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

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WRI India

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

Moderator:
Shravani Sharma
WRI India
Battery Safety

Advancing safer energy storage through science
About UL Battery Safety Group

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.

Judy Jeevarajan, Ph.D. / Underwriters Laboratories Inc.
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- 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 ceases, 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.

Cell Reaction: $\text{Li}_x\text{C} + \text{Li}_{1-x}\text{CoO}_2 \rightarrow \text{LiCoO}_2 + \text{C}$
Li-ion Battery Designs and Challenges

Low Voltage/ Low Capacity

High Voltage/High Capacity

Incidents of Li-ion Fires

Fire Incidents in Portable Applications

Fire Incidents in Cell Manufacturing Facilities

Lithium polymer fire burns down shop

Fire in Battery Recycling Facility

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Li-ion Cell Hazards

Thermal

Mechanical

Electrical
Hazard Causes - Electrical

- Overcharge
- Repeated Overdischarge/Overdischarge followed by charge
- External Shorts High and Low Impedance
- Extreme Thermal Environments High/Low temperatures
- Internal Shorts
- Manufacturing Defects
- Misuse in the Field
Hazard Causes - Electrical

Overcharge

- Over-voltage / High-rate Charge
- Electrolyte Decomposition (formation of gases such as H₂, CO and CO₂)
- Cathode destabilization and release of Oxygen
- High Temperatures
- Venting
- Fire
- Thermal Runaway
- Lithium metal dendrites (can pierce the separator causing short circuit)

Overdischarge

- Undervoltage / High Rate Discharge
- Dissolution of Copper Current Collector
- Benign Internal Shorts

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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

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Thermal Runaway – Single Cell Tests – Patch Heater

Nickel Manganese Cobalt (NMC) Cathode Lithium-ion Cell

Lithium Iron Phosphate (LFP) Cathode Lithium-ion

Cell 6 – Fire & Smoke

Variations in behavior between cells from the same battery

Cell 7 – Smoke only

Smoke only

NMC Single Cell

Venting Temperature

T = 200 °C

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Thermal Runaway – NMC Cell

- TC1 = Front (Under the heater)
- TC2 = Side (Unheated end)
- TC3 = Vent

$T_{max} = 603$ °C

$T_{TR} = 213$ °C

$T_{vent} = 200$ °C
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

NMC Module

Patch Heater Method

LFP Modules

Smoke only

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

Fire and Smoke

Smoke only

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Thermal Runaway – Battery Level

Patch Heater Method

Fire and Smoke

NMC Battery
15.2 V; 75 Ah

Smoke only

LFP Battery
15.2 V; 82.5 Ah

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Cell Gas Composition Test -NMC

<table>
<thead>
<tr>
<th>Component</th>
<th>Measured %</th>
<th>Component LFL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide</td>
<td>23.76% **</td>
<td>10.9%</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>26.65%</td>
<td>N/A</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>36.03% **</td>
<td>4.0%</td>
</tr>
<tr>
<td>Methane</td>
<td>3.55%</td>
<td>4.4%</td>
</tr>
<tr>
<td>Ethylene</td>
<td>3.20%</td>
<td>2.4%</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.57%</td>
<td>2.4%</td>
</tr>
<tr>
<td>Propylene</td>
<td>2.71%</td>
<td>1.8%</td>
</tr>
<tr>
<td>Propane</td>
<td>0.15%</td>
<td>1.7%</td>
</tr>
<tr>
<td>Propadiene</td>
<td>0.01%</td>
<td>1.9%</td>
</tr>
<tr>
<td>-</td>
<td>C₄ (Total)</td>
<td>0.83%</td>
</tr>
<tr>
<td>-</td>
<td>C₅ (Total)</td>
<td>0.09%</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.00%</td>
<td>1.0%</td>
</tr>
<tr>
<td>Dimethyl Carbonate (DMC)</td>
<td>1.08%</td>
<td>Not specified</td>
</tr>
<tr>
<td>Ethyl Methyl Carbonate (EMC)</td>
<td>0.46%</td>
<td>Not specified</td>
</tr>
<tr>
<td>Total</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>Individual C4 Components</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Butane</td>
<td>0.04%</td>
<td>1.4%</td>
</tr>
<tr>
<td>Butene</td>
<td>0.60%</td>
<td>1.5%</td>
</tr>
<tr>
<td>Butadiene</td>
<td>0.19%</td>
<td>1.4%</td>
</tr>
<tr>
<td>Individual C5 Components</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pentane</td>
<td>n-C₅H₁₂ 0.09%</td>
<td>1.1%</td>
</tr>
</tbody>
</table>

