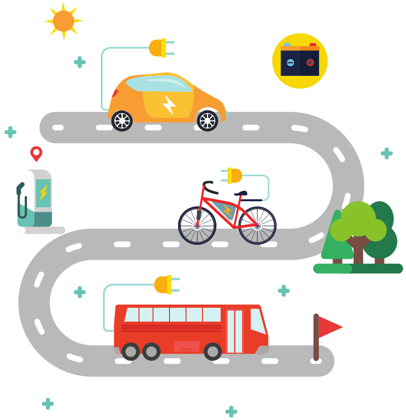
Summary

- Thermal runaway occurs due to hazard causes that can be electrical, mechanical or thermal in nature.
  - Fully characterizing a system under all credible off-nominal conditions will help with safer designs and usage limits
  - Carrying out a high-fidelity thermal analysis provides the data needed to design appropriate heat dissipation paths that lead to safer battery systems
- The events accompanying thermal runaway can vary quite a bit – venting or fire or smoke or combinations of these can be observed.
- Cell to cell variation in behavior is a challenge as that will require multiple tests from each cell lot to confirm worst case behavior.
- Toxic and flammable gases are released from lithium-ion batteries and battery systems.
  - Data obtained on the gases evolved should be analyzed for the volume of the chamber (room) or confined space that the battery system is located in, to understand worst case flammability and explosive as well as toxicity levels and help with the design of appropriate vent systems.
- Fire extinguishing methods need to be studied further and optimized for the size and nature of the battery as well as the design and environment of the application it is used in.

Acknowledgments

- Dr. Pravinray Gandhi, Alex Klieger and team (UL Northbrook)
- Dr. Daniel Juarez Robles and Saad Azam (UL Electrochemical Safety Team)

Thank you!



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Electric Vehicle Safety: Thermal Runaway and Fire Characteristics & Suppression in Lithium-ion Batteries

August 31 , 2020
7:00 PM - 8:00 PM (IST)
WRI India

Speaker:
Dr. Judy Jeevarajan
Research Director – Electrochemical Safety,
Underwriters Laboratories Inc.

Moderator:
Shravani Sharma
WRI India

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Back-up Charts

Water Mist Tests

- Same flow rate and pressure
- Same module position
- Same nozzle and nozzle position
- Early release water mist: discharged after first cell rupture
- Late release water mist: discharged at first sign of fire
- Tests were carried out with water released from the side as well as overhead.

N_2 Gas Tests

- Same Nozzle, nozzle position
- Same N_2 flow rate
- Early release: discharged at first cell rupture
- Late release: discharged at first fire

List of Safety Standards for EVs

Table 8-1. List of safety standards of Li-ion batteries.

Organization	Designation	Title	Year	Applicability	Summarized in this Chapter
Sandia Report	SAND2005-3123	FreedomCAR Electrical Energy Storage System Abuse Test Manual for Electric and Hybrid Electric Vehicle Applications (Doughty and Crafts 2006)	2006	Cell, module, or pack in a motor vehicle	
SAE International	SAE J2464	Electric and Hybrid Electric Vehicle Rechargeable Energy Storage Systems (RESS), Safety and Abuse Testing	2009	Cell, module, or pack in a motor vehicle	Table 8-4
	SAE J2929	Electric and Hybrid Vehicle Propulsion Battery System Safety Standard — Lithium-Based Rechargeable Cells	2011	System or whole vehicle	Table 8-3
International Organization for Standardization	ISO 6469-1	Electrically propelled road vehicles -- Safety specifications – Part 1: On-board rechargeable energy storage system (RESS)	2009	Cell, module, or pack in a motor vehicle	
	ISO 6469-2	Electrically propelled road vehicles -- Safety specifications – Part 2: Vehicle operational safety means and protection against failures	2009	System or whole vehicle	
Underwriters Laboratories	UL 1642	Standard for Lithium Batteries	2005		Table 8-6
	UL 2580	Batteries for Use in Electric Vehicles	2011	Packs, subassemblies and modules in a motor vehicle	Table 8-7
International Electrotechnical Commission	IEC 62133	Secondary Cells and Batteries Containing Alkaline or Other Non-acid Electrolytes — Safety Requirements for Portable Sealed Secondary Cells, and for Batteries Made from Them, for Use in Portable Applications	2002		
	IEC 62281	Safety of Primary and Secondary Lithium Cells and Batteries during Transport	2004	For transporting batteries	
United Nations	38.3 (E.09.VIII.3)	Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, Part III, Section 38.3	2010	For transporting batteries	Table 8-5
Institute of Electrical and Electronics Engineers	IEEE 1625	Rechargeable Batteries for Multi-Cell Mobile Computing Devices	2008	Not to vehicles	
	IEEE 1725	Rechargeable Batteries for Cellular Telephones	2011	Not to vehicles	Table 8-8