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

** Gases above combustible volume

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### Cell Gas Composition Test - LFP

<table>
<thead>
<tr>
<th>Component</th>
<th>Measured %</th>
<th>Component LFL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>0.0%</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO₂</td>
<td>21.60%</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H₂</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>CH₄</td>
<td>6.10%**</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C₂H₄</td>
<td>3.46%</td>
</tr>
<tr>
<td>Ethane</td>
<td>C₂H₆</td>
<td>1.13%</td>
</tr>
<tr>
<td>Propylene</td>
<td>C₃H₆</td>
<td>1.51%</td>
</tr>
<tr>
<td>Propane</td>
<td>C₃H₈</td>
<td>0.59%</td>
</tr>
<tr>
<td>Propadiene</td>
<td>C₃H₄</td>
<td>0.0%</td>
</tr>
<tr>
<td>-</td>
<td>C₄ (Total)</td>
<td>1.67%</td>
</tr>
<tr>
<td>-</td>
<td>C₅ (Total)</td>
<td>0.16%</td>
</tr>
<tr>
<td>Hexane</td>
<td>C₆H₁₄</td>
<td>0.05%</td>
</tr>
<tr>
<td>Dimethyl Carbonate (DMC)</td>
<td>C₃H₂O₃</td>
<td>3.35%</td>
</tr>
<tr>
<td>Ethyl Methyl Carbonate (EMC)</td>
<td>C₄H₅O₃</td>
<td>6.32%</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>100</td>
</tr>
<tr>
<td>Individual C₄ Components</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butane</td>
<td>C₄H₁₀</td>
<td>0.38%</td>
</tr>
<tr>
<td>Butene</td>
<td>C₄H₈</td>
<td>0.97%</td>
</tr>
<tr>
<td>Butadiene</td>
<td>C₄H₆</td>
<td>0.27%</td>
</tr>
<tr>
<td>Individual C₅ Components</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentane</td>
<td>n-C₅H₁₂</td>
<td>0.05%</td>
</tr>
</tbody>
</table>

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**

**Gases above combustible volume**
Gas Analysis for Battery Packs

### NMC 15.2 V; 75 Ah

<table>
<thead>
<tr>
<th>Gas Component</th>
<th>Peak Release Rate (L/min)</th>
<th>Non-flaming (L)</th>
<th>Flaming (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Hydrocarbons (Propane Equivalent)</td>
<td>113.3</td>
<td>17</td>
<td>165</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>471.1</td>
<td>&lt; 1</td>
<td>1403</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>33.8</td>
<td>&lt; 1</td>
<td>90</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>52.4</td>
<td>Below Detectable Limit (&lt; 17.3 L/min)</td>
<td>83</td>
</tr>
</tbody>
</table>

### LFP 15.2 V; 82.5 Ah

<table>
<thead>
<tr>
<th>Gas Component</th>
<th>Peak Release Rate (L/min)</th>
<th>Venting (L)</th>
<th>Thermal Runaway (L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Hydrocarbons (Propane Equivalent)</td>
<td>35.8</td>
<td>Below Detectable Limit (&lt; 0.01 L/min)</td>
<td>357</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>&lt; 1.8</td>
<td>Below Detectable Limit (&lt; 1.8 L/min)</td>
<td>Below Detectable Limit (&lt; 1.8 L/min)</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>&lt; 0.1</td>
<td>Below Detectable Limit (&lt; 0.1 L/min)</td>
<td>Below Detectable Limit (&lt; 0.1 L/min)</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>16.8</td>
<td>Below Detectable Limit (&lt; 8.0 L/min)</td>
<td>196</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline (1 mm and 0 mm spacing)</td>
</tr>
<tr>
<td>N₂ Early release</td>
</tr>
<tr>
<td>N₂ Late release</td>
</tr>
<tr>
<td>Water Mist Early (side) release</td>
</tr>
<tr>
<td>Water Mist Late (side) release</td>
</tr>
<tr>
<td>Water Mist Early (overhead)</td>
</tr>
<tr>
<td>Water Mist Late (overhead)</td>
</tr>
<tr>
<td>Stat-X Early release</td>
</tr>
<tr>
<td>Stat-X Late release</td>
</tr>
</tbody>
</table>

9P Module Configuration

Cells in contact physically and electrically to simulate worst case configuration

Cell with heater

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### Venting and Thermal Runaway Detection Cues

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

<table>
<thead>
<tr>
<th></th>
<th>$T_{\text{vent}}$</th>
<th></th>
<th>$T_{\text{thermal runaway}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>$\sim133^\circ$C</td>
<td>Baseline</td>
<td>$\sim210\ ^\circ$C</td>
</tr>
<tr>
<td>N$_2$ Early</td>
<td>$\sim129^\circ$C</td>
<td>N$_2$ Early</td>
<td>$\sim190\ ^\circ$C</td>
</tr>
<tr>
<td>N$_2$ Late</td>
<td>$\sim133^\circ$C</td>
<td>N$_2$ Late</td>
<td>$\sim200\ ^\circ$C</td>
</tr>
<tr>
<td>WM Early</td>
<td>$\sim136^\circ$C</td>
<td>WM Early</td>
<td>$\sim200\ ^\circ$C</td>
</tr>
<tr>
<td>WM Late</td>
<td>$\sim137^\circ$C</td>
<td>WM Late</td>
<td>$\sim197\ ^\circ$C</td>
</tr>
<tr>
<td>Stat-X Early</td>
<td>$\sim127^\circ$C</td>
<td>Stat-X Early</td>
<td>$\sim215\ ^\circ$C</td>
</tr>
<tr>
<td>Stat-X Late</td>
<td>$\sim137^\circ$C</td>
<td>Stat-X Late</td>
<td>$\sim210\ ^\circ$C</td>
</tr>
</tbody>
</table>

$T_{\text{vent}}$ & $T_{\text{thermal runaway}}$ 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

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Fire Suppression - Baseline Test – No fire Suppressant
Early water mist: cools cells near trigger cell, however all cells exceed $T_{\text{thermal runaway}}$ (~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.

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Early Release N₂

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

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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.

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<table>
<thead>
<tr>
<th>Experiment</th>
<th>$T_{\text{rupture}}$</th>
<th>$T_{\text{thermal runaway}}$</th>
<th>Propagation beyond cell 1</th>
<th>Flame outside box?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline</td>
<td>~133°C</td>
<td>~210 °C</td>
<td>Yes (all)</td>
<td>Yes; sustained fire</td>
</tr>
<tr>
<td>Water Mist Early (side)</td>
<td>~136°C</td>
<td>~200 °C</td>
<td>Yes (all)</td>
<td>Yes</td>
</tr>
<tr>
<td>Water Mist Late (side)</td>
<td>~137°C</td>
<td>~197 °C</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Water Mist Early (Overhead)</td>
<td>127 °C</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Water Mist Late (Overhead)</td>
<td>134 °C</td>
<td>~194 °C</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>N₂ Early</td>
<td>~129°C</td>
<td>~190 °C</td>
<td>No</td>
<td>Small or no sparks</td>
</tr>
<tr>
<td>N₂ Late</td>
<td>~133°C</td>
<td>~200 °C</td>
<td>No</td>
<td>Small or no sparks</td>
</tr>
<tr>
<td>Stat-X Early</td>
<td>~127°C</td>
<td>~215 °C</td>
<td>Yes (all)</td>
<td>Yes – at beginning and end</td>
</tr>
<tr>
<td>Stat-X Late</td>
<td>~137°C</td>
<td>~210 °C</td>
<td>Yes (2)</td>
<td>No; Small sparks</td>
</tr>
</tbody>
</table>
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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Research Director – Electrochemical Safety, Underwriters Laboratories Inc.