Toxicity

10.2.3 Secondary Toxic and Incompatible Materials Hazards

Toxic materials are those battery chemicals and byproducts that are toxic or corrosive by themselves or react with other materials to produce toxic, flammable, or heat-generating chemicals. As described in Chapters 2 and 3, the main components of Li-ion batteries share common health effects, material incompatibilities, and flammability characteristics. To determine the toxicity and incompatibilities of specific chemicals, readers should refer to MSDS and other safety information.

The data in Chapters 2 and 3 indicate that the cathode component appears to pose significant toxicity risks. However, the chance of human exposure to chemicals in the cathode could be considered low because these components are solids that possess high melting temperatures. Exposure to these chemicals would require the rupture of a battery with fragmentation or vaporization of the component chemicals, which is considered unlikely.

The more hazardous chemicals inherently present in a Li-ion battery are those comprising the electrolyte salt and electrolyte solvent. In the majority of Li-ion battery designs, the electrolyte salt ($LiPF_6$) is dissolved in the electrolyte solvent (EC, DMC, PC, or DEC); therefore, the more likely hazard would be ejection or leakage of electrolyte fluid from the battery. The primary hazards with the electrolyte solvents are the health effects noted in Chapter 3 and the flammability hazards. The combustion of any of the electrolyte solvents would also yield water (H_2O), which may influence the degradation of the $LiPF_6$ salt, and the asphyxiates CO and CO_2.

The primary hazards with the electrolyte salt $LiPF_6$ are health effects (noted in Chapter 3), and its incompatibility with water, which yields lithium fluoride (LiF), phosphoryl fluoride (POF_3), and hydrofluoric acid (HF) by the following reaction (Yang, Zhuang, & Ross , 2006):

$$LiPF_6 + H_2O \rightarrow LiF + POF_3 + 2HF.$$

If failure processes associated with thermal runaway occur within the battery, several hazardous chemicals may also be produced from various reactions. The significant hazardous products formed in these reactions include the flammable hydrocarbons (C_2H_4; C_3H_6; and C_2H_6); flammable gases and/or asphyxiates (H_2, CO_2, and CO); and LiF. Water can also be produced from the combustion of the electrolyte solvents, which could contribute to the formation of HF, POF_3, and additional LiF.

The primary hazards with LiF are its toxicity if ingested or inhaled and its incompatibility with water. Contact with water can result in the formation of HF, one of the other hazardous materials discussed in Chapter 3. The primary hazards with HF are its extreme toxicity and corrosiveness and its incompatibility with metal, glass, and rubber (common vehicle materials), which subsequently release flammable hydrogen gas upon contact. Little to no data exist on the specific toxicity and incompatibility of POF_3. POF_3 is assumed to have similar toxicity effects and material incompatibilities as $POCl_3$ given that both chemicals possess a halogen (chlorine or fluorine) and phosphorus.

Toxicity

10.2.4 Secondary Asphyxiation Hazards

The danger of asphyxiation is another concern with venting or ruptured Li-ion batteries. Asphyxiation may be a hazard in vehicle crashes when the battery casing has been compromised and there is little to no opportunity for external venting or air changeover within the vehicle (i.e., vehicle windows are in the up position and doors are closed). MSDS data for known asphyxiates state that the symptoms of asphyxiation (dizziness, nausea, etc.) can occur when oxygen levels are less than approximately 19.5 percent; levels under 8 to 10 percent can bring about rapid unconsciousness.

Chemicals that pose the highest threat of asphyxiation are the gases that are released when the battery casing is compromised and that displace the ambient vehicle air, such as H_2, C_2H_4, C_2H_6, C_3H_6, along with carbon dioxide (CO_2) and carbon monoxide (CO) produced from combustion. The threat of asphyxiation is also present for the volatile electrolyte solvents. For both the gases and solvents, the specific threat of asphyxiation is a function of the quantities of the chemicals released, their release rate, and the degree of accumulation in the vehicle. Most of the asphyxiates produced as a result of Li-ion battery failure are also flammability hazards, and can be present in both the flammability and asphyxiation ranges at the same time.