Moderator:
Shravani Sharma
WRI India
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>
<thead>
<tr>
<th>Organization</th>
<th>Designation</th>
<th>Title</th>
<th>Year</th>
<th>Applicability</th>
<th>Summarized in this Chapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAE International</td>
<td>SAE J2464</td>
<td>Electric and Hybrid Electric Vehicle Rechargeable Energy Storage Systems (RESS), Safety and Abuse Testing</td>
<td>2009</td>
<td>Cell, module, or pack in a motor vehicle</td>
<td>Table 8.4</td>
</tr>
<tr>
<td></td>
<td>SAE J2929</td>
<td>Electric and Hybrid Vehicle Propulsion Battery System Safety Standard — Lithium-Based Rechargeable Cells</td>
<td>2011</td>
<td>System or whole vehicle</td>
<td>Table 8.3</td>
</tr>
<tr>
<td>International Organization for Standardization</td>
<td>ISO 6469-1</td>
<td>Electrically propelled road vehicles — Safety specifications — Part 1: On-board rechargeable energy storage system (RESS)</td>
<td>2009</td>
<td>Cell, module, or pack in a motor vehicle</td>
<td>Table 8.4</td>
</tr>
<tr>
<td></td>
<td>ISO 6469-2</td>
<td>Electrically propelled road vehicles — Safety specifications — Part 2: Vehicle operational safety means and protection against failures</td>
<td>2009</td>
<td>System or whole vehicle</td>
<td>Table 8.3</td>
</tr>
<tr>
<td>Underwriters Laboratories</td>
<td>UL 1642</td>
<td>Standard for Lithium Batteries</td>
<td>2006</td>
<td>Packs, subassemblies and modules in a motor vehicle</td>
<td>Table 8.6</td>
</tr>
<tr>
<td></td>
<td>UL 2580</td>
<td>Batteries for Use in Electric Vehicles</td>
<td>2011</td>
<td></td>
<td>Table 8.7</td>
</tr>
<tr>
<td>International Electrotechnical Commission</td>
<td>IEC 62133</td>
<td>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</td>
<td>2002</td>
<td>For transporting batteries</td>
<td></td>
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<td></td>
<td>IEC 62281</td>
<td>Safety of Primary and Secondary Lithium Cells and Batteries during Transport</td>
<td>2004</td>
<td>For transporting batteries</td>
<td>Table 8.5</td>
</tr>
<tr>
<td>Institute of Electrical and Electronics Engineers</td>
<td>IEEE 1625</td>
<td>Rechargeable Batteries for Multi-Cell Mobile Computing Devices</td>
<td>2008</td>
<td>Not to vehicles</td>
<td>Table 8.5</td>
</tr>
<tr>
<td></td>
<td>IEEE 1725</td>
<td>Rechargeable Batteries for Cellular Telephones</td>
<td>2011</td>
<td>Not to vehicles</td>
<td>Table 8.8</td>
</tr>
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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 (LiPF₆) is dissolved in the electrolyte solvent (EC, DMC, PC, or DEC); if the batteries, 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 yield water (H₂O), which may influence the degradation of the LiPF₆ salt, and the asphaltenes CO and CO₂.

The primary hazards with the electrolyte salt LiPF₆ are health effects (noted in Chapter 3), and its incompatibility with water, which yields lithium fluoride (LiF), phosphoryl fluoride (POF₃), and hydrofluoric acid (HF) by the following reaction (Yang, Zhuang, & Ross, 2006):

\[
\text{LiPF}_6 + \text{H}_2\text{O} \rightarrow \text{LiF} + \text{POF}_3 + 2\text{HF}
\]

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 (C₂H₄, C₃H₆, and C₂H₆), flammable gases and/or asphaltenes (H₂, CO₂, and CO); and LiF. Water can also be produced from the combustion of the electrolyte solvents, which could contribute to the formation of HF, POF₃, 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 LiF are its extreme toxicity, health hazards, and its incompatibility with water, 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 POF₃. POF₃ is assumed to have similar toxicity effects and material incompatibilities as POCI₃ given that both chemicals possess a halogen (chlorine or fluorine) and phosphorus.
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 H₂, C₂H₆, C₃H₆, C₃H₄, along with carbon dioxide (CO₂) 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.